

Volume and Interface Studies of Complex Liquid Media

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Introduction

SINGLE-BEAM MULTIPLE SCATTERING SUPPRESSION BY CROSS-CORRELATION

A new method for characterizing particles in turbid media by cross-correlating the scattered intensity fluctuations at two nearby points in the far field is described. The cross-correlation function selectively emphasizes single scattering over multiple scattering. The usual dynamic light scattering capability of inferring particle size from decay rate is thus extended to samples which are so turbid as to be visually opaque. The method relies on single-scattering speckle being physically larger than multiple scattering speckle. With a suitable optical geometry to select nearby points in the far field or equivalently slightly different scattering wave vectors (of the same magnitude), the multiple scattering contribution to the cross-correlation function may be reduced and in some cases rendered insignificant. The viability of this technique has been confirmed at NASA and the University of Amsterdam (UvA), and recently combined with small angle X-ray scattering and dynamic X-ray scattering (Riese *et al.* [6] at UvA), allowing the measurement of hydrodynamic interactions.

ADVANCES IN SURFACE LIGHT SCATTERING SPECTROSCOPY INSTRUMENTATION AND ANALYSIS: NON-INVASIVELY MEASURING OF SURFACE TENSION, VISCOSITY, AND OTHER INTERFACIAL PARAMETERS

A new generation of vibration mitigating surface light scattering spectroscopy instrumentation has been designed and built. The computational application of an instrument function derived using Fourier optics is presented. We derived the necessary surface response function algorithms to study both simple fluids, and binary fluids at their wetting transition and near their critical points. This instrument and its accompanying suite of analysis software allow us to easily make accurate and non-invasive measurements of the interfacial tension, volume viscosity, and other interfacial parameters of fluids. These developments can be applied to study systems with liquid–vapor and liquid–liquid interfaces, including spreading monolayers whenever optical access for a laser beam is available. Theoretical and experimental results are provided for both simple fluids and asymmetric thin films.

Count them photons he said with a wave. – X. Druid

Volume Light Scattering (VLS) – (Section I)

VLS-1. Introduction

Beginning with the advent of the laser, dynamic light scattering has proved to be an invaluable technique for determining the dynamic properties of a variety of systems. It has been used to study order-parameter dynamics near the critical points of both pure fluids and binary mixtures. It provides the most accurate method known of determining the diffusion coefficient of macromolecules such as proteins and polymers, as well as that of colloidal particles. Because the radius of a spherical particle is determined very simply from knowledge of its diffusion coefficient, dynamic light scattering has become the method of choice for measuring the size of colloidal particles [7].

The method is not without problems however. In particular, for strongly scattering samples, not all of the scattered light originates as the result of single scattering. Under these conditions, it can be difficult to interpret data in any reliable way. One exception to this situation occurs in the limit of extremely strongly scattering samples, where the photons may be treated as diffusing throughout the sample [8-10]. In this case it has proved possible to deduce useful information regarding short time scale dynamics of the process giving rise to the scattering.

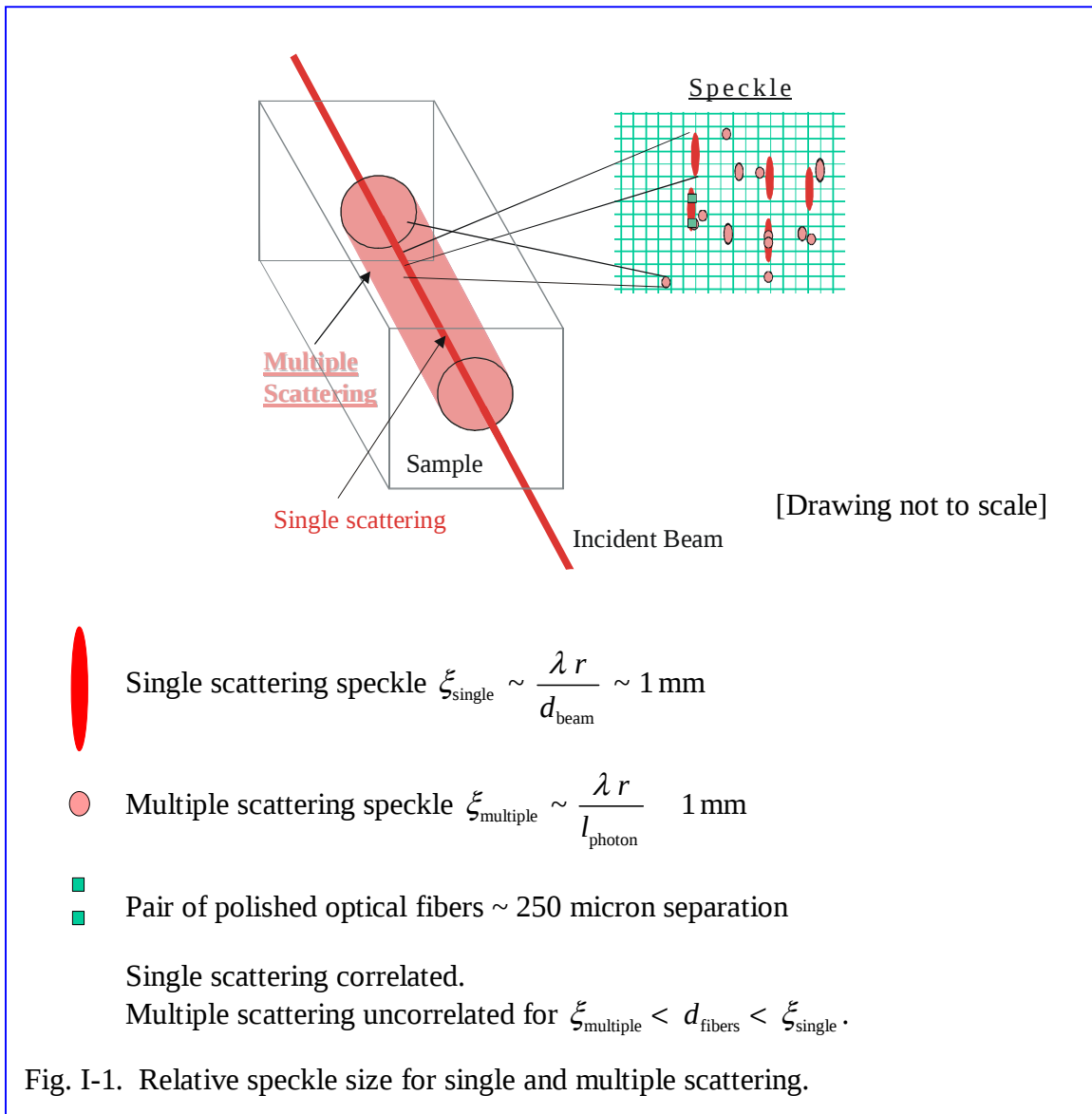
For dynamic light scattering in the intermediate regime where high order scattering is significant but the diffusing photon limit has not been reached, the most effective experimental method yet devised for dealing with multiple scattering is the cross-correlation technique invented by Phillies [11, 12], and extended by others [13-15]. Phillies' method relies on the fact that in order for the incident light to be scattered in a particular direction, the wave vectors of the incident and scattered light must be coupled by that of the dielectric constant fluctuation responsible for the scattering, in a scattered momentum transfer $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$ (see Ref. [7], p. 6). Here $\mathbf{k}_i$ is the wave vector of the incident light, $\mathbf{k}_s$ is that of the scattered light, and $\mathbf{q}$ is the wave vector of the fluctuation responsible for the scattering.

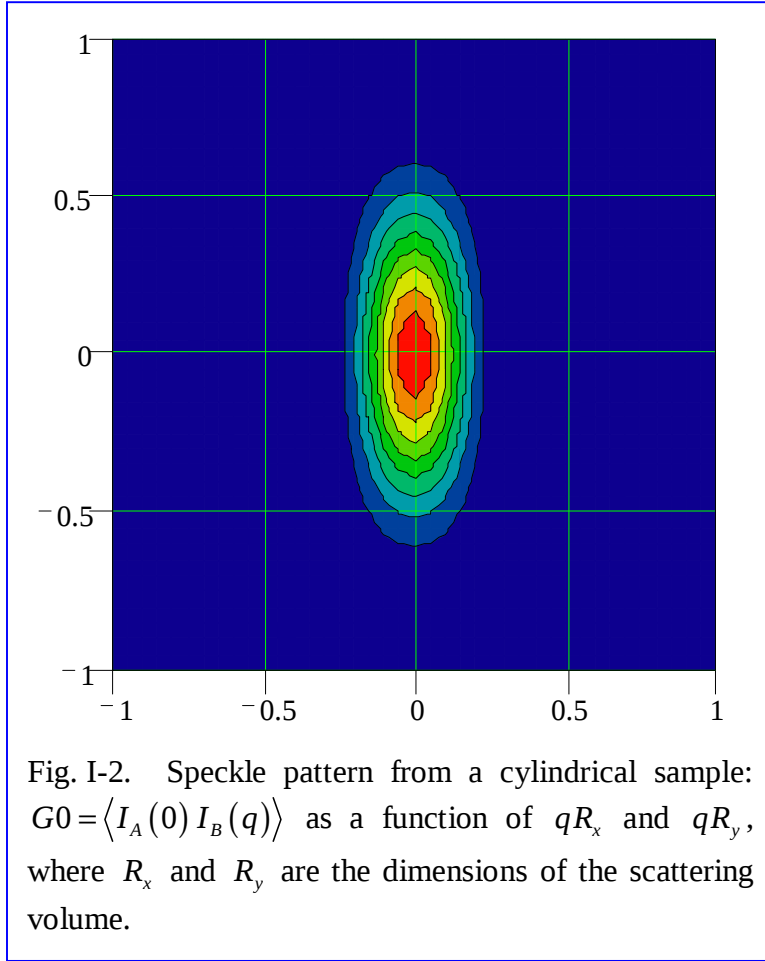
Because of the Bragg condition, two different beam-detector combinations can be aligned so as to simultaneously collect light which has been scattered by the same fluctuation. Of course, the two detectors also collect light which has been multiply scattered. This results in detector signals $i_A(t)$ and $i_B(t)$ which arise from both single and multiple scattering contributions. The single scattering contributions are strongly correlated with each other at all times, while the multiple scattering components are only weakly correlated. Measuring the temporal cross-correlation function of the two detector outputs $\langle i_A(\tau) i_B(0) \rangle$, then provides the same information as would be obtained in the single scattering limit using a conventional single-beam, single-detector arrangement to measure $\langle i(\tau) i(0) \rangle$.

Although feasible, the cross-correlation technique summarized above is expensive and difficult to align in practice. As a possible alternative, we [1, 16-23] and later others [24, 25] explored the possibility of using a single-beam, two-detector system. The basic idea hinges on the observation shown in Fig. I-1 that single scattering originates exclusively from the region of

primary illumination, typically the small cross-section of a focused laser beam. Multiple scattering however arises from a broader ‘halo’ surrounding the incident beam, and thus appears to come from a significantly larger source.

Because scattered light arises from a spatially incoherent source, its spatial coherence properties are determined by the apparent dimensions of the source as viewed by the detector (van Cittert-Zernike theorem [26]). Consequently singly scattered light gives rise to correlated patches (time-dependent speckle) which are typically much larger in one dimension than they are in the other. As shown in Figs. I-1 – I-3, they are large in the dimension in which the source appears small, namely transverse to the incident beam, and small in the dimension in which the source appears large, that is parallel to the incident beam. Multiply scattered light also gives rise to time-dependent speckle, but since the smallest source dimension for multiple scattering is larger than that for single scattering, the multiple scattering speckles are smaller than the single scattering speckles in the direction transverse to the incident beam.





We have demonstrated experimentally that this idea, regarding the relative sizes of speckle arising from single versus multiple scattering, can be used to discriminate single from multiple scattering. This was accomplished by using two optical fibers leading to two separate detectors to collect scattered light at two closely spaced positions. We used optical fibers which were single-mode for 632.8 nm to collect scattered light at 514.5 nm. However single mode behavior is not necessary for the results reported below because each fiber only conveys light to a detector, with the fiber core acting as a small physical aperture stop. The fibers were not terminated with lenses, and thus served simply to collect light at two small regions. The two fibers were placed sufficiently close together to lie within one speckle of the singly scattered light, but not within one speckle of the multiply

scattered light. Under these conditions we found that the cross-correlation function of the two detector outputs yielded useful data for the diameter of colloidal spheres, even when sample concentrations were so large as to render the 10 mm diameter samples visually opaque.

A detailed theoretical analysis has been provided elsewhere [27, 28] by our collaborator J. A. Lock.

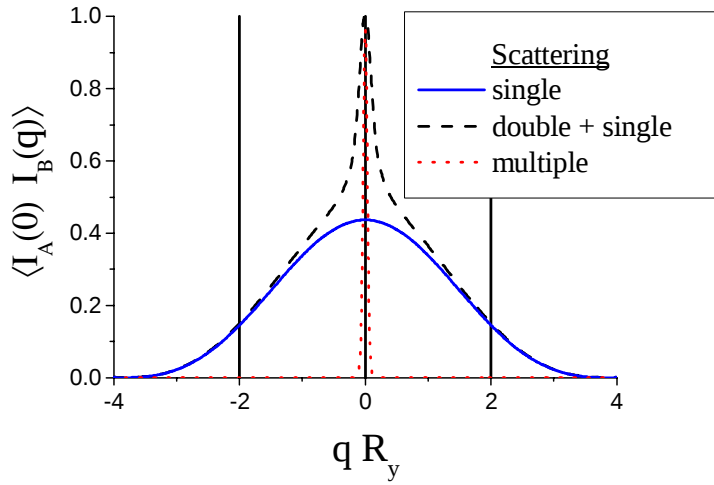


Fig. I-3. Horizontal cut through the speckle. The solid black lines designate the positions of the detectors. When the detectors are placed this far apart only single scattering will contribute to the time correlation function obtained by cross-correlating the signal from the two detectors. The measured correlation function is: $\langle I_A(0,0) I_B(\varepsilon, \tau) \rangle_q$, where ε is the small wavevector difference determined by the angle between the detectors A and B.

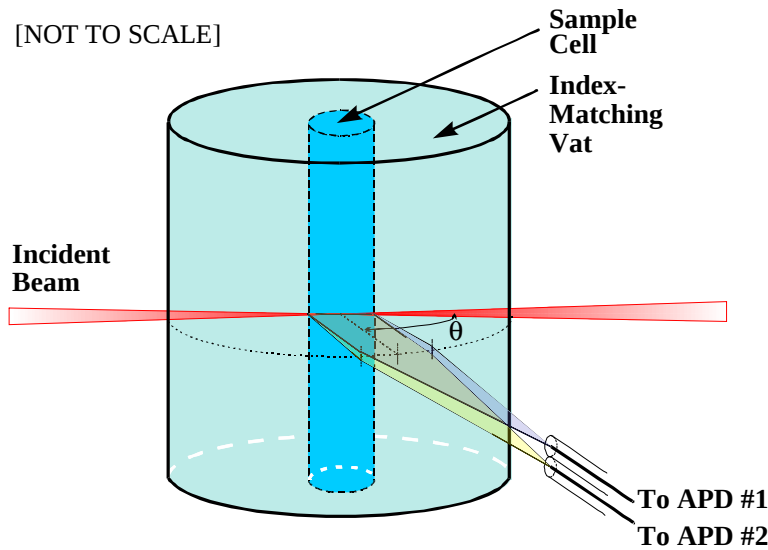


Fig. I-4. Optical geometry used to verify the concept of multiple scattering suppression by spatial cross-correlation.

VLS-2. Experimental Method

Our experimental arrangement is shown schematically in Fig. I-4. The cylindrical sample cells were 10.1 mm inner diameter glass test tubes of 11.6 mm outer diameter, held rigidly on the axis of a cylindrical glass vat containing either water or decalin as index matching fluid. The vat had an inner diameter of 80 mm and an outer diameter of 84.6 mm. Light from an argon-ion laser of vacuum wavelength $\lambda_0 = 514.5$ nm was brought to a focus near the axis, with a $1/e^2$ diameter of about $88 \mu\text{m}$ using a lens of focal length 100 mm. The beam entered the vat through a small polished flat area (not shown in Fig. I-4). Since the samples were suspensions of colloidal particles in water, some distortion of the focus occurred upon entering the sample cell when decalin (refractive index 1.48) was used as the matching fluid, but this had no observable effect on the results. Better optics for scattering from highly concentrated systems may be envisaged using square cuvette (which we discuss later), but this change does not affect the conclusions reported here. Our present geometry uses the sample cell and optional index matching vat as a cylindrical lens [29, 30], as shown in Fig. I-5, and thus collects light

of a single scattering angle from along the entire beam path (when the illuminating beam has not been extinguished by turbidity). A ray-trace for this optical design is shown in Fig. I-5. Note that for a cylindrical lens the focus, f , for scattering from a single scattering angle is at

$$f = R \frac{n}{n-1},$$

where R is the radius of the cell (the index matching vat in this case) and n is the

index of refraction of the liquid. For water, where $n = 1.33$ and a cell of radius $84.6 \text{ mm} / 2 \text{ mm}$ the focus is at approximately 170 mm . In actual practice, this positioning of the detection fibers is quite forgiving. From the ray-trace shown in Fig. I-5, it is evident that the addition of an iris to stop the outermost rays from the edge of the sample cell provides highly collimated light at the detection fiber. For scattering from dilute single scattering samples the amount of light scattered does not change with angle. This has advantages that we will discuss in a later section when we address a technique for flare rejection that involves adding a sufficiently strong local oscillator.

To collect scattered light from two nearby points in the far field, we arranged the polished ends of two optical fibers, which are single-mode for 633 nm , to touch at the cladding diameter so that the cores were 0.25 mm apart. We placed the end of this fiber pair 170 mm from the system axis just above the horizontal plane containing the incident beam, with the fibers one above the other; that is, separated in the direction transverse to the beam, the direction in which the single scattering speckle is large. Being slightly above the plane reduced the flare effects of multiple internal reflections for this geometrical configuration. Flare effects need to be avoided since they can act as a local oscillator which can deleteriously move the measured decay times away from the self-beat regime toward the homodyne regime [1, 4, 31]. Given a beam diameter of $88 \mu\text{m}$, the vertical extent of the single scattering speckle should be of order $(\lambda_0/d)R \cong 1.0 \text{ mm}$

at a distance of 170 mm . Consequently the two fibers, separated by only 0.25 mm , should collect light which is well correlated provided it originates only within the incident focused beam. For our geometry, the scattered light consists of small speckles which are much taller than they are wide, and which fade in and out of existence continually at any one place as the particles

diffuse. Since the two fibers often lie within a single speckle the optical powers they each collect tend to be correlated.

Careful visual observation of samples which exhibit multiple scattering reveals an apparent bright line (scattered light emerging directly from the beam itself) lying within a much larger and more diffuse region. This diffuse source is light which has been scattered out of the illuminating beam and has subsequently been rescattered one or more times, with the final scattering event directing it into the eye. Since this source appears larger than the beam, we expect it to produce speckle which is much shorter vertically than the 0.25 mm separation of the fibers,

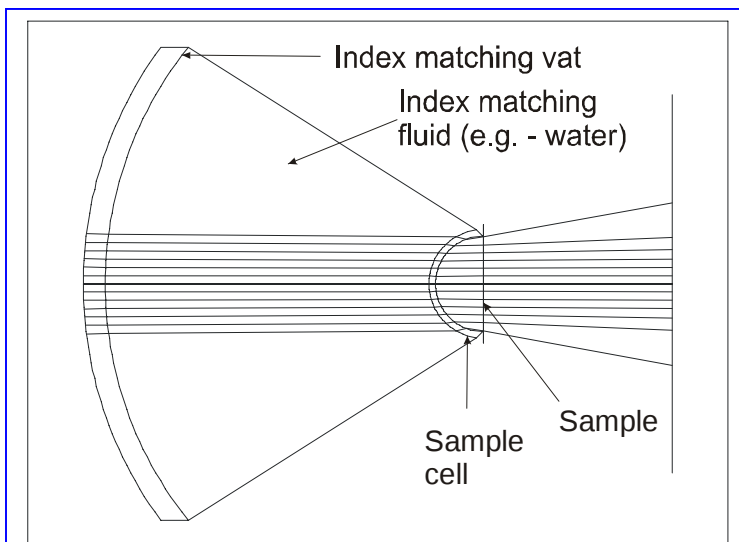


Fig. I-5. Ray-trace for a cylindrical sample cell in a water-filled vat. The cylindrical vat focuses the light scattered at any one angle to a vertical line.

and thus to contribute little to the cross-correlation of optical powers collected by the two fibers. Because both the single and multiple scattering sources have about the same dimension parallel to the incident beam, we would not expect to discriminate single scattering were the fibers separated horizontally rather than vertically.

We have not yet attempted to optimize the fiber spacing chosen using the rough criteria described above. This is partly because no single optimum angular separation may exist. The optimum depends not only on the optical geometry, but also on the scattering cross section, because its magnitude and angular dependence clearly affect the apparent source dimension for multiple scattering. Thus from a practical point of view optimization will also probably depend on the nature and concentration of the sample. See however the paper by Nobbmann *et al.* [24] which reports results obtained using our method but with variable fiber spacing.

The light collected by each fiber was delivered to an actively-quenched silicon avalanche photodiode (EG&G Optoelectronics Canada, model SPCM-AQ-141-FL) capable of single photon counting. These detectors produce ~ 10 ns TTL level pulses at rates proportional to the instantaneous optical power reaching each detector. The resulting pulse streams $n_A(t)$ and $n_B(t)$ were fed to a Brookhaven Instruments model BI-9000AT digital correlator which can compute either the temporal auto-correlation function

$$G(\tau) = \langle n(t + \tau) n(t) \rangle \quad (\text{I.1})$$

for either pulse stream, or the temporal cross-correlation function

$$G_{AB}(\tau) = \langle n_A(t + \tau) n_B(t) \rangle = \langle n_B(t + \tau) n_A(t) \rangle \quad (\text{I.2})$$

for both.

The correlator determines the number of counts received during each interval $(t, t + T)$, which we have denoted by $n(t)$ in Eqs. (I.1) and (I.2). By simultaneously forming the products of the current n value and the n values corresponding to 256 different delay times τ , and accumulating these products for a sufficient time, an acceptably accurate measurement of either $G(\tau)$ or $G_{AB}(\tau)$ can be formed. Note that the correlator actually computes an approximate correlation function since the time series is of bounded length and averaged over a finite number of time series.

The nominally 107 nm or 204 nm diameter particle samples obtained from Bangs Laboratories were suspensions of polystyrene latex spheres in distilled water. (The particle sizes we quote are based on hydrodynamic radii. When electron microscopy is used to verify dynamic light scattering standards, the polystyrene latex spheres are dried before being measured, thus giving a reduced value for the measured diameter.) We show data with concentrations that range from 0.0017 weight % to as high as 5 weight % in some cases. We initially measured particle diameters for dilute suspensions that were essentially free from multiple scattering by using

conventional optics at a 90° scattering angle. The extremely dilute samples scattered so little light compared with residual flare that more consistent measurements were obtained from 0.01 weight % samples which were still essentially transparent. Samples of different concentrations were prepared by diluting a suspension of polystyrene latex spheres, supplied at a nominal concentration of 10 weight %, determined by the manufacturers by evaporation to dryness and stated to vary by as much as $\pm 10\%$. The diluent was distilled water filtered with a pore size of 0.22 microns, to remove dust. It was not found necessary to further filter the samples after dilution. The specimen tubes were rinsed with similarly filtered water before charging and sealing with 'parafilm'.

VLS-3. Results

To quantify the way multiple scattering affects the auto-correlation function, we measured $G(\tau)$ for a number of suspensions of the nominally 107 nm diameter spheres with concentrations ranging from 0.0017 weight % initially up to 1 weight %. The measurements were made at a 90° scattering angle using one of the two optical fibers to collect the scattered light. Results for the normalized auto-correlation functions $G(\tau)/B-1$ versus delay time τ , are shown on a semilog plot in Fig. I-6 for six different concentrations. Fig. I-6 was prepared using baseline values determined by fitting a single exponential where intercept, baseline and exponential coefficient were all allowed to float. Typically the fitted baseline and the baseline calculated within the correlator from the sample time and actual number of pulses received agreed to within a few tenths of a percent or better. As we shall see later, this difference should not be ignored for

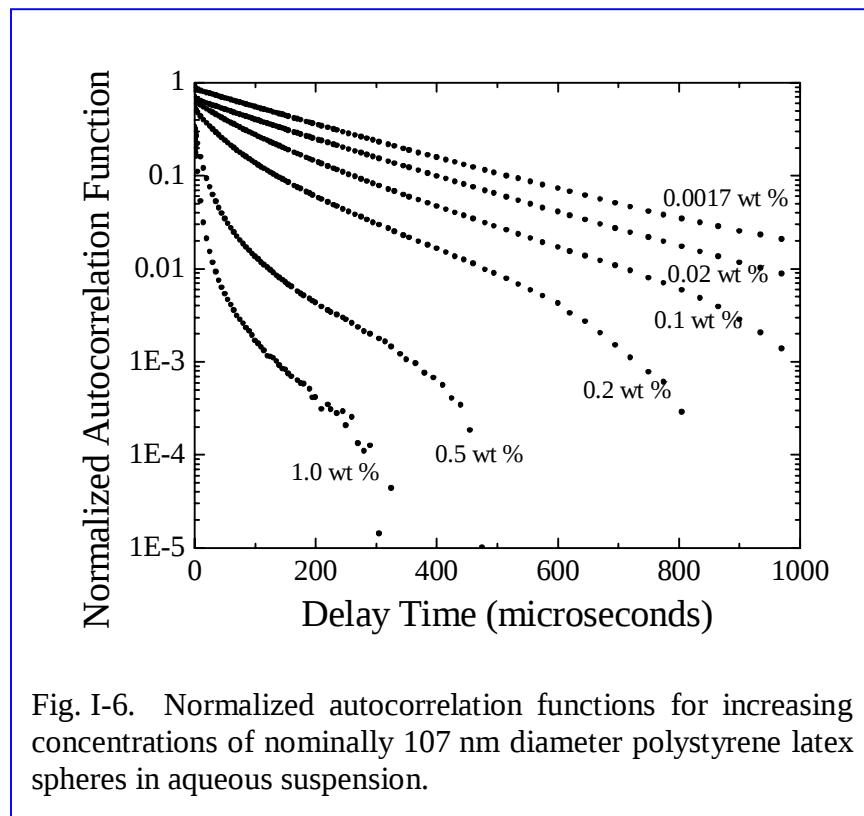


Fig. I-6. Normalized autocorrelation functions for increasing concentrations of nominally 107 nm diameter polystyrene latex spheres in aqueous suspension.

the later cross-correlation functions from which it is possible to extract good size measurements even when the zero delay time intercept becomes extremely small.

For monodisperse samples of sufficiently low concentration that they are free from multiple scattering, plots such as those shown in Fig. I-6 should be linear, and indeed those corresponding to the two lowest concentrations appear very nearly so. Examining the auto-correlation functions of the higher concentration samples reveals that $G(\tau)$

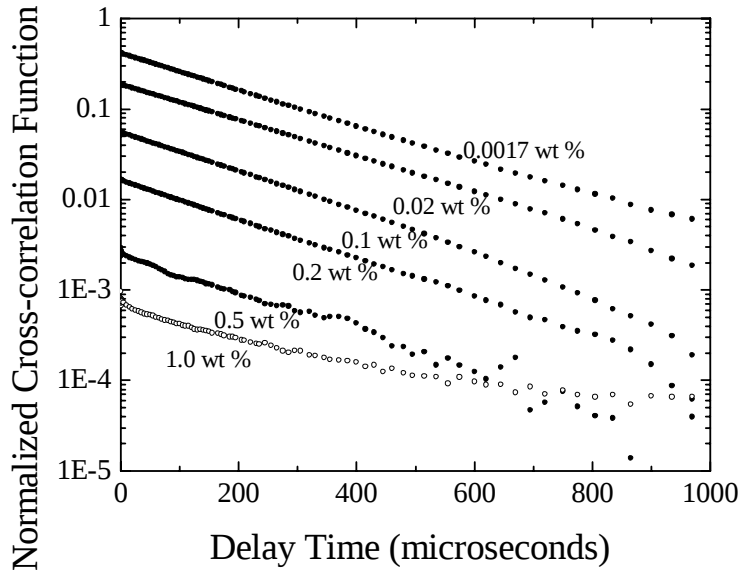


Fig. I-7. Normalized cross-correlation functions for increasing concentrations of nominally 107 nm diameter polystyrene latex spheres in aqueous suspension.

becomes increasingly non-exponential. The rapid initial decay evident for the 0.5 and 1.0 weight % samples is characteristic of strong multiple scattering [8-10], supported by the obvious visual opacity of the samples.

Cross-correlation functions $G_{AB}(\tau)$ for the same samples were measured using each of the fibers to collect the scattered light at nearby points. Some of these measurements are presented in Fig. I-7, which shows $G_{AB}(\tau)/B-1$ versus τ on a semilog plot. Because the decaying portion of $G_{AB}(\tau)$ is only a small fraction of the

baseline B for the cross-correlation data, especially for the higher concentration samples, we determined B for each data set by fitting to a single exponential decay plus a baseline. That the curves of $G_{AB}(\tau)/B-1$ presented in Fig. I-7 are linear to within experimental accuracy shows that the cross-correlation data for all the concentrations studied are consistent with single exponential decay. This is in marked contrast with the results for the auto-correlation measurements shown in Fig. I-6, which clearly contain a broad spectrum of decay rates for the higher concentration samples.

Quantitative analysis of the data was performed on the measured cross- and auto-correlation functions by the two-cumulant expansion given by

$$G_{AB}(\tau) = A \exp \left[-2 \left(K_1 \tau - \frac{K_2}{2} \tau^2 \right) \right] + B \quad (\text{I.3})$$

with A , B , K_1 , and K_2 adjustable. This method of analysis is commonly used for polydisperse samples that exhibit a range of decay rates, as do our auto-correlation functions. For the many sets of cross-correlation data, fits including the second cumulant, show a consistent value of about 0.028 for the reduced second cumulant. This low value, conventionally associated with polydispersity justifies the validity of a single exponential fit as a method of estimating relaxation time and hence particle diameter. We related the first cumulant to an effective diffusion coefficient D [32], by

$$K_1 = D q^2 \quad (\text{I.4})$$

where $\mathbf{q}$ is the scattering wave vector given by

$$\mathbf{q} = \frac{4 \pi n}{\lambda_0} \sin \left(\frac{\theta}{2} \right) \quad (\text{I.5})$$

Here n is the refractive index of the suspension, and θ is the scattering angle. We obtained an apparent particle diameter from

$$D = \frac{k_B T}{6 \pi \eta a} \quad (\text{I.6})$$

Here k_B is Boltzmann's constant, T the absolute temperature, η the viscosity, and a the apparent particle radius. The results of this analysis are summarized in Fig. I-8, which presents the apparent particle diameter versus sample concentration derived from both the auto- and cross-correlation functions. The results from auto- and cross-correlation agree reasonably well at the lowest concentrations, but disagree seriously for the higher concentration samples. Two main conclusions can be drawn from Fig. I-8. Firstly, multiple scattering can so severely distort auto-correlation function data as to result in apparent particle diameters more than an order of magnitude smaller than the true diameter. Secondly, the simple artifice of cross-correlating the scattered intensity at two nearby points virtually eliminates this effect.

Further results from the data analysis are shown in Fig. I-9, which displays the zero delay time intercept for each correlation function analyzed to produce the results already shown in Fig. I-8. Here we see that while the auto-correlation intercept changes little for the more concentrated samples, the intercept for cross-correlation falls steeply. This occurs because a smaller fraction of the detected light is correlated for the more turbid samples as the ratio of multiply scattered light to singly scattered light increases. We find that excellent estimates of particle diameter are obtainable from cross-

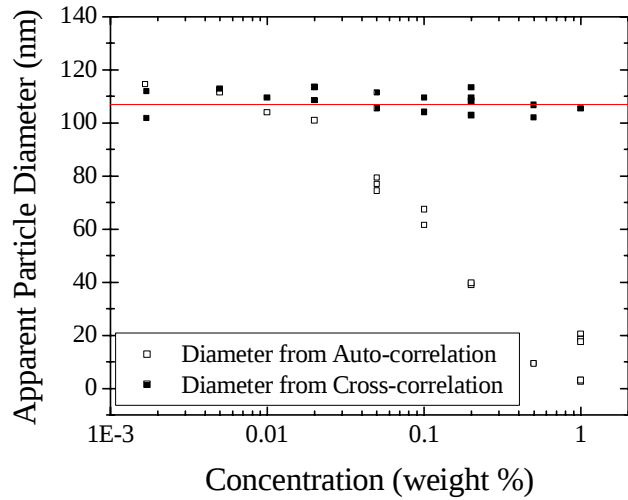


Fig. I-8. Particle diameter inferred from auto- and cross-correlation functions using a two-cumulant fit. Particles nominally 107 nm in diameter.

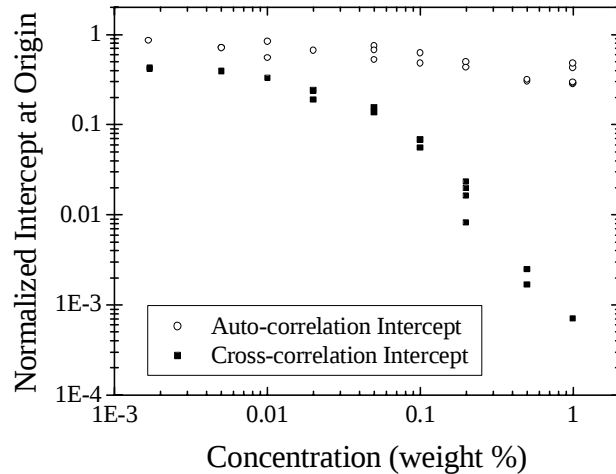
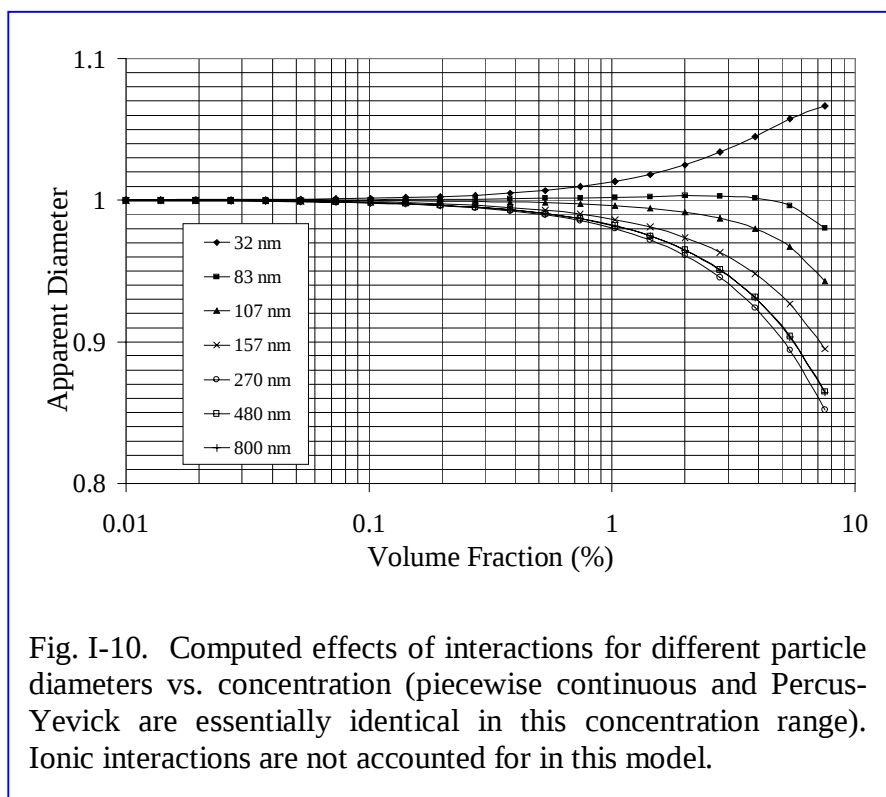


Fig. I-9. Zero delay time of normalized auto- and cross-correlation functions for increasing concentration.

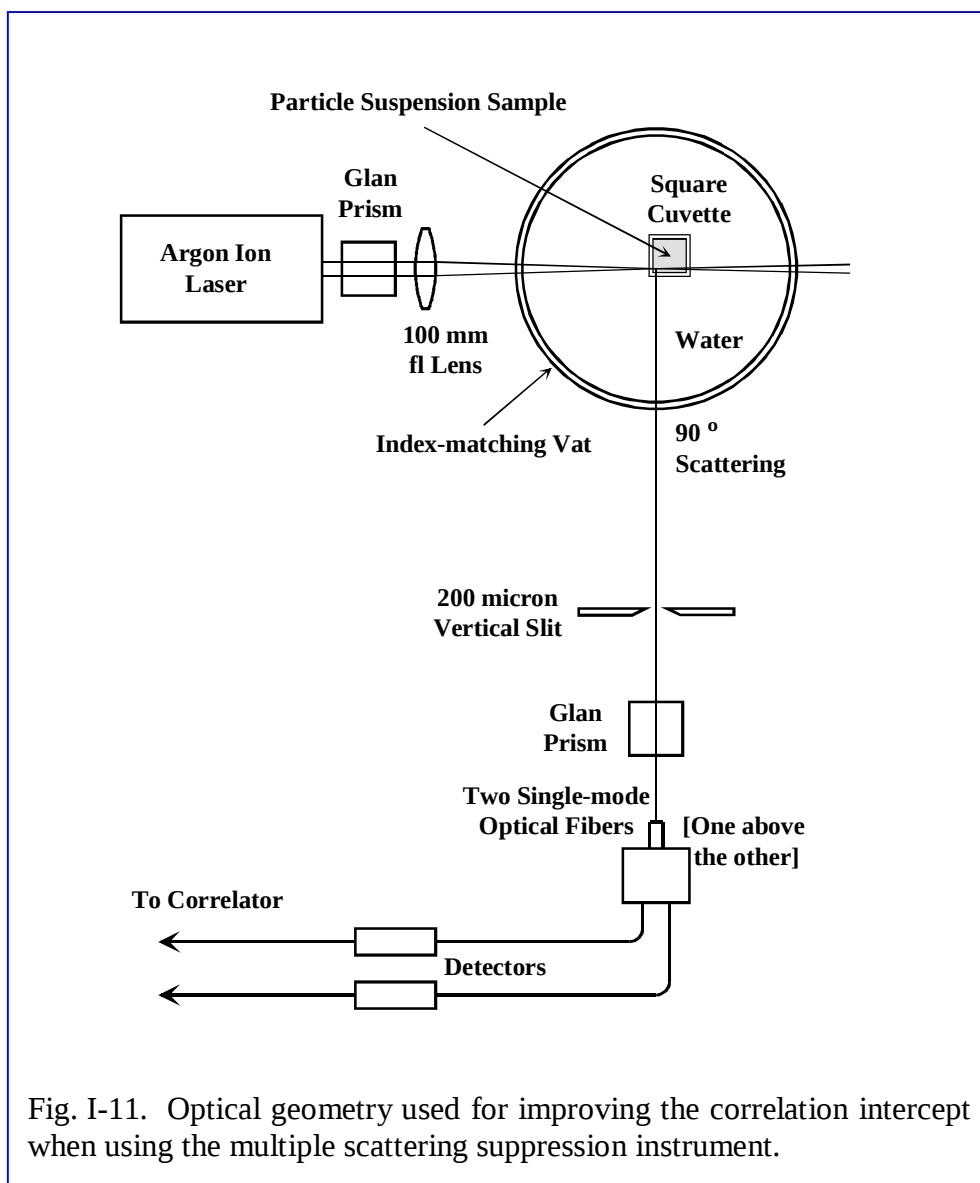
correlation functions acquired in times not significantly longer than those conventionally used for auto-correlation and dilute suspensions. This is the case even for the cross-correlated signal for the more concentrated samples, which have an extremely small signal amplitude. Both theory and our experience with samples having an even higher concentration than those shown in Fig. I-8 have shown that for the case of even higher concentrations either a longer run time or a smaller diameter sample cell may be required. Note that because of the rapid initial decay of the auto-correlation functions for the more concentrated samples, the near constancy of the zero delay time intercept is not apparent when the data are displayed as they are in Fig. I-6.

There appears a small, but noticeable drop in the particle sizes derived from cross-correlated data at the higher concentrations. Results of modeling for hard-sphere interactions are shown in Fig. I-10. For volume fractions below 5 % the difference between the piece-wise continuous model used by Pusey and Tough [33] and the Percus-Yevick model differ only in the third decimal place, and these models are nearly identical for our concentration range. However, neither of the models represented in Fig. I-10 accounts for ionic potential, which increases with volume fraction. Please note that FORTRAN software for the Beenakker-Mazur model, which works at higher concentrations than those shown in Fig. I-10, is provided in Appendix I-A. The hard-sphere interaction model shows the right trend to explain the droop, but this appears quantitatively insufficient to account for the changes seen in the effective particle size. Since all multiple scattering suppression schemes have some ‘leakage’ we have addressed this concern [34] by optical masking to remove some of the excess multiple scattering. For this we have also added a vertical slit, instead of the circular iris that was used for obtaining the data in Fig. I-8. With this approach, a significant additional improvement is realizable by examining the sample confined near the corner of a square cuvette. These two additions, shown in Fig. I-11,



result in much enhanced intercept values, that is, we can now use shorter data acquisition times to acquire for data of a similar quality. Alternatively, data of higher quality should now be obtainable from highly concentrated systems using the measurement times previously required.

With industrial applications in mind, we pursued using our multiple scattering suppression technique with these two additions changes when for rapidly sizing particles over a large range of concentrations. We were able to get reasonable diffusion coefficient measurements in two minutes, as shown in Fig. I-13, because the vertical slit blocked a significant amount of multiple scattering that would have been in the field of view on either side of the detection fibers and because there is less multiple scattering near the entrance of the sample cell. The improved intercepts obtained are shown in Fig. I-12. While the data that we acquired using measurement times longer than two minutes was of higher quality, a careful reacquisition of those same data sets could achieve data of similar quality in much less time by using the approach just outlined. Without belaboring this point, we will refer to our higher quality data to as we continue our



discussion.

To give some impression of the quality of the fits in Figs. I-6 and I-7, Fig. I-14 and Fig. I-15 shows deviation plots of the difference between fit and data, normalized by the amplitude A_1 of the decaying portion of the correlation function. Fig. I-14 is for the cross-correlation data of Fig. I-7 corresponding to sample concentrations of 0.2, 0.5, and 1.0 weight %.

Eq. (I.3) provides a good, but perhaps not perfect, description of the cross-correlation function when the detection of multiple scattering is suppressed. For comparison, Fig. I-15 displays similar plot for the three auto-correlation functions of Fig. I-6 for the same high concentration samples. As expected, these data are clearly and systematically non-exponential.

A quantitative measure of the overall scattering power of the various samples may be obtained from the fraction of the incident beam power transmitted through the 10.1 mm diameter samples. Results of our attempts to make such measurements for various concentration samples of the nominally 107 nm diameter particles are shown in Fig. I-16. The points show the results of two separate measurements of transmission for the same samples taken some weeks apart and with different optics. The measurement of the ratio of scattered intensity, I_s , (or power) to incident intensity, I_i , (or power) is referred to as the Beer-Lambert law when high concentrations are not involved. When high concentrations are not

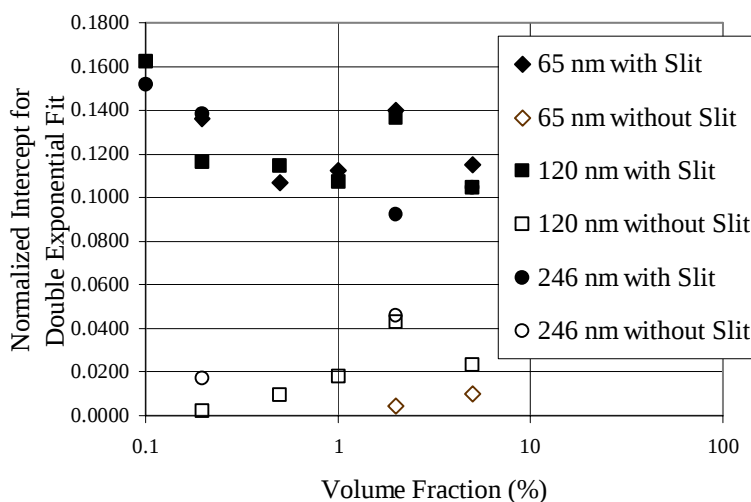


Fig. I-12. Normalized Intercept with reduced cross-correlation data acquisition time (raised correlation intercept value) after adding a vertical slit in front of the detection fibers.

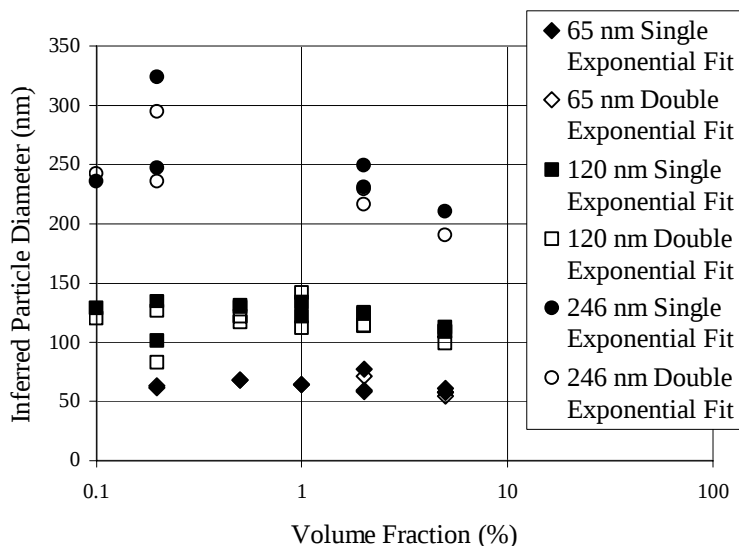


Fig. I-13. Particle diameter with reduced cross-correlation data acquisition time (raised correlation intercept value) after adding a vertical slit in front of the detection fibers.

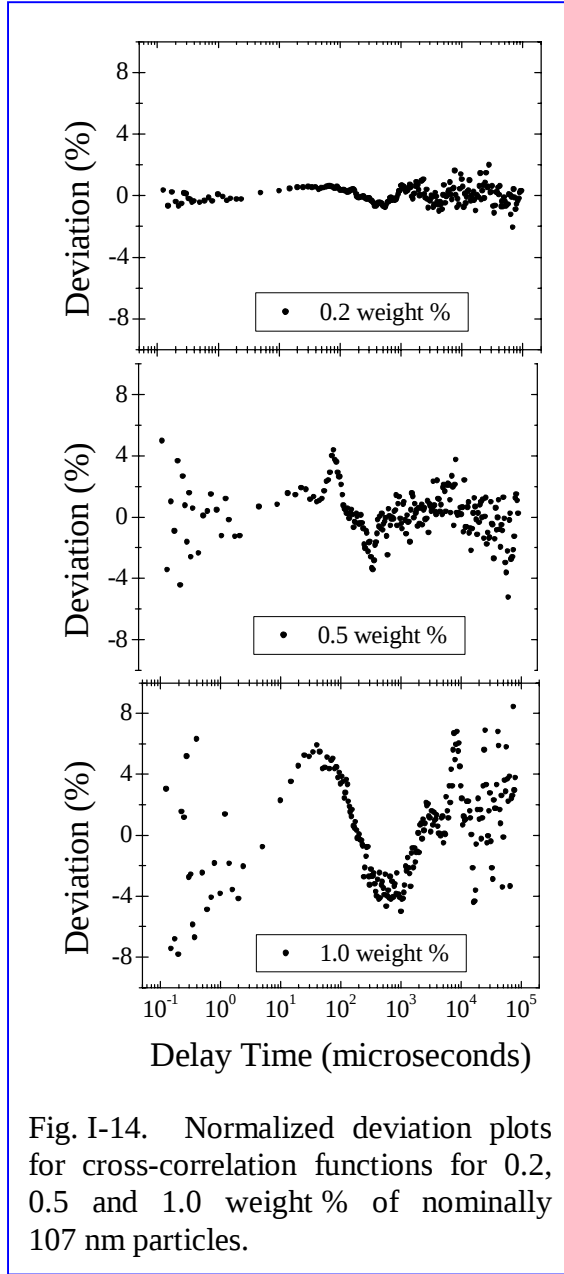


Fig. I-14. Normalized deviation plots for cross-correlation functions for 0.2, 0.5 and 1.0 weight % of nominally 107 nm particles.

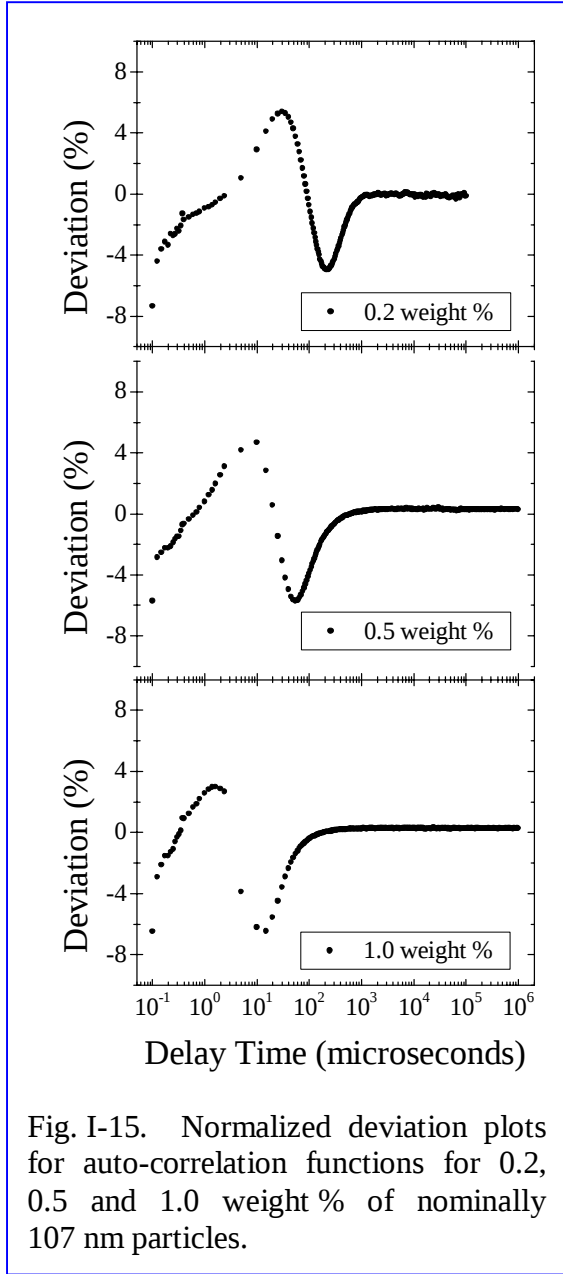


Fig. I-15. Normalized deviation plots for auto-correlation functions for 0.2, 0.5 and 1.0 weight % of nominally 107 nm particles.

involved this ratio is related to turbidity, τ^* , for the pathlength R , by $\frac{I_s}{I_t} = \text{Exp}[-R \tau^*]$. This is

related to the Rayleigh ratio, $\Re = \frac{I_s}{I_t} \frac{R^2}{V}$ (where V is the scattering volume), by the integration

of $\Re$ over the whole solid angle: $\tau^* = \int_{\Omega} \Re d\Omega(\theta, \phi)$ [35]. The solid curve in Fig. I-16 is

calculated from the theoretical Mie scattering cross-section. The calculated and measured results agree reasonably for concentrations below about 0.5 weight %, but above that concentration the measurements lie increasingly above the theory. We believe that the increasing excess of

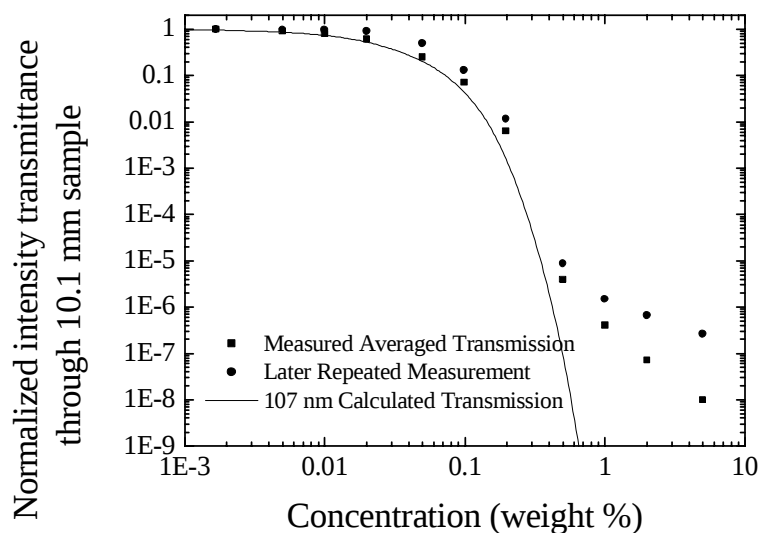


Fig. I-16. Measured and calculated transmittance through a 10.1 mm diameter sample cell containing particles of nominally 107 nm in diameter.

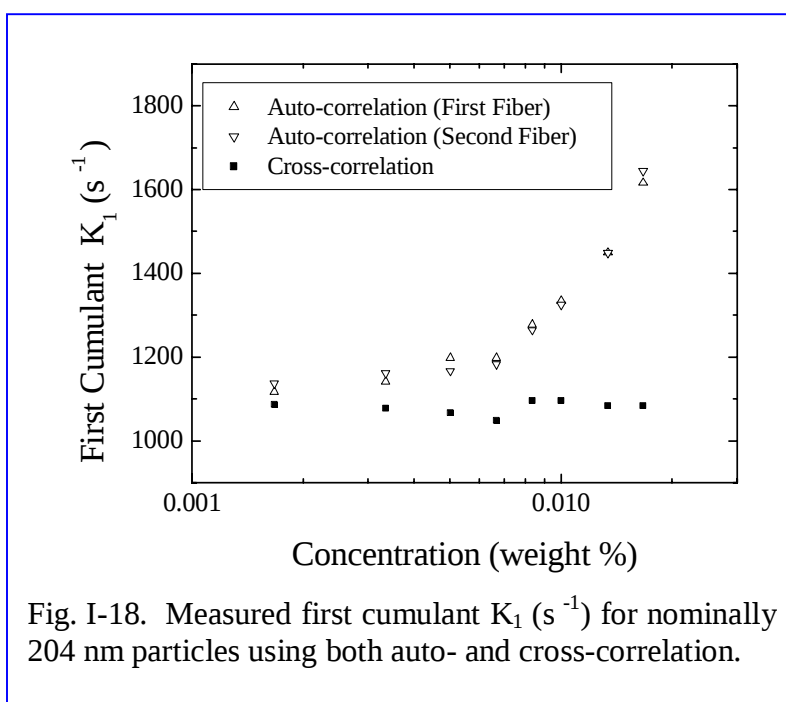
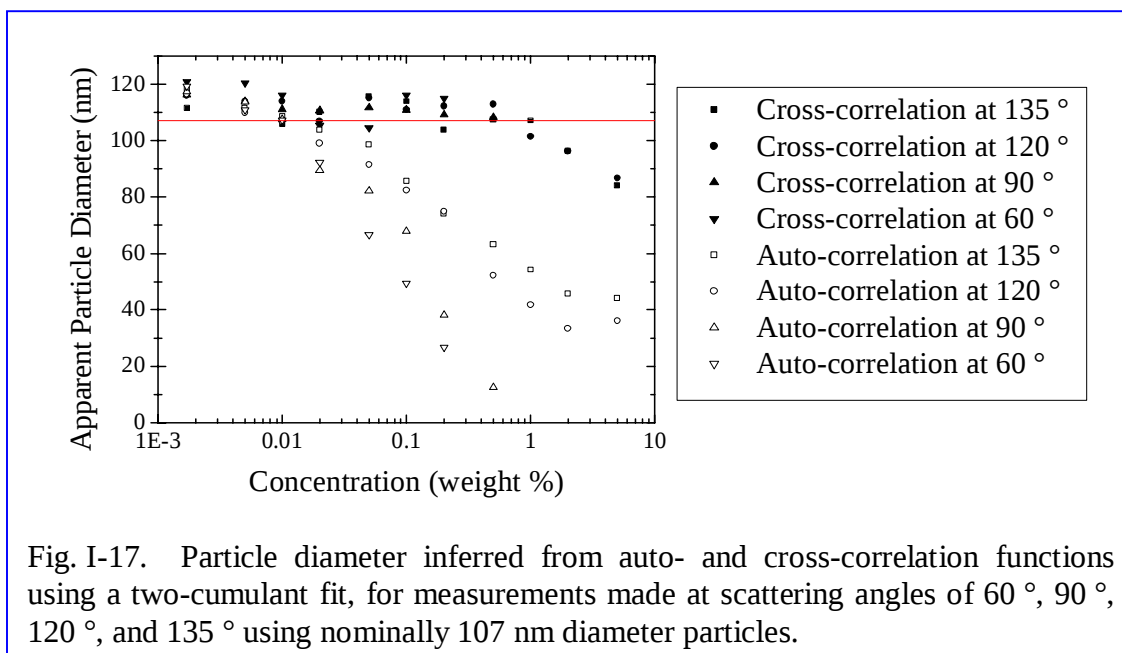
measured power over the Mie model is the result of the detector observing a small amount of scattered light, which becomes increasingly more significant as the transmittance reduces.

The main conclusion from these results is that even for samples transmitting less than one part per million of the incident power, spatial cross-correlation allows accurate determination of particle size. Note however, that under such strong scattering conditions most of the single scattered light detected must have originated within a millimeter or so of the point where the beam

enters the samples.

We now extend the measurements to angles other than 90°. We measured both auto- and cross-correlation functions for the same set of various concentration samples of the nominally 107 nm spheres at scattering angles of 60°, 90°, 120°, and 135°. These data were analyzed by fitting the correlation function using Eq. (I.3) as before, with A , B , K_1 , and K_2 adjustable. The apparent particle diameters are presented in Fig. I-17. The values of diameter inferred from the auto-correlation functions are severely influenced by multiple scattering for the higher concentration samples. They are also dependant on scattering angle, yielding a systematic underestimate of the particle size which gets worse as the angle is moved more to the forward direction. In contrast, values of diameter inferred from the cross-correlation functions show no systematic dependence on scattering angle even at the highest concentrations. However the values of diameter estimated from the cross-correlation functions do show a progressive decrease at concentrations of 1 weight % and above. This effect could arise from repulsive interactions among the particles, or it might be an artifact of our optical geometry.

To verify the applicability of the method to particles of a different diameter we present results in Fig. I-18 for 90° scattering from particles of a similar material but a nominal diameter of 204 nm. The stability of the first cumulant from the cross-correlation function, and hence the inferred particle diameter, as the suspension concentration increases to opacity, is encouraging. The rapid increase in value of the first cumulant from the auto-correlation functions shows the usual particle size underestimate from the auto-correlation function when multiple scattering is significant. The cross-correlation results correspond to a diameter of 214 nm in very reasonable agreement with the nominal value.



VLS-4. Discussion

Our experimental results demonstrate the promise of the new method of spatial cross-correlation originally proposed [16] and described by Meyer *et al.* [17-19]. The ability to make reliable easily interpretable dynamic light scattering measurements on strongly scattering samples is valuable in both basic research and in industrial applications. Examples of research areas where multiple scattering is significant, and measurements currently difficult, include the study of particle dynamics in

strongly interacting systems, critical point phenomena, and in vivo biological and medical studies. Examples of the many industrial applications include characterization of various slurries used for grinding and polishing, paint particle studies, sizing of particles in concentrated suspensions, and quality control of products which may involve colloidal intermediate stages.

In this text, we have emphasized and demonstrated the feasibility and reliability of the method as applied to colloidal suspensions. We have used simple collection optics consisting of adjacent bare fibers without collimation lenses. Each fiber collects light from along the entire sample,

which is not the most effective way to selectively discriminate against multiply scattered light. A better method might be to use collimating lenses to restrict the accepted light to that originating in a localized portion of the sample or, as we showed, placing a vertical slit in front of the detection fibers. Using bare fibers has the advantage, however, of being extremely easy. We calculated and confirmed experimentally that the distance of the fibers from the focus formed by the sample cell or the sample cell and its accompanying index matching vat is rather forgiving. The only critical alignment is the vertical alignment of the fibers so that the line joining the centers of their exposed faces is perpendicular to the beam. In practice we achieved this by rotating the fiber pair about an axis parallel to the fiber axes to maximize the amplitude of the cross-correlation function measured for a single scattering sample. No other alignment was necessary, and the fibers remained aligned for many months.

For isotropic particles, single scattering is highly polarized; multiple scattering is not. An analyzer allowing the fibers to accept only I_{vH} restricts the sensitivity of the cross-correlation function to multiple scattering only. This rather simple test was used to confirm that the chosen fiber spacing was adequate to suppress the multiple scattering contribution to the cross-correlation function. For our fiber spacing, corresponding to an angular separation of 1.5 mrad, the multiple scattering contribution was immeasurably small. By making such measurements as a function of the fiber spacing, or equivalently the angular separation of the two fibers, one can quantify exactly how the multiple scattering contribution to the cross-correlation function reduces with increasing fiber separation. Such measurements have been made both for I_{vv} and I_{vH} by Nobbmann *et al.* [24], using an arrangement nearly identical with ours, but with each fiber terminated by a collimating lens. Their results clearly demonstrate the correctness of the physical ideas which guided our invention of this technique, specifically the relatively much greater extent of single scattering speckle as opposed to multiple scattering speckle, in the direction transverse to the beam.

As our results show, the amplitude of the cross-correlation function relative to the baseline falls dramatically as multiple scattering increases (see Fig. I-9). This is because the baseline is proportional to the square of the detected total intensity, while the amplitude of the decaying portion is proportional to the square of the detected intensity from single scattering alone. This observation leads to the possibility of using the measured zero delay time intercept for cross-correlation to deduce the fraction of the total scattered intensity arising from single scattering. Specifically, the ratio of the measured intercept to its value for single scattering dilute from samples, is equal to the square of the ratio of the detected single scattered intensity to the total intensity.

Applying this reasoning to the data for the 1 weight % sample, for example, suggests that only about 4 % of the light reaching the detectors was singly scattered. If this sort of analysis proves robust in practice, spatial cross-correlation may make static light scattering measurements usefully quantitative even for very strongly scattering samples.

VLS-5. Future Applications in Volume Light Scattering

Considering future applications of our work on multiple scattering suppression, the obvious application of significantly extending the concentration range of dynamic light scattering has been augmented by the insights inspired by the recent availability of high brilliance X-ray sources from a synchrotron. A partially coherent beam of X-rays can now be formed to perform dynamic X-ray scattering (DXS) [23, 36-38] on length scales, until recently the sole domain of light scattering [7, 39]. The combination by Riese *et al.* [6, 23, 40-42] at UvA of the cross-correlated dynamic light scattering [18] introduced above with DXS and Small Angle X-ray Scattering (SAXS) allows optically opaque colloidal suspensions to be probed in a way that reveals novel physics: the phenomenon of hydrodynamic screening [40]. See Fig. I-19 on the next page for proof that dynamic cross-correlation and dynamic X-ray scattering obtain the same results in a multiple scattering solution, where dynamic autocorrelation breaks down.

We have also looked at combining cross-correlation with a local oscillator to address the ill-conditioning problems introduced by flare light [1, 2, 4, 31]. Essentially the local oscillator pushes the scattered light signal to an asymptotic limit and cross-correlation provides the added benefit of mitigating the affects of multiple scattering. The advantages of adding a local oscillator include an increased signal-to-noise, reduction of stray light effects, a larger allowed angular range and the ability to use smaller specimens due to the reduction of stray light effects, improved resolution of multiple particle sizes because only the cross-terms of the beating process are then significant, the signal no longer has to be Gaussian, and weak signals benefit from the gain supplied by the local oscillator [1]. While the gain of adding a local oscillator is significant, combining our cross-correlation technique described above to a local oscillator using monomode fibers and couplers for wavefront matching deserves future studies, as outlined by Meyer *et al.* [1, 2] and Smart *et al.* [4] in their papers and patent (pending).

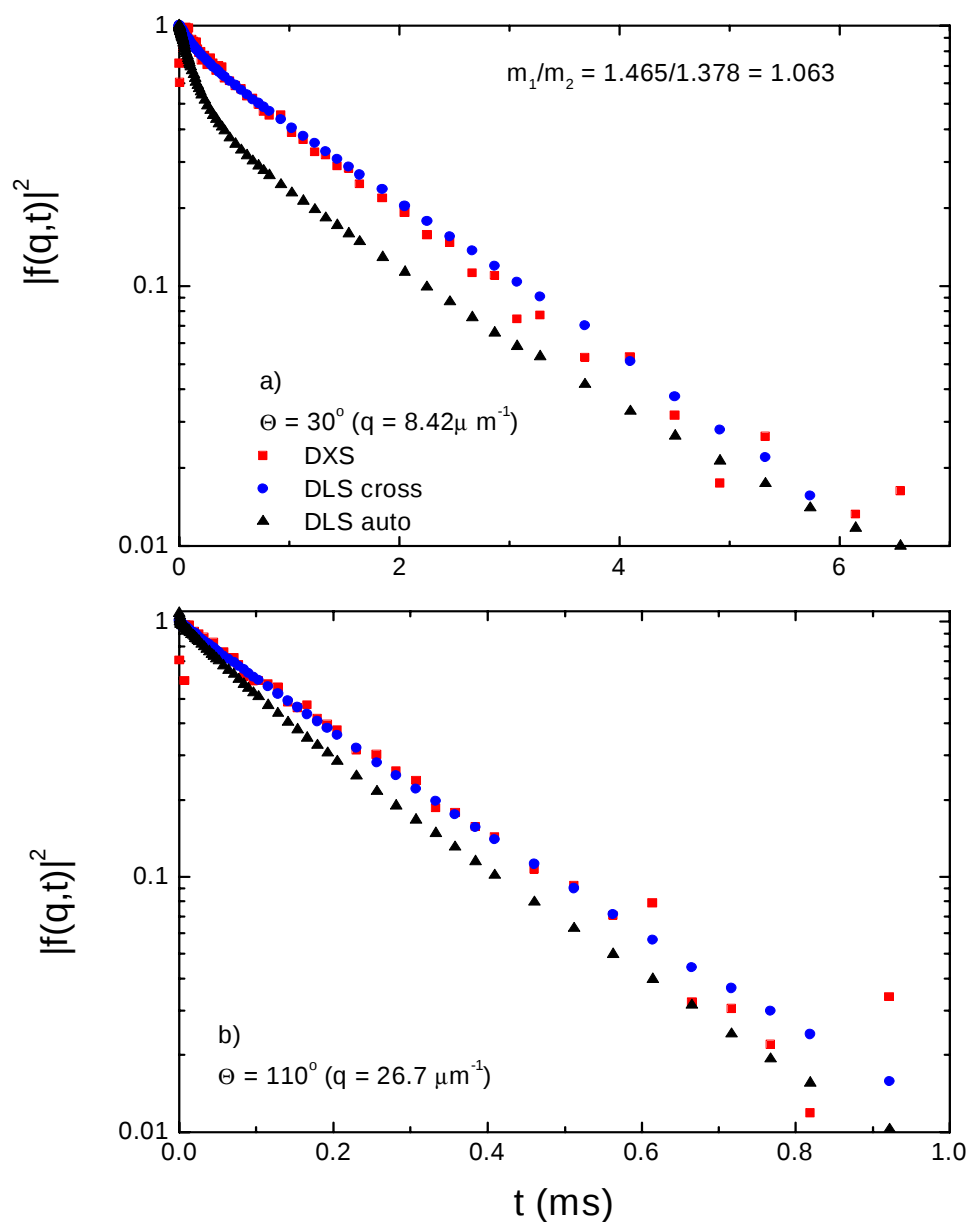


Fig. I-19. A comparison of Dynamic Light Scattering (DLS) using autocorrelation and cross-correlation with Dynamic X-ray Scattering (DXS). This shows that autocorrelation breaks down due to multiple scattering, which results from the difference in index of refraction of the particles (m_1) and solvent (m_2) and sample thickness traversed before exiting at a particular scattering angle in Fig. (a) being greater for much of the scattered light than in Fig. (b). Figs. I-19 (a) and (b) indicate results obtained for scattering angles of 30° and 110° , respectively. DXS is not susceptible to multiple scattering and provides the same results as our cross-correlation technique, *i.e.*, a straight line on a semi-log plot. Because of multiple scattering, the decaying exponential (whose semi-log plot is a straight line) is not the signature of the autocorrelated signal.

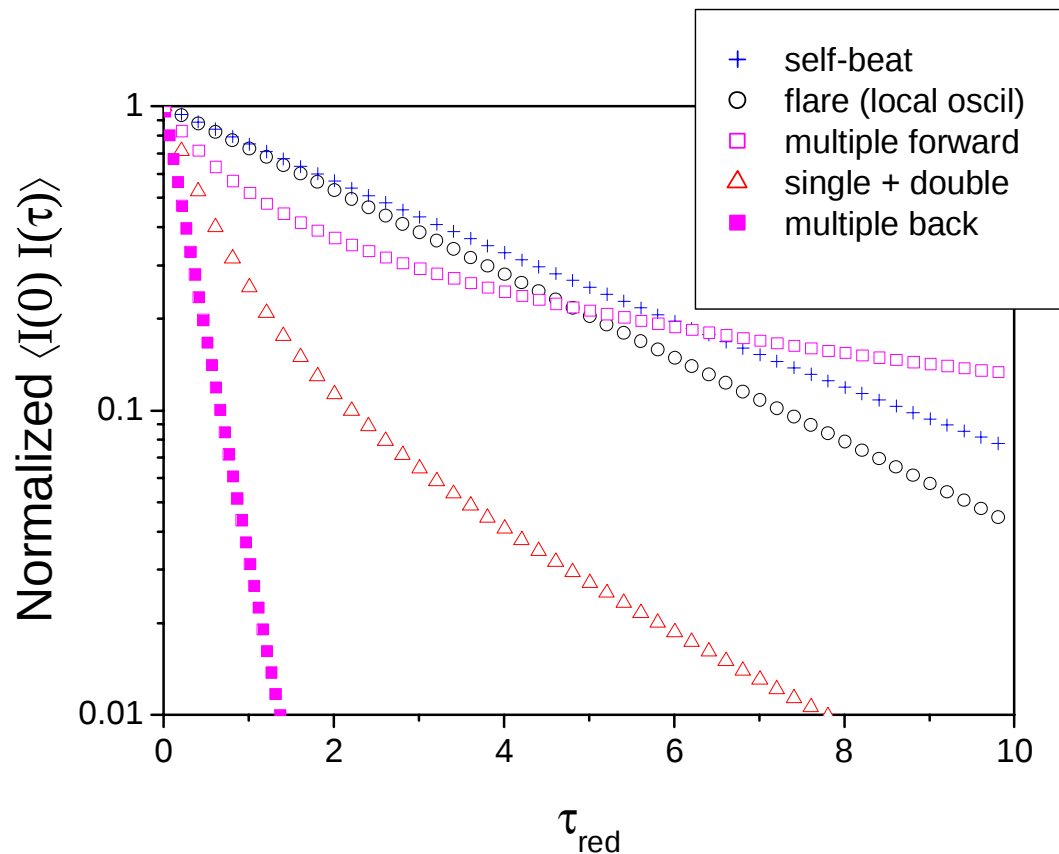


Fig. I-20. As noted above, in Meyer *et al.* [1, 2], and in Smart *et al.* [4], the addition of a local oscillator allows one to move out of the equation fitting region where small amounts of flare light corrupt the data analysis. Additional benefits of this approach are described in section VLS-5, which is entitled “Future Applications in Volume Light Scattering”. To aid in identifying the symbols in the figure above, only every 20th data point is shown for the hollow symbols and every 5th data point for the solid symbols.

VLS-6. Appendix I-A: Hard Sphere Diameter Compensations

Existing models for hard sphere interactions from Pusey and Tough, and from Percus and Yevick have been examined, in certain specific cases and up to a volume concentration of 0.075, and shown to be similar, but not identical. Circumstantial evidence was available from the original Applied Optics data and its reprocessed versions to suggest the importance of correction of measured diameter, using some external knowledge. To become useful, this work must be extended. The cross-correlation technique has now been sufficiently improved by using square cuvettes and optical masking slits to make better measurements in volume concentrations comparable with the limits of the above calculations, offering the possibility of empirical closure

where none was previously available. Also it would be useful to study the Beenakker model, which purports to handle higher concentrations, with a view to its correspondence with both the Pusey-Tough and Percus-Yevick predictions, in the regions where they have common territory. The Percus-Yevick source code used in Fig. I-10 is included as an Appendix on the CD ROM that accompanies this text.

Surface Light Scattering Spectroscopy (SLSS) – (Section II)

SLSS-1. Introduction and Background

We begin this section (Section II) with a discussion of the applicability of surface light scattering spectroscopy for measuring a wide range of interfacial parameters. This is followed by a presentation of our vibration mitigating design with its Fourier-optics-based [43-47] instrument function, which we use for the optics of our new surface-light-scattering spectrometer. There follows a sequence of discussions on how to apply the instrument function computationally, the use of the fast-Fourier-transform (FFT) algorithm to minimize uncertainty in the derived power spectrum, some of the standard analysis routines used in this paper, along with the results of our work with the surface response function (SRF), which is derived and included as Appendix II-C on the accompanying CD ROM. We follow this by comparing the results of some analysis routines, using data taken at a simple fluid interface. We then bring empirical and analytic closure to our surface-light-scattering instrument discussion by showing three-dimensional power spectrum plots of our data and theory for an asymmetric thin film of pentane on water, where the film thickness is varied using an accurate thermostat (temperature controller) designed and built at the University of Amsterdam. Our surface light scattering instrument allowed us to experimentally see a power spectrum bifurcation occur as a result of a change in the pentane film thickness on water (see Fig. II-24 and the paper by Fenistein *et al.* [48] for more details). This observation is supported by our SRF theory and its power-spectrum plots (see Fig. II-26, below). We provide the theoretical underpinnings elsewhere [5] and the several hundred typed pages of the computational derivation (included as Appendix II-D on the accompanying CD ROM) for our analytical SRF solution and results for the asymmetric double-interface problem provided later in this work.

The instrument function is an integral transform that relates the correlation function of surface fluctuations to the correlation function that is detected as a photocurrent fluctuation. The most general theory of surface fluctuations is derived through SRF formalism. We exploit both the formalism of the Meunier and Bouchiat SRF [49], and the stream and potential function SRF formalism first used by Mann for the forced wave experiment [50] and developed more extensively for SLSS the companion paper [5], which provides the theoretical background for the work discussed here in an experimental context. This SRF formulation provides a power spectrum, which is most easily fit to an experimental power spectrum. The experimental power spectrum is obtained from the correlator as a Fourier transform of its time-domain data into the frequency domain. The correlator is effective in providing an accurate approximation for the correlation function of the surface fluctuations. However, the FFT of such data to the frequency domain must be done carefully to avoid distortion due to finite record length, for example.

An argument can be made for transforming the SRF by FFT to a correlation function as part of the fit process. Unfortunately, an analytical transformation of the theoretical SRF does not appear possible as a result of a branch cut in the complex plane of the response function. A numerical procedure is possible. This thesis will put the emphasis on transforming the correlogram to an accurate approximation of the spectrogram. Here, we use the terminology that the correlogram is a point-wise, experimental representation of the theoretical correlation function.

The correlogram that is measured is a finite approximation of the correlation function; the correlogram is a random variable, whereas the correlation function is not. This property merits the inclusion of a weight factor in the maximum likelihood method used to determine the parameters in the theory of the correlations. This weight factor is determined empirically in this text and analytically in an accompanying paper by Smart *et al.* [4]. The results of applying the FFT to the correlogram to obtain a power spectrum is not exact and can be subject to errors, due in part to the finite length of the correlogram. This concern with the FFT and our approach for mitigating this concern is discussed below and is addressed in more detail in Ref. [4] and its references therein.

The principle of surface-light-scattering technology is the non-invasive detection of interference patterns caused by ubiquitous, small-amplitude surface waves that scatter an incoming laser beam. The process can be thought of as the scattering of photons by quantized surface waves called ripplons. The three-dimensional solid-state analog is the scattering of photons from phonons. The ripplon properties of wavelength and band shape can be established and related to surface tension, surface visco-elastic response, bulk viscosities, and densities, characteristics that act on the ripplons as the surface restoring forces and damping mechanisms.

Surface tension is an elusive phenomenon that controls many individual processes and everyday phenomena. For single-component simple fluids, it is the two-dimensional analog of pressure, and it acts to maintain the smallest possible surface area. When other components contribute to an interfacial film of monomolecular thickness, the surface tension must be generalized to the surface tension tensor [5]. Surface-light-scattering spectroscopy reports the dynamics that can be analyzed in terms of this more general surface property [5]. This paper will deal analytically with both simple and complex interfaces; the generalization to complex interfaces has been written about by several authors [43], [5], [49], [51], [50]. While the stream and potential function approach was first used in Ref. [50] for driven waves, it has now been analytically generalized for complex interfaces discussed and outlined herein and in more detail by Mann *et al.* in Ref. [5] (see Appendix II-D on the accompanying CD ROM for the full derivation).

SLSS-2. Uses for Surface Light Scattering Spectroscopy

While NASA's interest in funding this development through its Advanced Technology Development program is to support possible space experiments, such as, critical point studies, surface wetting, free-surface phenomena experiments, pool boiling experiments, surface tension induced instabilities experiments, and surface tension driven convection experiments, the University of Amsterdam and Case Western Reserve University see this work leading to an instrument also capable of ascertaining fundamental fluid interface properties on earth. These include the properties of simple fluids, fluid-fluid interfaces, and the forces acting between the interfaces, as in wetting films, namely, the Van der Waals forces and the fluctuation-induced critical Casimir forces.

Surface properties affect cooking, cosmetics (improved formulation), tertiary oil recovery (20 to 30 % more oil can be pumped from the ground), detergents (better wetting of fibers),

controlled release and targeted drug delivery (for example, liposomes, that can determine what travels through cellular surfaces), materials processing, such as steel making, and many other activities. This instrument provides not only a non-invasive measurement of surface tension from which surface temperature can be extracted but also information about volume viscosity close to the interface for simple liquids.

SLSS-3. Instrumentation

For many years now surface light scattering has held the promise of being an easy way to non-invasively measure the surface tension and viscosity of a fluid–fluid interface (either liquid–vapor or liquid–liquid). When optical access to a fluid surface is available, this technique should be both quick and easy and also free of difficult calibration protocols. Yet until recently a number of problems have plagued the implementation of this technique. External vibrations have been one of the major problems, since small vibrations have often caused the scattered signal and grating spots coming from the fluid interface to move back and forth across the face of the detector, an optical lever effect. The reflected or transmitted laser beam has a Gaussian intensity profile, so angular movement of the reflected and scattered light causes the intensity being measured at the detector to change, and this in turn shows up as the addition of a low-frequency modulation indistinguishable from the data. At times, external vibrations can cause the signal to be lost completely, showing that no data is better than bad data for improving an instrument design. To address this problem, some researchers have had entire sections of the building housing their laboratories floated upon pylons sunk into the earth; alternatively one can use an active control table to help eliminate slosh or use an actively controlled mirror to control the reflected beam direction to eliminate this effect; these approaches come with considerable cost or complexity. We report here a new remedy for vibration problems that addresses external vibration concerns.

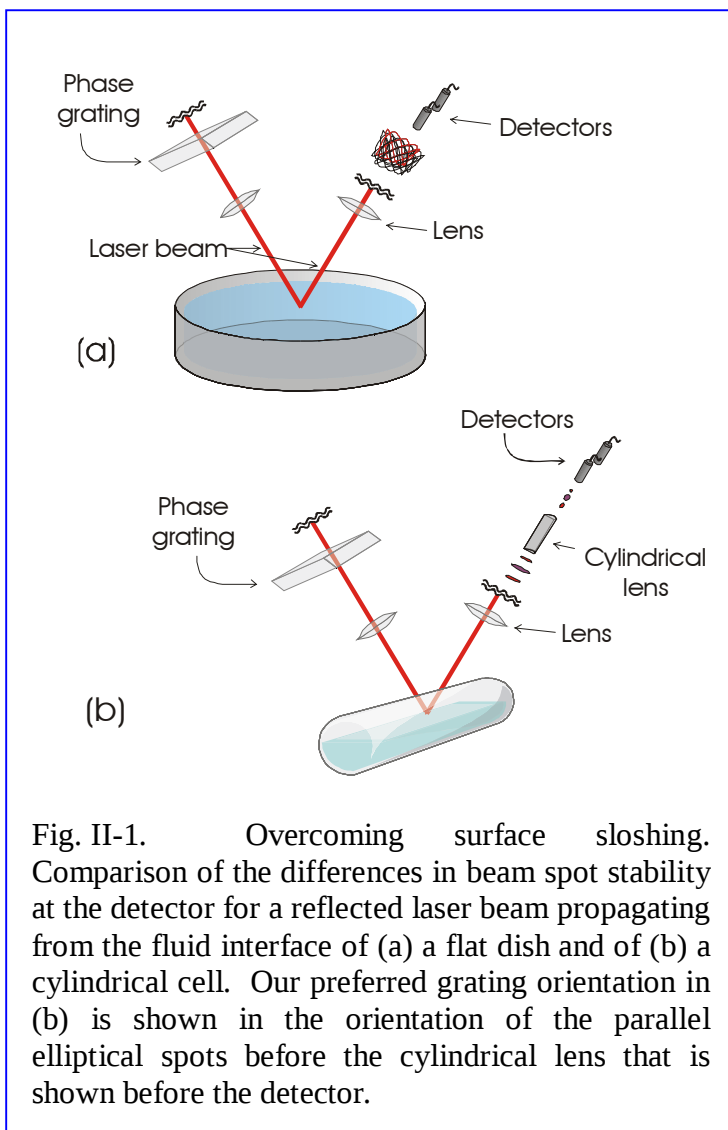


Fig. II-1. Overcoming surface sloshing. Comparison of the differences in beam spot stability at the detector for a reflected laser beam propagating from the fluid interface of (a) a flat dish and of (b) a cylindrical cell. Our preferred grating orientation in (b) is shown in the orientation of the parallel elliptical spots before the cylindrical lens that is shown before the detector.

SLSS-3.1 Traditional Instrument Design and the Problem with External Vibrations

To help explain the problem, before presenting a solution, we introduce a typical surface light scattering instrument setup. This is shown in Fig. II-1 (a). We choose to image a phase grating (amplitude gratings also work) onto the liquid interface to pick out a narrow range of wavelengths on the fluid surface for detection. Note that the same information can be obtained by either using a lens to project through the interface or by reflecting from the interface, where both approaches deliver an optical Fourier transform of the grating at the detector. Our design has an f-number that is relatively forgiving to changes in the interface height that result from evaporation, ocean wave studies, etc. Moreover, an instrument function can be derived that simply requires knowledge of the grating constant, the beam diameter (its shape at the interface) and the magnification of the optical system [see Eq. (II.1), below].

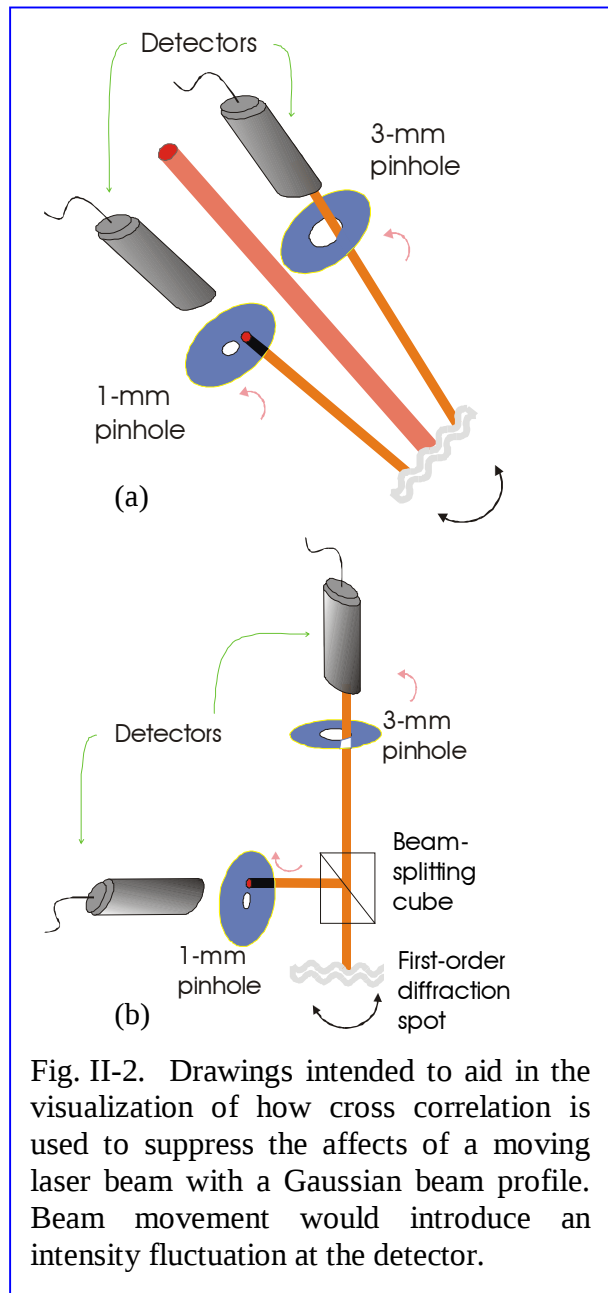
The operation of the surface-light-scattering spectrometer can be understood by recognizing that the surface fluctuations behave much like a weak phase grating. Since a fluid has a temperature above absolute zero, thermal fluctuations generate an ensemble of capillary waves (ripples) that do or do not propagate on the interface and damp out in space and time. It has been shown that all wavelengths exist at the fluid interface down to molecular scales, where these later wavelengths have been detected using X-ray reflectometry. The ripple field modulates the image of the grating so that only a narrow range of capillary wavelengths is detected at the first- (and higher-) order spots. When the fluid surface does tip or slosh because of external vibrations the grating spot and the scattered light of the same wavelength move together. This ensures that, except for the intensity modulation of the optical lever effect caused by external vibration, only a narrow range of wavelengths defined by the grating is detected. To optimize the homodyne gain provided by the grating spot without exceeding the dynamic range of the detectors, we used a set of low-efficiency holographic phase-gratings that were fabricated for us by L. Lading's group while he was at the Risø National Laboratory in Denmark. To limit the amount of noise at the detector, a small-diameter (as large as 3 mm) detector is used to collect the light scattered by the wavelengths that match the grating wavelength (and spot size). Because the zero- and first-order spots from the grating, typically $250 - 1500 \text{ cm}^{-1}$ (we often magnify the later to bring it down to 500 cm^{-1}) are so close together, a second lens system is used to separate these beams. It is important that the detector capture the entire first-order spot in the direction perpendicular to the grating lines. Our instrument function assumes this intensity to be Gaussian, which it is in our design.

With a small-diameter container, the surface tipping and sloshing that comes from external vibrations is significantly reduced; or when appropriate wetting conditions exist the liquid may be spread as a thin film (approximately a mm thickness range) on a substrate such as glass. However, when the container diameter is reduced, the surface tension that we are trying to measure causes the fluid to form a meniscus that turns the surface into something like a spherical mirror. This changes the parallel spacing between the grating lines that are being imaged onto the interface in a way that is functionally akin to a Mercator projection of the earth, where the Earth's Polar Regions are stretched on a flat map. This would give us a large spread in wavelength resolution (the range of q values). We now discuss the optical approach devised by Meyer to address this concern.

SLSS-3.2 New Instrument Design to Mitigate External Vibration Problems

One instrument design uses a cylindrical cell and cross correlation to suppress unwanted low-frequency contributions introduced into the signal by external vibrations. This design permits the use of a much-smaller diameter container. An approximately 25-mm-diameter cylindrical cell (with an optically uniform and thin wall) minimizes the meniscus-induced curvature in one dimension. By aligning the projected fringes perpendicular to the axis of the cylinder, we simply elongate the grating lines without changing their parallelism. This optical effect is shown in the bottom of Fig. II-1 (b). This also ensures that the spacing between the image lines does not change as a function of scattering angle, which is not a concern when a backscatter or forward-scatter (*i.e.* – transmission) mode is used. If the grating spots at the detector have been elongated into lines by the equivalent astigmatism of the curved surface, they can be refocused to points at the detector with a cylindrical lens, thus recovering much of the power density. Using a cylindrical cell (or equivalent pinning edge) addresses the problem of surface sloshing in one dimension normal to the cylinder axis. Even though the cylindrical geometry by itself reduces slosh both around and along the cylindrical axis, the addition of cross correlation can be used to address any residual surface sloshing problems along the axis of the cylinder.

We have tried two cross correlation approaches for addressing the surface tipping (sloshing) problem along the axis of the cylindrical sample cell. With a different size pinhole in front of each detector, one can cross-correlate either the +1 and –1 first-order grating spots or one can beam split one of the first-order spots and cross-correlate its two images. For either cross-correlation approach to be effective, a different size pinhole (< 3 and 3 mm in diameter for our detector distances) is placed in front of each detector (Fig. II-2). Cross correlation only exploits the signals that are common to both inputs and this is used to advantage. When the +1 and –1 first-order grating spots are cross correlated, while the grating spot being observed by the detector with the big pinhole is moving off of the detection area of this detector, the other detector with the smaller pinhole has already completely masked this grating spot. This also occurs when only one of the



first-order spots and a beam splitting cube are used. When a beam-splitting cube is used and the detector with the small pinhole is in play, as the Gaussian intensity profile of the reflected and scattered beam starts to move off the small pinhole, the detected grating spot at the other pinhole moves in the opposite direction. We have verified both cross correlation approaches empirically. By combining the use of a cylindrical cell and cross correlation, we have been able to mitigate the presence of spurious low-frequency information in the data where it would otherwise distort the correlogram and its associated power spectrum. In our experience, simply using the cross-correlation technique with a large container (without the advantage of a cylindrical cell), does not allow the grating spots to remain positioned on the detectors long enough to acquire a good signal in a reasonable amount of time (seconds to minutes). The combination of these two instrument design features allows a good signal to be acquired in a short time, even when external vibrations are present. For samples that do not have a low viscosity by nature, the technique of using a cylindrical cell, an appropriately oriented grating, and autocorrelation will often suffice. This implies that along with grating orientation little more than the bottom half of the cylinder or an equivalently shaped pinning edge may be all that is actually required to address surface sloshing problems in many experiments.

Note that when correlating, one must be sure that a significant temperature gradient does not exist perpendicular to the grating lines that are being projected onto the surface. This is because in this case ripples traveling to the right and those traveling to the left for underdamped fluids can lead to a power spectrum composed of two shifted Lorentzians (those of both the measured positive and “negative” frequencies) that do not perfectly overlap.

SLSS-4. Analysis and Experimental Results

SLSS-4.1 Instrument Function Advances

In addition to the problems with external vibrations, instrument function effects have limited the widespread use of surface-light-scattering hardware. One must trade-off between a relatively large laser beam power and large spot size at the fluid interface, which requires no instrument function correction, and a good signal-to-noise ratio in the correlogram. A large spot size diminishes the modulation depth in the correlation function, as a result of adding more signals that are not in phase (the central limit theorem). By providing an analytical formula, based on first principles, for the instrument function we can use a reasonable spot size and laser power (~ 1 mm, 100 mW) while still acquiring clean data in seconds to minutes. This instrument function provides accurate results and is derived from a Fourier optics analysis based on the paper of Lading, Mann and Edwards [44], [45], [47]. Its only approximating assumptions are that the beam profile is Gaussian and that the optical system is paraxial, which are the case experimentally.

When a collimated Gaussian laser beam is sent through a grating and projected onto a fluid interface, the size of the resulting spot size at the fluid interface is connected with the angular resolution of the waves propagating through the grating. A small spot size (like the approximately mm one we often use) leads to a spread in detected q values. To understand this, imagine seeing the resulting beats when sliding two identical parallel-ruled moiré patterns over

each other when their lines are parallel. Then repeat the experiment while rotating one of the moiré patterns through a small range of angles. Viewing this through a small hole (like that provided by hole-punched paper) placed on top of the patterns and then repeating the experiment without the hole present is like watching a changing grating image spot size being imposed on the moving ripples; in this way, it is possible to see the spread in q values or, equivalently, the change in angular resolution allowed to reach the detector. When this spread in capillary wavelength is present it is possible to model it by Fourier analysis. This spread in detected ripplon wavelengths at the detector can and must be corrected by applying an instrument function. The imaging system we advocate provides an instrument function that is simple to analyze. When the grating is placed before the surface (which is preferred since a sloshing surface no longer passes the probe light through the grating at different angles, effectively changing its line spacing), essentially all of the important instrument function effects take place at and before the fluid interface. The significance of the instrument function can be gauged by a dimensionless parameter, referred to as N , which equals the grating constant times the beam

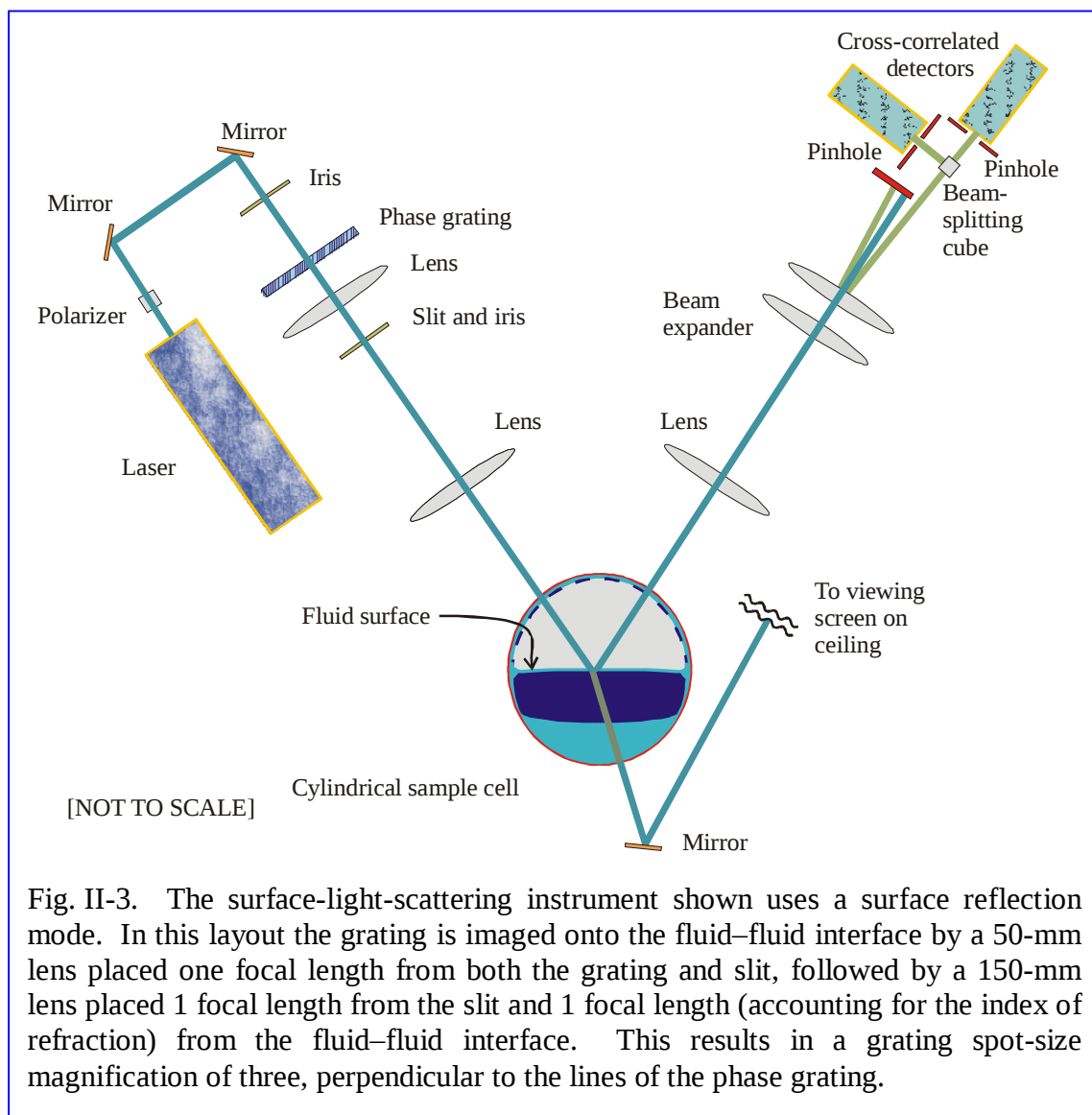


Fig. II-3. The surface-light-scattering instrument shown uses a surface reflection mode. In this layout the grating is imaged onto the fluid–fluid interface by a 50-mm lens placed one focal length from both the grating and slit, followed by a 150-mm lens placed 1 focal length from the slit and 1 focal length (accounting for the index of refraction) from the fluid–fluid interface. This results in a grating spot-size magnification of three, perpendicular to the lines of the phase grating.

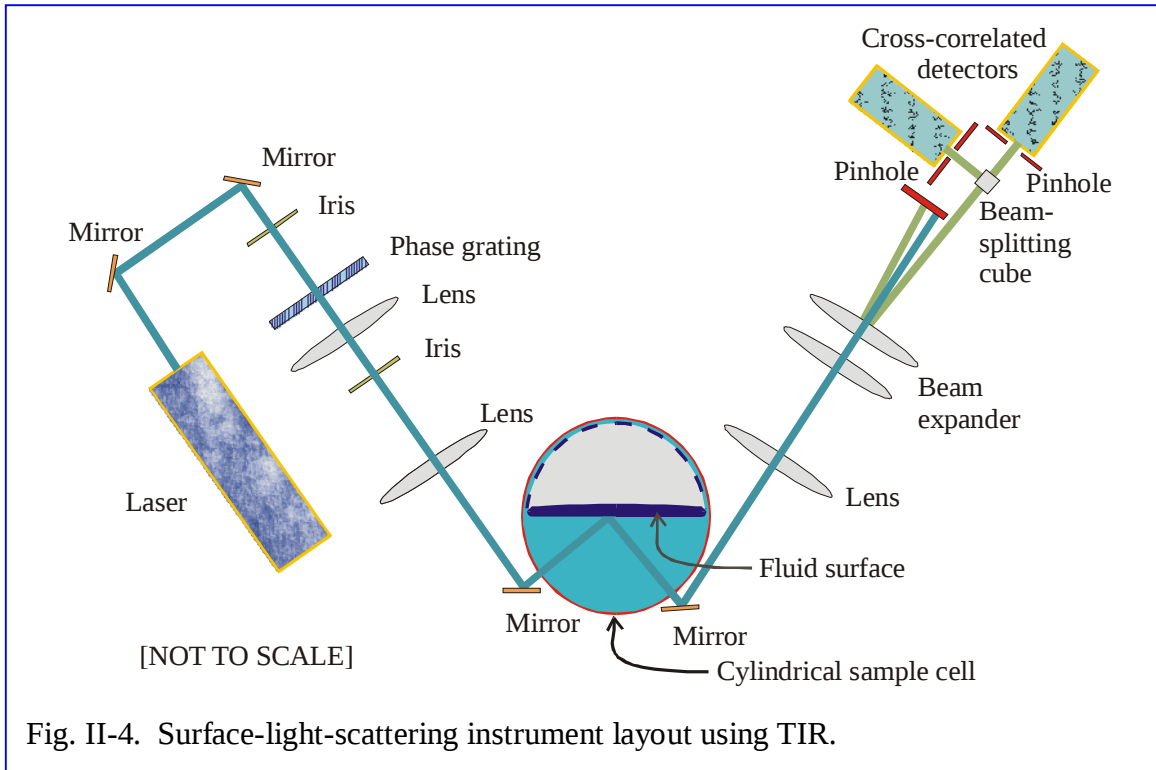


Fig. II-4. Surface-light-scattering instrument layout using TIR.

diameter at the grating and is a measure of the number of grating lines projected onto the surface [43]. This is equivalent to measuring N at the fluid interface after magnifying the beam diameter (which demagnifies the grating constant by an equal amount). The Fourier analysis published in several papers [44], [45], and [47] traces the effects on the laser beam as it passes through the grating, lenses, interface and finally reaches the detector. See Figs. II-3 and II-4 for a schematic of the general optical design. Please note that a total internal reflection version of the instrument shown in Fig. II-4 was needed to acquire the thin-film data presented in Fig. II-24 below. This design was used to avoid reflux problems at the upper glass interface and it also provided a much stronger signal at the detectors (~ 25 times stronger than for the reflection mode), which for many applications provided the possibility of shortening the data acquisition times from minutes to seconds.

This leads to an instrument function equation like that obtained by Edwards *et al.* [43], Lading *et al.* [44], Mann [47], and Meyer *et al.* [45], which has the form of $R_i = \int_{A_d} F^2 R(q, \tau) d\mathbf{q}$. The beam is Gaussian so that when A_d is sufficiently large the integral can be taken to infinite limits without an appreciable loss in accuracy, if the beam is not sloshing on and off the detector(s). We show the application of this instrument function in the backscatter and transmission modes in our Applied Optics paper [47]; these equations can be extended to allow for the rotation of the grating by an angle ϕ_g , where ϕ_g is 90° in the instrument setups shown in Figs. II-3 and II-4. The traditional kernel of the instrument function given by Edwards *et al.* is [43]:

$$F^2 = Q^2 \exp \left[- \left(\frac{\sigma_{gMag}}{\epsilon_x} \right)^2 (K_s - q_{sx})^2 \right] \exp \left[- \sigma_{gMag}^2 (q_{sy})^2 \right], \quad (II.1)$$

where F is the kernel of the surface light scattering instrument function, Q is an instrument scaling factor that includes factors such as the quantum efficiency of the detector (Q can be set equal to 1 for our purposes), q_{sx} is the surface wave number in the x direction always taken in the plane of the interface perpendicular to the grating lines, q_{sy} is the surface wave number in the y direction taken in the plane of the interface parallel to the grating lines, $\epsilon_x^2 = \cos^2 \theta_x$, where ϵ_x is the cosine of the angle between the surface normal and the incoming laser beam for a flat interface (experimentally, it also accounts the ellipticity of the beam spot at the interface, which can be affected by surface curvature which elongates the grating lines when using geometries like Fig. II-3), σ_{gMag} is the magnified beam width just before the surface, normal to the magnified beam propagation direction, and K_s is the wave number of the grating in the plane of the fluid interface. We rewrite the Edwards' instrument function, Eq. (II.1), in a form that will later allow easy comparison with the enhanced instrument function:

$$F^2 = Q^2 \exp \left[- \left(\frac{\sigma_{gMag}}{\epsilon_x} \right)^2 \left((q_{sx} - K_s)^2 + (\epsilon_x q_{sy})^2 \right) \right]. \quad (II.2)$$

After about 80 pages of algebra (included as Appendix II-A on the accompanying CD ROM), W. Meyer (with assistance from J. Lock) produced an enhanced instrument function, which handles both the traditional grating orientation and the rotated grating used with the cylindrical cell design for working correctly with scattering angles other than backscatter and forward scatter angles. Please note that for backscatter and forward scatter angles the grating orientation provides the same results when a flat interface is being measured; this is a result of the grating spot being circular, rather than elliptical. When the interface is not flat, than an additional distortion arises (see Edwards *et al.* [43]), which is relatively easy to correct for when using a cylindrical cell and a grating line orientation perpendicular to the cylindrical cell axis so that the grating constant remains unchanged, but elongated. For a grating oriented with its lines parallel to the cylindrical cell axis (which is not what we are advocating here) the periodicity of the grating can be distorted by a cylindrically curved interface. Our preferred grating orientation has obvious advantages over a traditional cell, since the traditional round dish with its potentially spherically curved interface produces a spread of k values at that interface. The use of adaptive optics may provide the ultimate “simple” solution by allowing the image of the grating to be preconditioned in such a way that parallel grating lines result on any stable surface, allowing the surface properties of fluid drops (even levitated molten metal drops) to be measured. When simply imaging a grating onto an interface, only the positive q grating orientation is used in the data analysis program (about seven megabytes of *Mathematica*[®] source code written by W. Meyer) that was developed for this work and included as Appendix II-F on the accompanying CD ROM. Also note that for the coordinate system orientation used in the data analysis program, we have changed the sign on the “ $\epsilon_x K_{sy}$ ” term given in the final result of the instrument function derivation to match the coordinate systems of the surface response function and instrument function. This change of sign in the instrument function simply interchanges the first-order grating spots so that the positive q values are used for both the surface response

function and the instrument function. This selects the correct direction of the propagating capillary wave (the negative q values provide zero signal for the present surface response function coordinate system) since only the appropriate first-order spot (+ q) acts as a local oscillator for the surface response function spot that we are correlating. When the y-axis grating orientation term is included (represented by the $\mathcal{E}_x K_{sy}$ term in Eq. (II.3)), an enhanced instrument function is written as:

$$F^2 = Q^2 \exp \left[- \left(\frac{\sigma_{gMag}}{\mathcal{E}_x} \right)^2 \left((q_{sx} - \mathcal{E}_x K_{sx})^2 + (\mathcal{E}_x q_{sy} + \mathcal{E}_x K_{sy})^2 \right) \right] + \exp \left[- \left(\frac{\sigma_{gMag}}{\mathcal{E}_x} \right)^2 \left((q_{sx} + \mathcal{E}_x K_{sx})^2 + (\mathcal{E}_x q_{sy} - \mathcal{E}_x K_{sy})^2 \right) \right] \quad (II.3)$$

Eq. (II.3) includes a term for the -1 spot from the phase-grating and for the $+1$ spot from the physical phase-grating. We rotate the coordinate system for the instrument function to match our algorithms (which use the $+1$ spot from the phase-grating) and obtain:

$$F^2 = Q^2 \exp \left[- \left(\frac{\sigma_{gMag}}{\mathcal{E}_x} \right)^2 \left((q_{sx} - \mathcal{E}_x K_{sx})^2 + (\mathcal{E}_x q_{sy} - \mathcal{E}_x K_{sy})^2 \right) \right]. \quad (II.4)$$

For the surface light scattering instruments shown in Figs. II-3 and II-4, the grating for the enhanced version of the instrument function is either orientated along the x-axis or the y-axis, which turns K_s in Eqs. (II.1) and (II.2) into either K_{sx} or K_{sy} . In this case the grating is rotated so that its orientation is either perpendicular to or parallel to the scattering plane, where K_{sx} is set to equal the grating constant at the surface then K_{sy} is equal to zero, and vice-a-versa. The $\mathcal{E}_x$ term in $\mathcal{E}_x K_{sx}$, in Eq. (II.3) above, disappears when we define K_s to be the projection of K_{sx} in the interface ($\mathcal{E}_x K_{sx} = K_s$ and $K_{sy} = K_s$). This accounts for the remaining difference in the two instrument function formulations when we include the rotated grating orientation term $\mathcal{E}_x K_{sy}$. The $\mathcal{E}_x$ in the equations accounts for the ellipticity of the grating spot at the fluid interface; this impacts the value of K_{sx} detected at the interface by changing the spacing between the grating lines when the grating lines are oriented perpendicular to the scattering plane; this spacing between the grating lines is not changed at the interface when the grating lines are oriented parallel to the scattering plane, hence the projection of q_{sy} does not change with angle. We note that $\sigma_{sx} = \frac{\sigma_{gMag}}{\mathcal{E}_x}$ represents the major axis of the elongated ellipse projected onto the fluid interface when the laser beam illuminates the fluid interface at an angle. K_{sx} is changed to a smaller value at the fluid interface by a factor of $\mathcal{E}_x$ when projected onto the surface at an angle. σ_{sy} , the minor axis of the elongated ellipse projected onto the fluid interface, and q_{sy} are not affected by the scattering angle. For actually implementing the enhanced surface light scattering

instrument function, it is simpler to define ϕ_g as the angle of orientation of the grating, which accounts for the angle between the direction of the grating lines and the scattering plane of the incoming and detected light. We can then write the enhanced kernel of the instrument function as:

$$F^2 = Q^2 \exp \left[- \left(\frac{\sigma_{gMag}}{\varepsilon_x} \right)^2 \left(\left(q_{sx} - K_s \left| \cos[\phi_g] \right| \right)^2 + (\varepsilon_x)^2 \left(q_{sy} - K_s \left| \sin[\phi_g] \right| \right)^2 \right) \right]. \quad (II.5)$$

We need to take the absolute value of the $\cos[\phi_g]$ and $\sin[\phi_g]$ terms to ensure that the correct first-order instrument function grating spot is maintained, regardless of grating rotation direction, for the direction of the surface wave we have selected to correlate at the fluid interface (for the selected sign, *i.e.*, direction, of q_{sx} and q_{sy} in Eq (II.4)). If we have the incorrect sign in the instrument function algorithm, we will not have a local oscillator to beat the scattered signal against, since ripplon waves traveling in one direction show up at one first-order grating spot and the ripplon waves traveling in the opposite direction show up at the other first-order grating spot.

Now we discuss the application of the instrument function to the surface response function. In the correlation data analysis program and in Appendix II-F (of the accompanying CD ROM) of this work, the application of the instrument function to both the correlation function and power spectrum is worked out and also applied to underdamped (propagating), critically damped, and overdamped systems (*e.g.*, using models like the damped cosine for an underdamped system).

Note that for the backscatter data shown in Tables II-1 and II-2, $K_s = K_g / M$ and $\sigma_s = M \sigma_g$ where M is a magnification factor that may include misfocusing effects, and that for our grating orientation $N = K_g \sigma_g = K_s \sigma_s$. Note that when N is independent of M , this allows the beam profile data collected close to the grating, g , to be used for estimating N with the cell in place. However the magnification M must be determined since K_s determines the ripplon wave numbers detected by the optical system. Additionally, when the grating lines are oriented perpendicular to the axis of the cylindrical sample cell, the angle of scattering and surface curvature changes resulting from surface tension changes with temperature (which can fit by floating the σ ellipticity parameter, ε_x , during data analysis) can affect the relationship for N between σ_g and σ_s . One of the advantages of using a cylindrical cell is that it does not change the parallel line spacing of the grating with changing surface tension, but elongates the grating lines and simply impacts the ellipticity of σ . Formula (II.5), like the Edwards' instrument function was derived for light reflecting from the top of the interface. When entering the sample cell from below, as we will choose to do with the water-pentane data (see Fig. II-4), the additional lensing effects of using a cylindrical sample cell can have an impact on the grating line spacing (with our grating orientation), and the index of refraction of the curved interface will significantly impact the value one back-calculates or measures for the length of the grating lines, *i.e.*, σ in the y-direction. This lensing effect can be mitigated by putting flat windows in the cylindrical sample cell, but the change of index encountered when entering the sample cell will still effectively move the liquid surface closer to the Fourier transform lens, thus changing σ in

both dimensions, if this is not compensated for by changing the optical path length. Should a non-cylindrical sample cell without a pinning edge or a levitated drop require a surface light scattering examination, adaptive optics could be used to image parallel grating lines onto the surface. Moreover, surface anisotropic behavior can be detected and measured by rotating the grating.

The instrument function is obtained after integration of the square of the field over the face of the detector. Since the Gaussian beam intensity can be ignored beyond the area of the detector, the limits of the integral can be extended over the entire plane. The result and the integral to be approximated in the time domain is

$$R_i(K_s, \tau) = (1/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R_{\zeta}[q, \tau] F^2[q_{sx} - K_s, q_{sy}] dq_{sx} dq_{sy}$$

when the grating lines are oriented perpendicular to the plane containing the incident and scattered light, and

$$R_i(K_s, \tau) = (1/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R_{\zeta}[q, \tau] F^2[q_{sx}, q_{sy} - K_s] dq_{sx} dq_{sy}$$

when the grating lines are oriented parallel to the plane containing the incident and scattered light;

(II.6)

and in the frequency domain this becomes a power spectrum that can be obtained by a Fourier transform on τ :

$$P_i(K_s, \omega) = (1/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_{\zeta}[q, \omega] F^2[q_{sx} - K_s, q_{sy}] dq_{sx} dq_{sy}$$

when the grating lines are oriented perpendicular to the plane containing the incident and scattered light, and

$$P_i(K_s, \omega) = (1/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_{\zeta}[q, \omega] F^2[q_{sx}, q_{sy} - K_s] dq_{sx} dq_{sy}$$

when the grating lines are oriented parallel to the plane containing the incident and scattered light,

(II.7)

where F^2 is the instrument function kernel given above, which is the same in both cases. From the definition of the dimensionless variable N , it is then clear that when N is sufficiently large, the kernel behaves as a delta-function and the undistorted correlation function and power spectrum are recovered. In practice this is reached when $N > \sim 50$. This corresponds to more than 50 grating lines focused on the interface inside the footprint of the laser beam. Practical spectrometers often work at $30 > N > 20$ so as to yield a reasonable signal-to-noise ratio in the correlogram. The correlation function for thermal fluctuations in surface elevation is required to complete Eqs. (II.6) and (II.7). The response function formalism [5, 44, 49, 51] (discussed below) provides an expression for the power spectrum that is not directly applicable in the time domain of the correlation function, whereas the early formulation of Mann [51] provides a general dispersion equation for determining the center frequency (ω_q) and decay coefficient (Γ_q), assuming a Lorentzian spectrum. Langevin [49] clearly points out the limits of this

approximation through the use of a type of capillary number, $Y=1/(2 N_{ca})^2$, where $Y=(\omega_0/\Gamma_0)^2$ and N_{ca} is the capillary number, with $N_{ca} = \frac{\omega_q}{|q|} \left/ \left(\frac{\gamma}{\eta_u + \eta_b} \right) \right.$, which is a ratio of velocities. Here Γ_0 and ω_0 are defined in terms of the properties of each liquid phase as $\Gamma_0 = 2 q^2 \left(\frac{\eta_u + \eta_b}{\rho_u + \rho_b} \right)$ and $\omega_0 = \left[\gamma q^2 |q| / \left(\rho_u + \rho_b \right) \right]^{1/2}$, where γ is the interfacial tension, ρ_u, ρ_b, η_u , and η_b are the density and viscosity numbers for the upper u and bottom b phases. If $Y > 100$, the ripples are propagating and the spectrum of the fluctuations is nearly Lorentzian. If $Y < 0.01$, the spectrum is again nearly Lorentzian, but the center frequency is zero, and the ripples are non-propagating. If $Y \sim 1$, the spectrum is no longer Lorentzian (but is propagating), and the spectrum derived from the SRF must be used (*e.g.*, Figs. II-19 and II-20). In this work we will analyze data from simple fluids. For simple fluids such as acetone ($Y = 826$) and water ($Y = 349$) the deviation from the Lorentzian spectrum is small. For ethanol ($Y = 61.3$) this might no longer be true. And for the water/glycerol mixtures that we discuss later, we will control the Y value by adjusting the concentration or temperature.

It is now practical to use the full spectrum function to fit data, which automatically takes into account deviation from a Lorentzian response. However, to provide a much more concise fitting function when presenting the implementation of the instrument function, the case for large Y is discussed next using a Lorentzian model. This also provides a pedagogical tool that makes contact with what has been done in the past. Assuming a sufficiently large Y , the autocorrelation function is to a reasonable approximation

$$R_\zeta = \frac{k_B T}{\gamma q^2 + g \Delta \rho} \exp(-\Gamma_q \tau) \cos(\omega_q \tau), \quad (\text{II.8})$$

where k_B is the Boltzmann constant, T the temperature, g the acceleration due to gravity, and $\Delta \rho$ the density jump across the interface. The two parameters sought from the correlograms, Γ_q and ω_q , are solutions of the dispersion equation that has the form

$$\hat{D} \left(\Gamma, \omega, q, \rho_u, \rho_b, \eta_u, \eta_b, \gamma \right) = 0, \quad (\text{II.9})$$

where $\hat{D}$ is the eigenvalue matrix, giving the complex eigenvalues of the problem. For more complicated interfaces other parameters are required. See Refs. [5, 43, 49, 51], and [50] for additional details and references to the original papers. The simple equation often used for fitting data in the time domain is for the Lorentzian model, therefore (using the case where the grating lines are oriented perpendicular to the plane containing the incident and scattered light)

$$R_i(K_s, \tau) = \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{K_B T}{\gamma q^2 + g \Delta \rho} \exp(-\Gamma_q \tau) \cos(\omega_q \tau) F^2(q_{sx} - K_s, q_{sy}) dq_{sx} dq_{sy}. \quad (\text{II.10})$$

However, this example equation is rather awkward to use in fitting as it stands, so a transformation was devised that provides an efficient algorithm without a significant loss of accuracy.

First, numerical experiments showed that for the beam diameters on the order of 2 mm, ignoring the integration over q_{sy} when using a backscatter or transmission mode did not degrade the accuracy of the fit. Second, an assumption was made as to the q dependence of ω_q and Γ_q . Often, the Kelvin equation is a reasonable approximation so the conjecture is that if one uses the Lorentzian function and the dispersion equation for underdamped systems

$$\omega_q \approx \left(\frac{\gamma K_s^2 |K_s|}{\rho_u + \rho_b} \right)^{1/2} \left(\frac{q}{K_s} \right)^{3/2} = \omega_K \left(\frac{q}{K_s} \right)^{3/2} \quad \text{and} \quad (\text{II.11})$$

$$\Gamma_q \approx \Gamma_K \left(\frac{q}{K_s} \right)^2, \quad (\text{II.12})$$

can be used to rewrite Eq. (II.10) in a form that can be numerically integrated using standard quadrature formulas. The first approximation, Eq. (II.11), is often quite good, with an error between 1 % and 5 %, and our fitting routines are designed to use q_{sy} , when requested; but this increases the computational overhead by one-dimension when both x and y are used in the Gauss-Hermite quadrature (GHQ) expansions. This additional computational overhead of calculating both x and y may be needed when scattering at an angle that produces an elliptical spot for the grating image at the interface. The second approximation, Eq. (II.12), is not so good, but if these functions are used only in the instrument function the q dependence is captured with gratifying accuracy; that is, when ω_K and Γ_K computed with formula (II.13), and values for ρ_u , ρ_b , and η_u are input into the full dispersion equation(s), good estimates of γ and η_b result as long as the capillary number, N_{ca} , is sufficiently small. With modern desktop computers, computational speed is not as much of an issue, so the general SRF should be used for even extreme values of the capillary number. Nevertheless, the Lorentzian model is provided as a simple example for the processing algorithm.

After a change of integration variables, the fitting function, Eq. (II.10) becomes

$$R_i(A, B, N, \Gamma_K, \omega_K, \tau) = A \int_{-\infty}^{\infty} \exp(-x^2) \frac{\exp\left(-\Gamma_K \left(1 - \frac{x}{N}\right)^2 \tau\right)}{\left(1 - \frac{x}{N}\right)^2 + \alpha} \cos\left(\omega_K \left|1 - \frac{x}{N}\right|^{3/2} \tau\right) + B \, dx. \quad (\text{II.13})$$

Here, $\alpha = \frac{g \Delta \rho}{\gamma (K_g / M)^2}$, which does depend on the interfacial tension and represents the gravity

contribution to the ripplon spectrum. With few exceptions, this term is small enough that an estimate of this number is quite satisfactory and so it may be kept fixed in the fitting algorithm. Additional fitting cycles using refined values of γ provide negligible change.

Mann pointed out that the above integral Eq. (II.13) containing an instrument function may be approximated by GHQ, as shown in Eq. (II.14).

$$\int_{-\infty}^{\infty} \exp(-u^2) f(u) du = \sum_{i=-n}^n \omega_i^{(n)} f(u_i^{(n)}) + R_n \quad (\text{II.14})$$

The use of GHQ is described by W. H. Press *et al.* [52]*. See also Ref. [53].

We use an odd number of terms in our Gauss-Hermite polynomial (that is, n is chosen to be an odd integer) to have the $u_i^{(0)} = 0$ term in Eq. (II.10). An interpretation of this formula is that of a weighted sum of the correlation function at different values of q . The weights and zeros were initially generated with 24 places of precision, up through $n = 19$, and tested in our surface light scattering data analysis program written in *Mathematica* (which is capable of carrying any requested precision). Little benefit seems evident from carrying more than $n = 11$ terms in the expansion; for example, when $n = 13$ the Mann and Meunier surface tension and viscosity values

* Note that formula 4.5.9 in Ref. [52] for determining the weights $\omega_i^{(n)}$ is missing a factor of 2 in the numerator. This can be confirmed by comparing $\int_{-\infty}^{\infty} \exp[-x^2] x^2 dx = \pi^{1/2} / 2$ to

$$\sum_{i=-n}^n \omega_i^{(n)} f(u_i^{(n)}); \text{ other even powers of } u \text{ in } f(x) = x^u \text{ will also show this. Moreover,}$$

$$\pi^{1/2} = \sum_{i=-n}^n \omega_i^{(n)} \text{ to 13 significant figures.}$$

change in the fourth decimal place and the precision limit of the Yaws standards tables [54][†] for surface tension only given to two decimal places (with the other values given for viscosity, density, and vapor pressure are only given to three or four decimal places). This may lead one to wonder why we have shown the extended precision we have in Tables II-1 and II-2 below. This is to allow comparison of the Mann and Meunier SRFs when applied to experimental data while using an instrument function; this yields results that are numerically identical to at least five decimal places in the tables and which match to the epsilon of the computers utilized. When comparing the Mann and Meunier SRFs computationally they are identical to the precision of the computer. One might also be tempted to judge the quality of the Fourier transform, which is good; but this is better-done using synthetic data [4] and comparing center frequencies and linewidths, rather than results obtained after applying a dispersion equation or SRF.

Fig. II-5 shows the effect of the instrument function for water, $Y = 349$. The GHQ algorithm fails at $N = 5$, but is satisfactory for $N > 10$ and very good for $N > 20$.

Eq. (II.9) written as a GHQ was used to fit experimental data collected on several standard liquids, water,

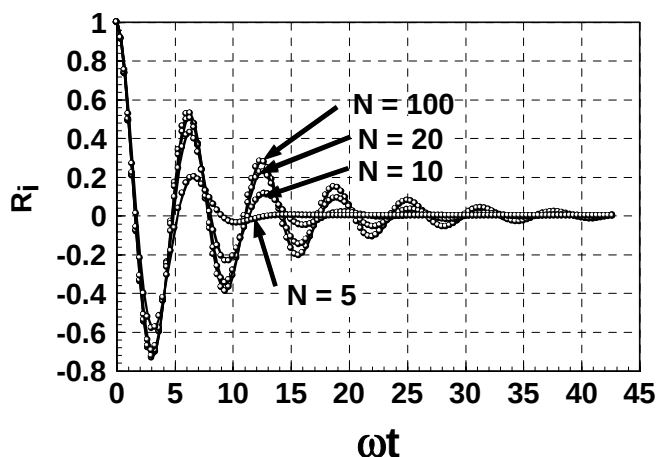


Fig. II-5. Correlograms for water, $T = 20\text{ }^{\circ}\text{C}$, $q = 500\text{ cm}^{-1}$, with different N values illustrate the effect of the instrument function. Most spectrometers operate between $N = 20$ and $N = 30$. For some experiments N down to ~ 10 allows the spot size imaged on the surface to be smaller than 1 mm.

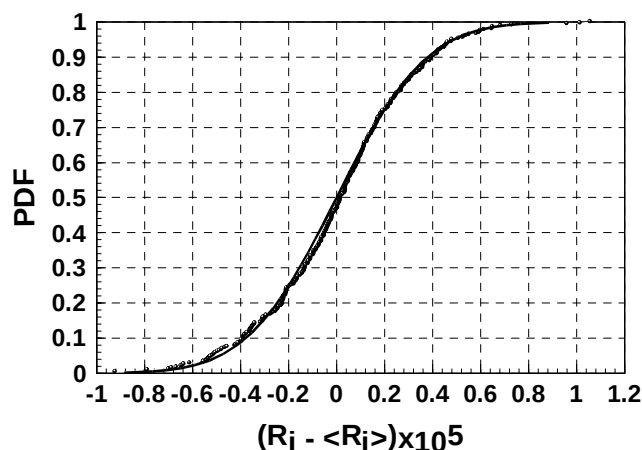


Fig. II-6. Fit of the normal probability distribution function (PDF) to the experimental PDF estimated from replicate data of the correlogram for toluene. The data is shifted slightly from zero at $\text{PDF} = 0.5$.

[†] Note that other literature values for acetone indicate that the correction shown below is needed for the exponent for the Yaws acetone surface tension extrapolation formula in Ref. [54]:

$$\text{surfaceTensionLitValue} = \text{surfaceTensionAtRefTempInKelvin}$$

$$\times \left(\frac{\text{criticalTempInKelvin} - \text{tempInKelvin}}{\text{criticalTempInKelvin} - \text{refTempInKelvin}} \right)^{1.4728}.$$

acetone, toluene, and ethanol. The scattered light was collected using Hamamatsu S3072 PIN silicon photodiodes mounted to Analogue Modules Model 341-4INV, 10 pf preamplifiers that were electrically isolated (using nylon screws and washers). These preamplifiers were cabled to EG&G 5113 preamplifiers, which provided ac coupling and optional band-pass filtering (often set to -12 dB at 300 Hz or lower with underdamped fluids). The conventional maximum likelihood algorithm was implemented in *Mathematica*. The data taken at the University of Amsterdam were collected

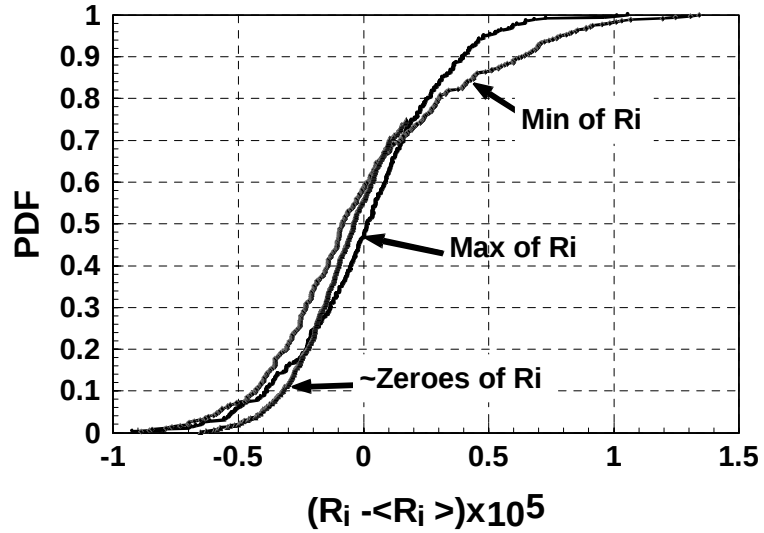


Fig. II-7. Experimental PDF computed from replications of the correlogram for toluene. Three PDF estimations were made: The residuals for the first three maxima beyond $R_i(0)$, the first three minima, and three lag-times where R_i was close to zero.

using a Brookhaven 9000AT correlator with a piggyback analog input card. At NASA Glenn Research Center we use both the Brookhaven Instruments correlator card and an analog input digital correlator from Correlator.com. Scripts were used to allow the collection of multiple correlograms while the temperature was controlled to considerably better than millidegrees Kelvin. Care was taken to keep the optical alignment constant during the collection of replicate correlograms. The doubled Nd:YAG laser (Coherent/Adlus Model DPY 315M) was reasonably well stabilized so that the statistics of the data collection would be time stationary. We note that the correlator by its nature generates a sample of R_i that is a random variable of variance

$\langle (R_i - \langle R_i \rangle)^2 \rangle$ where the average is $\langle R_i \rangle$. It was straightforward to estimate these numbers as a

function of lag-time τ . Fig. II-6 shows the result of this estimation using 119 replications on toluene. The fit is good enough to demonstrate that each channel of the Brookhaven correlator is delivering a Gaussian-random sample of the actual correlation function. However, there are still hints of a low-level systematic noise contribution in the data. Fig. II-7 shows the probability distribution function data for three features in a typical correlogram: at the maxima, the minima, and at the zero-crossing.

It is evident from this data that the distribution function changes some with lag time and that this data set confirms the Gaussian character of the distribution function, but there still is a bit of uncontrolled error in the data since each data set should go through 0.5 for 0 residual.

The fitting algorithm is based on the maximum likelihood of Gaussian distributed channel uncertainty:

$$\text{Minimize } \left\{ \sum_{n=1}^{\#} \Lambda_n \left[R_i(n) - R_i(A, B, N, \Gamma, \omega, \tau_n) \right]^2 \right\}, \quad (\text{II.15})$$

where the weight factor $\Lambda_n = 1/\sigma_n^2$ requires the variance $\sigma^2 = \left\langle \left(R_i - \langle R_i \rangle \right)^2 \right\rangle$ for the n^{th} channel. R. V. Edwards [55] derived a formula for the variance in the data. This is what we have used for the weight factor that is plotted along with a correlogram in Fig. II-8. Edwards [4, 31] recently extended this weighting function (which previously applied just the diagonal of the covariance matrix) so that his weighting function is now based on the more general inversion of the covariance matrix. Experimentally, we estimated σ_n^2 directly from the set of correlograms for toluene, and the variance is plotted against channel number in Fig. II-8 (b). The Edwards weight factor is plotted for comparison. The comparison data was computed using part of a set of APL programs written by R. V. Edwards and J. A. Mann, Jr. and these algorithms were implemented and tested in *Mathematica* by W. V. Meyer. The correspondence is reasonably good considering the number of data sets and the small systematic background that had to be subtracted from the experimental data.

SLSS-4.2 Mann Surface Response Function for a single interface

The theoretical background provided later for the Mann SRF is based on the ideas published by Mann *et al.* in Ref. [5]. The full derivations for both

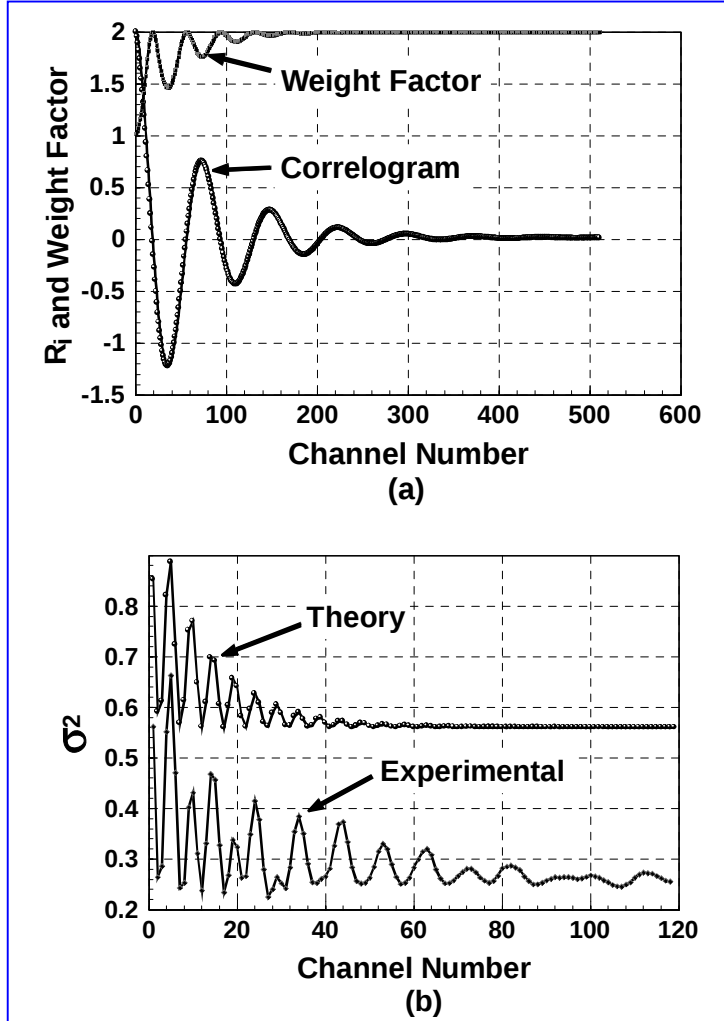


Fig. II-8. (a) The Edwards weight factor $\Lambda_n = 1/\sigma_n^2$ used in the maximum likelihood fitting algorithm is compared with the correlogram for water. (b) The channel variance computed from multiple runs of correlograms compared to $1/\Lambda_n$ as computed in a least-squares fitting program first written by Edwards. The two curves were displaced slightly for this comparison. A small systematic variation in the baseline was subtracted from the residuals before plotting.

the single interface Mann SRF and the asymmetric thin film SRF are provided in Appendices II-C and II-D, with the resulting algorithms and their applications included in this text. The analytical and computational results, to which we apply the instrument function using Mann's

Gauss–Hermite quadrature suggestion outlined in Eq. (II.7), follows for the $\left\langle \zeta_{q,u,b}^*[0] \zeta_{q,u,b}[s] \right\rangle$

surface response function matrix component that we measured with our surface light scattering spectrometer (all matrix components and their derivation provided in Appendix II-C). The Mann surface response function for a simple fluid–fluid interface follows. Notice the symmetry between the numerator and the denominator. The denominator differs from the main term in the numerator simply by an additional factor of s (which equals $i\omega$) and by an additional $-q^2 \bar{\gamma}$ term. So the Mann surface response function for a single interface which follows can be written in the form:

$$\left\langle \zeta_{q,u,b}^*[0] \zeta_{q,u,b}[s] \right\rangle = A \frac{\text{Term01}(-q^2 \bar{\gamma}_v + s(\text{Term02})) + s(\text{Term03})}{\text{Term01}(-q^2(\bar{\gamma} + s\bar{\gamma}_v) + s^2(\text{Term02})) + s^2(\text{Term03})} + B$$

powerSpectrumFitUsingMannSRF

$$\begin{aligned}
 &= P_{\zeta} [q, \omega] = \left\langle \zeta_{q, u, b}^* [0] \zeta_{q, u, b} [s] \right\rangle \\
 &= \left(\frac{1}{\pi} \right) \text{Re} \left[\left(\frac{\text{powerSpectrumAmplitude } k_B \text{ temperature}}{q^2 \bar{\gamma}} \right) \right. \\
 &\quad \left(\left(-q^2 (K_e + s K_v) - s \left(\frac{m_b \eta_b}{q^2 - |q| m_b} + \frac{m_u \eta_u}{q^2 - |q| m_u} + |q| \left(\frac{\eta_b}{q^2 - |q| m_b} + \frac{\eta_u}{q^2 - |q| m_u} \right) \right) \right) \right. \\
 &\quad \times \left(-q^2 \bar{\gamma}_v + s \left(\frac{m_b \rho_b}{q^2 - |q| m_b} + \frac{m_u \rho_u}{q^2 - |q| m_u} \right) \right) \\
 &\quad + s \left(|q| \left(-\frac{m_b \eta_b}{q^2 - |q| m_b} + \frac{m_u \eta_u}{q^2 - |q| m_u} \right) - q^2 \left(-\frac{\eta_b}{q^2 - |q| m_b} + \frac{\eta_u}{q^2 - |q| m_u} \right) \right) \\
 &\quad \times \left(2 \left(-\frac{\eta_b}{q^2 - |q| m_b} + \frac{\eta_u}{q^2 - |q| m_u} \right) + s \left(\frac{-\rho_b}{q^2 - |q| m_b} + \frac{\rho_u}{q^2 - |q| m_u} \right) \right) \Bigg) \\
 &\quad \times \left(\left(-q^2 (K_e + s K_v) - s \left(\frac{m_b \eta_b}{q^2 - |q| m_b} + \frac{m_u \eta_u}{q^2 - |q| m_u} + |q| \left(\frac{\eta_b}{q^2 - |q| m_b} + \frac{\eta_u}{q^2 - |q| m_u} \right) \right) \right) \right. \\
 &\quad \times \left(-q^2 (\bar{\gamma} + s \bar{\gamma}_v) + s^2 \left(\frac{m_b \rho_b}{q^2 - |q| m_b} + \frac{m_u \rho_u}{q^2 - |q| m_u} \right) \right) \\
 &\quad + s^2 \left(|q| \left(-\frac{m_b \eta_b}{q^2 - |q| m_b} + \frac{m_u \eta_u}{q^2 - |q| m_u} \right) - q^2 \left(-\frac{\eta_b}{q^2 - |q| m_b} + \frac{\eta_u}{q^2 - |q| m_u} \right) \right) \\
 &\quad \times \left(2 \left(-\frac{\eta_b}{q^2 - |q| m_b} + \frac{\eta_u}{q^2 - |q| m_u} \right) + s \left(\frac{-\rho_b}{q^2 - |q| m_b} + \frac{\rho_u}{q^2 - |q| m_u} \right) \right) \Bigg) \\
 &\quad \left. + \text{powerSpectrumBaselineOffset} \right]
 \end{aligned}$$

We define the function for the positive real root as

$$\text{positiveRealRoot } [z_-] := \frac{\sqrt{x + |x + i y|} + i \text{Sign}[y] \sqrt{-x + |x + i y|}}{\sqrt{2}}$$

and we use the following replacement rules $\{x \rightarrow \text{Re}[z], y \rightarrow \text{Im}[z]\}$

$$\left\{ \begin{array}{l} \bar{\gamma} \rightarrow \gamma + \frac{|\rho - \rho_u|}{q^2} g + B_e q^2, \quad \bar{\gamma}_v \rightarrow \gamma_v + B_v q^2, \\ m_b \rightarrow \text{positiveRealRoot} \left[q^2 + \frac{i \omega \rho_b}{\eta_b} \right], \quad m_u \rightarrow \text{positiveRealRoot} \left[q^2 + \frac{i \omega \rho_u}{\eta_u} \right] \end{array} \right\}$$

$$\left\{ \begin{array}{l} (* \text{ Comment: For a monolayer free interface, we take the surface viscoelastic} \\ \text{coefficients to be zero.} *) \\ s \rightarrow i \omega, B_e (* \text{ bending modulus} *) \rightarrow 0, B_v (* \text{ bending viscosity} *) \rightarrow 0, \\ \gamma_v (* \text{ transverse surface viscosity} *) \rightarrow 0, \\ K_e (* = \bar{G} + \bar{K}, \text{ surface shear and dilational elastic modulus} *) \rightarrow 0, \\ K_v (* = \bar{\eta} + \bar{\zeta}, \text{ surface shear and dilational viscosity modulus} *) \rightarrow 0, \\ q \rightarrow \text{surfaceWaveNumber}, \\ \rho_u \rightarrow \text{densityUpperPhase}, \rho_b \rightarrow \text{densityBottomPhase}, \\ \eta_u \rightarrow \text{viscosityUpperPhase}, \eta_b \rightarrow \text{viscosityBottomPhaseSought}, \\ \gamma \rightarrow \text{interfacialTensionSought}, g \rightarrow \text{gravitationalAcceleration}, \\ k_B \rightarrow 1 (* \text{ Drop Boltzmann constant scalefactor.} *), \\ \omega \rightarrow 2 \pi \text{ selectedFrequencyValuesForPowerSpectrumAxis} \end{array} \right\}$$

The Mann and Meunier SRFs provide identical results, as confirmed with a point-by-point power spectrum comparison over a wide range of temperatures. After applying our instrument function, essentially identical results are again obtained. Any small differences are due to the discrete-grid nature of the instrument function and the need to carry a lot more terms if additional accuracy is desired. Although these two SRFs represent the same physics, they were derived using different analytical methods. These differences must be kept in mind when defining how the gradients are to be determined in the NonlinearRegress fitting routine in *Mathematica*. Without the gradient definition replacement rules we provide in Appendix II-B later in this work (also found in Ref. [3] and on the accompanying CD ROM), the *Mathematica* NonlinearRegress routines will simply not run with either SRF.

SLSS-4.3 Using the Fast Fourier Transform to Obtain a Power Spectrum

For surface light scattering, the application of a surface response function is desirable to optimize information recoverable from the measured data, and this function is known only in the frequency domain, since a branch-cut in the complex plane prevents Fourier transformation to a simple function applicable in the time domain, as can be done with the Lorentzian spectrum function. With this constraint, we need to know how many decay times are required in the correlation data to obtain a good numerical Fourier transform for frequency domain analysis. We may examine estimates obtained in both the time and frequency domains from an analytic form of the single exponential compared with a synthesized form, which includes channel-to-

channel correlations. This type of analysis gives a ‘best-case’ test of the Fourier transform process by excluding uncontrolled variables encountered in real experiments, such as zero-channel corruptions from dead-time, after-pulsing, noise, possible problems with high frequency aliasing, and other potentially unknown empirical imperfections. With synthetic data, we can find the best accuracy of obtaining frequency data from correlation data acquired over different numbers of decay times. This is typically not possible with real experimental data, constrained by the limitations of real analog or even digital correlators, for example, intentional or implicit low-pass filtering.

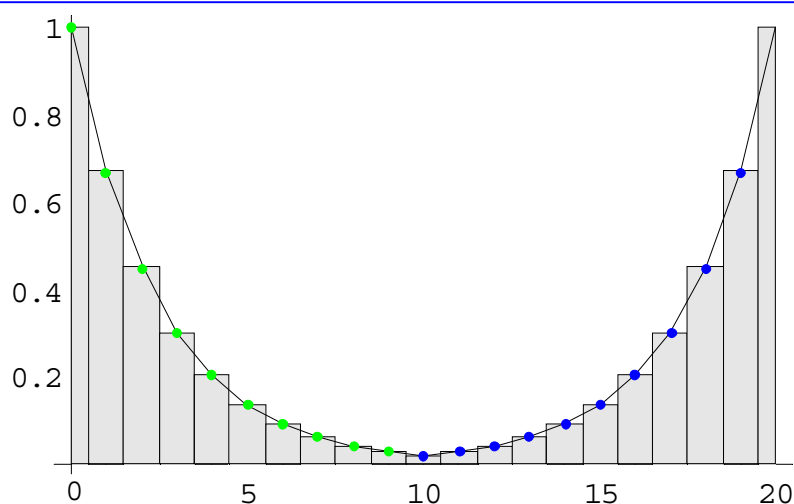


Fig. II-9. An example of folding the correlation function about the baseline before Fourier transforming to obtain the power spectrum. This requires that the two redundant data points (overlapping end-channels from each half of the folded correlogram) be dropped when the original and folded correlation functions are merged. The figure above shows how folding a correlogram with 11 data points (including the zero-channel) would provide 20 data points to Fourier transform. Note that the zero-channel has a width of one-half of a correlation channel.

To obtain the power spectrum we first fold the correlation function (see Fig. II-9) before applying a prime-number-decomposition fast Fourier transform (see Fig. II-10). This form of fast Fourier transform (FFT) does not assume 2^n data points, where n is an integer, and hence does not require ‘zero’ padding, which may otherwise bias our analysis. Since an FFT assumes that the pattern being transformed covers all frequencies (infinite bandwidth) and that it is a pattern that repeats ‘forever’ we fold the data before transforming to avoid introducing a step that would otherwise add spurious high frequency components to the

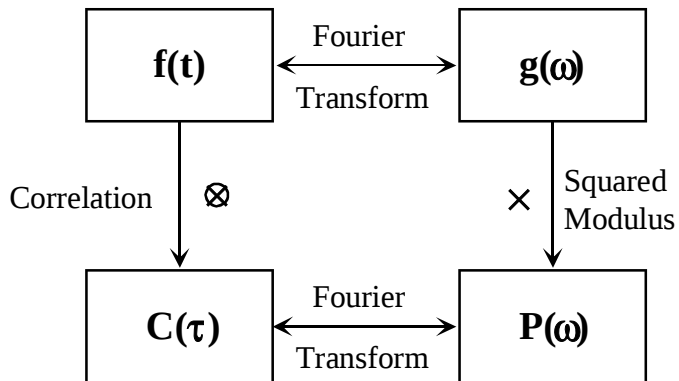


Fig. II-10. Wiener-Khinchine relationship showing the association between the detected signal, $f(t)$; the correlation function $C(\tau)$; and the power spectrum $P(\omega)$. t indicates time, τ indicates correlation delay time, and ω indicates frequency. The operation indicated in the figure by the words “Squared Modulus” consists of taking the Fourier transform of the signal times its complex conjugate to obtain the power spectrum.

power spectrum. Because we intend to work with correlation functions that decay to what should be a flat baseline, this approach avoids the need to apply a windowing function or roll-off filter to suppress the effects of the step, possibly biasing the results. It is well known that folding the correlation function requires some care to ensure that the fold, particularly at the zero channel, does not introduce spurious phase effects. A value at zero delay time is necessary, which for real experiments can be extrapolated with minimum impact. [Note that by subtracting an extrapolated ordinate value for the zero-channel from the measured value for the zero-channel, we are able to directly measure the noise in the experiment; and hence determine the signal-to-noise, which is the extrapolated zero-channel value (signal) divided by the noise.] To give an example regarding the folding of a correlogram we start, for example, with 257 data points, which include the zero-channel; we will find 512 data points in the Fourier transform after folding, but half of these are redundant (see Fig. II-9). The 512 points in the transform result from dropping the redundant data points from the unfolded and folded data sets before they are concatenated. Two simple criteria for successful folding are that the value and its gradient should both be continuous at the ends of the input data, and that establishing this condition should not introduce spurious phase effects.

Simply folding a data set to Fourier transform it is not sufficient to guarantee an accurate result. The accuracy of the result can be significantly affected by the total length of the correlogram function in comparison to the decay time (line width) of that correlation function. Fig. II-11 shows the line-width in reciprocal time ticks estimated in each of the time and frequency

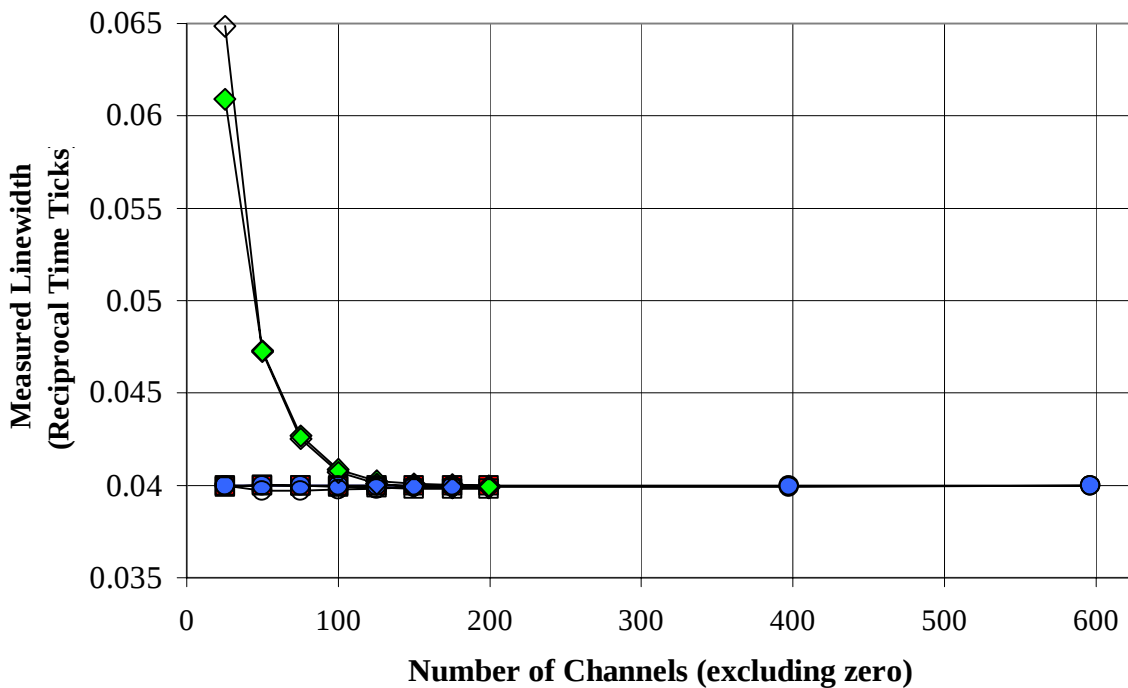


Fig. II-11. Estimate of linewidth in time and frequency domains from analysis of analytic data in the time domain, ■; the frequency domain with unextended baseline, ◆; and extended baseline, ●; and for synthesized data in the time domain, ; the frequency domain with unextended baseline, ; and extended baseline, .

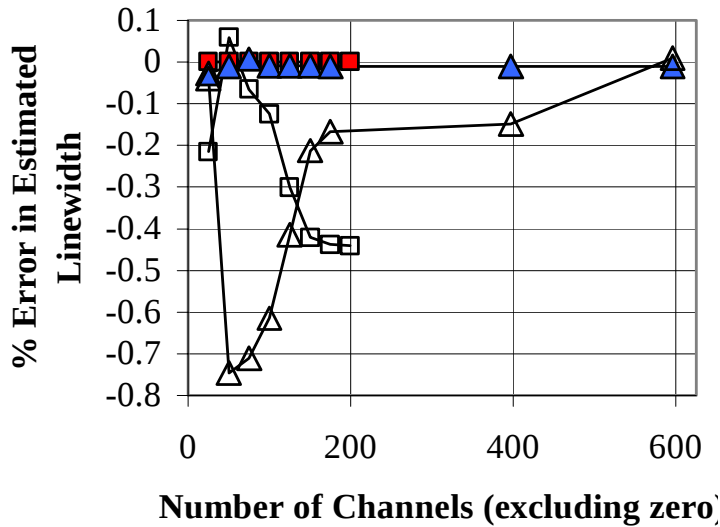


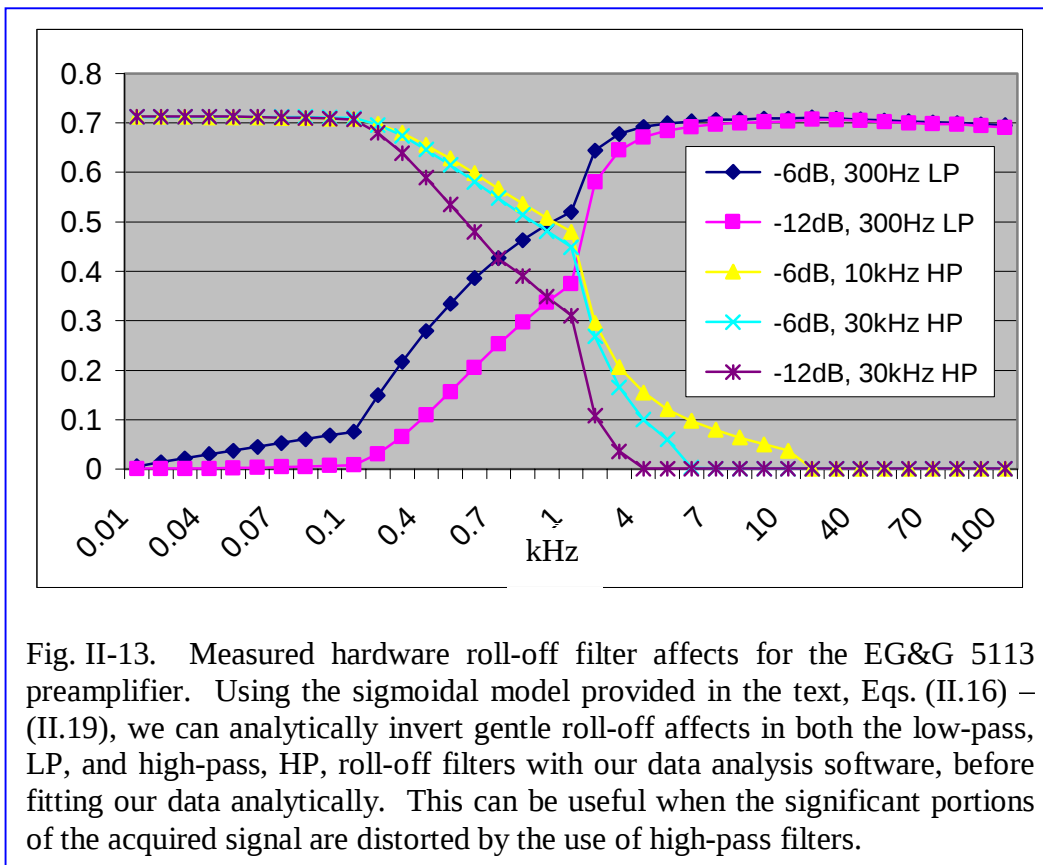
Fig. II-12. Percentage errors in linewidth from fitting in the time domain for analytic, ■; and synthesized, □ data; and in the frequency domain for analytic, ▲; and synthesized, △ data with an extended baseline. The symbols for an unextended baseline have been omitted to allow reasonable scaling. Synthesized data includes the additional effects of correlated channel-to-channel noise.

domains using increasing lengths of the correlogram from one decay time up to the eight decay times available from the synthetic data [4]. Estimates are shown for the analytic data without correlated errors and the synthetic data generated as explained by Smart *et al.* in Ref. [4]. In the frequency domain where the data were folded directly with an unextended baseline before Fourier transformation, large errors appear for the short segments of the correlogram. Errors are much reduced by extending the baseline (extrapolating it with an exponentially damped cosine algorithm) to 597 points before folding. This extensions has a very small amplitude, but gets rid of the cusp that might otherwise be introduced at the fold.

Fig. II-12 shows the percentage errors in the estimated line-width, excluding the extreme errors from the unextended baseline set. We observe that without baseline extension the errors do not reduce to as little as 1 % until the correlogram extends for at least five times the decay time, and therefore advise against this procedure unless the appropriate conditions are met. For the analytic version in the time domain the errors are zero, but for the synthetic data set the values jump about until they converge to an error of about - 0.4 %, an error actually present in the data synthesized for a limited time. In the frequency domain the analytic version has a small residual error of about 0.01 %, which we believe is associated with residual imperfection in the extended baseline. In the frequency domain, the synthetic data show larger errors initially, but then proceed to an almost perfect estimate. This appears to be a subtle artifact of the baseline being extended on the basis of *a priori* knowledge, and hence supplying spurious extra accuracy not present in the original data.

For the synthesized data, where correlated channel-to-channel noise is present, there is likely to exist a small residual step where the data is spliced to an extrapolated baseline. Since this is typically small compared with the cusp introduced at the fold point when the correlation function is too short, it is still a useful procedure if we are constrained to fit our model in the frequency domain. Only modest improvement is possible where data sets are already longer than six decay times. The traditional wisdom of requiring only four times the decay time for the recorded correlogram abscissa appears less than adequate where a model is to be fitted in the frequency domain, unless care is taken to extend the data by analytic continuation before transformation. It is better to record a correlogram at least eight times the decay time of the slowest process [4].

Because we are working with experimental correlation functions (correlograms) which decay to an essentially flat baseline or which can be extrapolated to an essentially flat baseline [4], this approach rids us of the need to use a low-pass roll-off filter to get rid of the step affects (and applying such a filter can distort the data). However, bandpass filters often prove useful when one wants to exclude noise, which has sources outside of the fluctuating interface. For example, coupling of the 60 Hz (in North America, 50 Hz in Europe) electric main frequency and its harmonics through the laser driver or detector circuit leads to a curved baseline in the correlogram. This is not in the model and therefore difficult to handle without bandpass filters when one does not have the fortune to have battery powered equipment. When gentle roll-off filter settings are used, our data analysis routines allow us to invert their affect, provided the filter has not zeroed some of the data to be inverted. For the most part, with underdamped systems, the judicious use of high-pass roll-off filters will not impact the data inversion, while flattening the correlation baseline. Fig. II-13 shows the measured affects of the roll-offs filters



for the EG&G 5113 preamplifiers we use. The algorithms needed to invert the affects of the roll-off filters (potentially important for overdamped, critically damped, and underdamped systems where significant amounts of information exist at low frequencies) are summarized with Eqs. (II.16) – (II.19). The resulting roll-off filter curves are normalized to lie between zero and one. In the data analysis program (provided as Appendix II-F), we have the option of deconvolving the hardware roll-off filter effects in the frequency domain, were the SRF is applied.

	filterInitialValue	filterFinalValue	
lowpass filter	1.0	0.0	(II.16)
highpass filter	0.0	1.0	

$$\text{filterPower} = \sqrt{\frac{|\text{filterRollOffSetting} (* \text{ in dB } *)|}{3.0}}, \quad (\text{II.17})$$

$$\text{filterCenterFreq} = \frac{\text{filterFreqSetting} \times |\text{filterRollOffSetting}|}{12.0}, \quad (\text{II.18})$$

$$\begin{aligned} \text{hardwareFilterSettings} = & \frac{\text{filterInitialValue} - \text{filterFinalValue}}{1.0 + \left(\frac{\text{freqAxisValues}}{\text{filterCenterFreq}} \right)^{\text{filterPower}}} \\ & + \text{filterFinalValue} \end{aligned} \quad (\text{II.19})$$

SLSS-4.4 Single Interface Algorithm Comparisons with Experimental Data

Examples of some correlation functions and their accompanying power spectra follow. These are data sets that were taken in consecutive runs on the same sample of acetone, first using cross correlation and then autocorrelation. With cross correlation the small low-frequency band at the bottom left of the power spectrum disappears. Without the special cell geometry (or pinning edge geometry) or extensive vibration isolation techniques, this low-frequency pollution would be much bigger and it would significantly affect the measured linewidth, where vibrations to allow us to acquire data at all. FFT data analysis results for acetone are presented in Tables II-1 and II-2.

In Figs. II-14 – II-19 and in Tables II-1 and II-2, we compare cross correlation and autocorrelation with an acetone sample chosen from our hundreds of data sets acquired for simple fluids. The acetone data sets in Tables II-1 and II-2 were taken in a backscatter mode with the system shown in Fig. II-4 (with the possible addition of an optical diode consisting of a

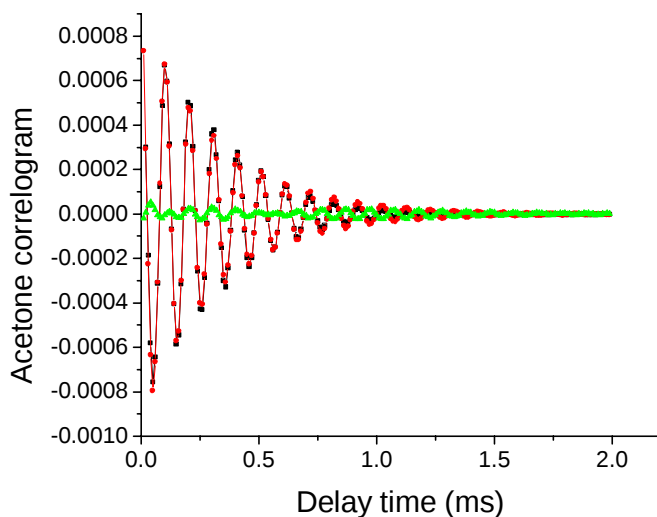


Fig. II-14. Acetone data taken with cross-correlation. Data fit with an exponentially damped cosine model and no instrument function: $\omega = 9756.850$ Hz, S.E. 3.312 Hz; $\Gamma = 488.723$ Hz, S.E. 4.819 Hz; surface tension, 23.244 dynes/cm (mN/m); viscosity, 0.53082 cP; data, ■; fit, ●; residuals, ▲.

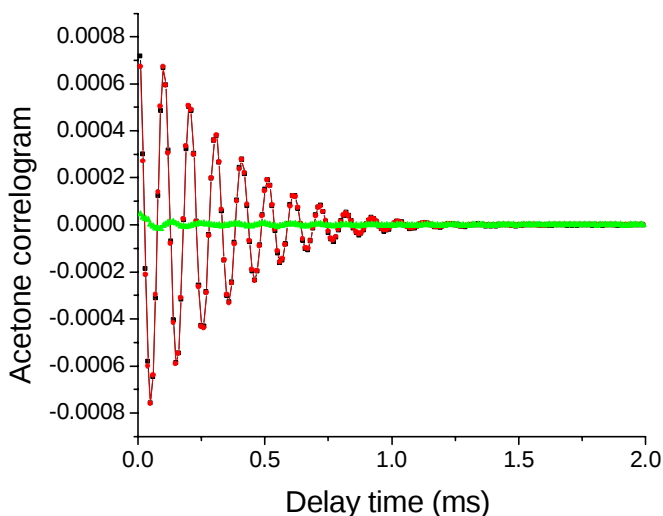


Fig. II-15. Acetone data taken with cross-correlation. Data fit with an exponentially damped cosine model and the Mann GHQ (MGHQ) instrument function: $\omega = 9780.510$ Hz, S.E. 1.645 Hz; $\Gamma = 304.265$ Hz, S.E. 2.577 Hz; surface tension, 23.194 dynes/cm (mN/m); viscosity, 0.31703 cP; data, ■; fit, ●; residuals, ▲.

polarizing beam-splitting cube followed by a quarter-wave plate when in a direct backscatter mode). For these particular data sets we used a laser for which we back-calculated N to equal 33.6271. Using the Mann SRF and literature values for the thermal-physical coefficients (at 23.0475 °C the density of liquid acetone = 0.786436 g/ml, the density of acetone vapor = 0.0006633 g/ml at 210.958 mm Hg (28.1 kPa), and the viscosity of acetone vapor = 0.00743965 cP), we find that $K = 505.401 \text{ cm}^{-1}$ (after magnification), which gives us a spot size measured perpendicular to the beam of $\sigma_s = 0.066535 \text{ cm}$ (intensity measured at the $1/e^2$ points = $4 \sigma_s$). We have also used this approach for determining values for K_s and σ_s with other standards for the same optical system, and with single samples at a range of temperatures for a single grating constant. For the data sets shown in Figs. II-14 – II-18, whose analyses are listed in Table II-1, we use Mann's dispersion equation to obtain values for the interfacial tension and viscosity when fitting with an exponentially damped cosine in the time domain and the Lorentzian (the Fourier transform of the exponentially damped cosine) in the frequency domain. Next, in Table II-2, we show the more general results provided by the SRF. The SRF generalizes the Lorentzian model and, for example, does not require sorting of the zeros of the dispersion equation to make the algorithm work for overdamped, critically damped, and underdamped systems. Indeed, the Lorentzian

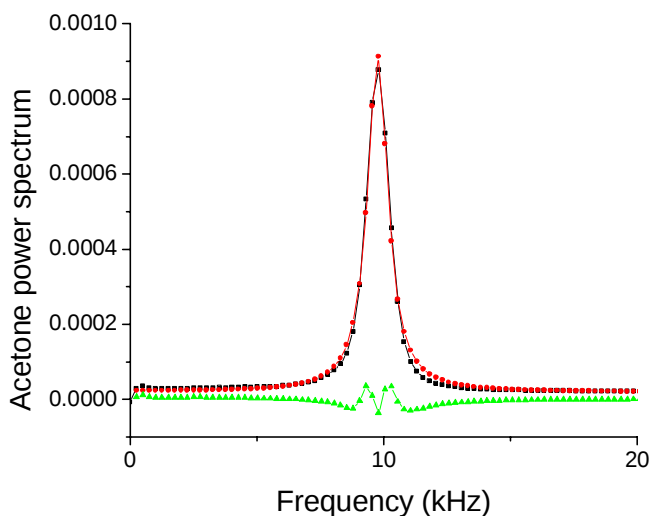


Fig. II-16. Acetone data taken with cross-correlation. Data fit with a Lorentzian model and no instrument function: $\omega = 9756.700$ Hz, S.E. 3.290 Hz; $\Gamma = 488.983$ Hz, S.E. 4.768 Hz; surface tension, 23.244 dynes/cm (mN/m); viscosity, 0.53113 cP; data, ■; fit, ●; residuals, ▲.

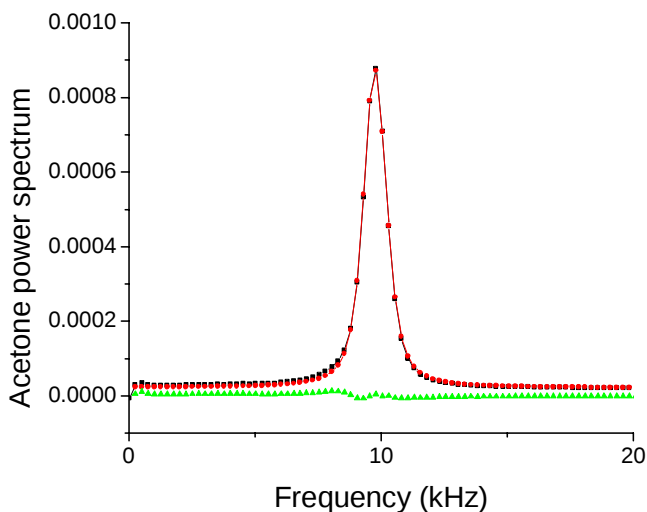


Fig. II-17. Acetone data taken with cross-correlation. Data fit with a Lorentzian model and the MGHQ instrument function: $\omega = 9780.180$ Hz, S.E. 1.620 Hz; $\Gamma = 305.733$ Hz, S.E. 2.394 Hz; surface tension, 23.194 dynes/cm (mN/m), viscosity, 0.31869 cP; data, ■; fit, ●; residuals, ▲.

model fails as fluctuations become critically damped. For the data sets shown in Fig. II-19, which are listed in Table II-2, we compare both the Mann [5] and the Meunier [49] SRF, which fit the data to the Fourier transform of the temporal correlation function. While these provide identical results, we implemented the Mann SRF using a different approach.

Theoretically, the exponentially damped cosine model (used in Table II-1) for data analysis in the time domain and its Fourier transform (a Lorentzian) used in Table II-1 for data analysis in the frequency domain should provide results that are quite close to those of the SRF for samples like acetone, where $Y > 100$ (as discussed above). However, computationally the SRF is a more complete model and it has the advantage that all the independent variables (*e.g.* - interfacial tension, lower phase viscosity, or other choices of variables, along with the power spectrum amplitude, and power spectrum baseline offset) are found simultaneously (which helps in error analysis). Table II-2 supports our preferred use of the SRF formalism (both that of Mann and Meunier) by providing SRF analysis results for acetone data that can be directly compared with Table II-1.

Note that the results we obtain are for fluids in sealed sample cells, prepared so that acetone is measured in acetone vapor alone and not in air, as were the literature values. These samples are in a thermostat that controls the temperature to

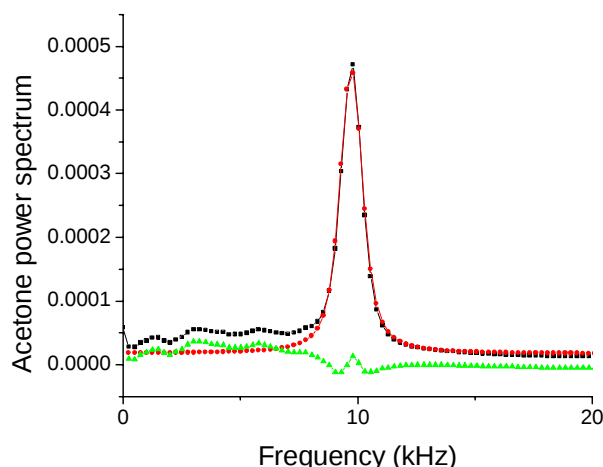


Fig. II-18. Acetone data taken with autocorrelation. Data fit with a Lorentzian model and the MGHQ instrument function: $\omega = 9753.070$ Hz, S.E. 10.615 Hz; $\Gamma = 347.622$ Hz, S.E. 16.275 Hz; surface tension, 23.098 dynes/cm (mN/m); viscosity, 0.36639 cP. Notice the low-frequency band of noise to the left of the peak when not cross correlating as in Fig. II-17 – and this is a fairly clean data set; data, ■; fit, ●; residuals, ▲.

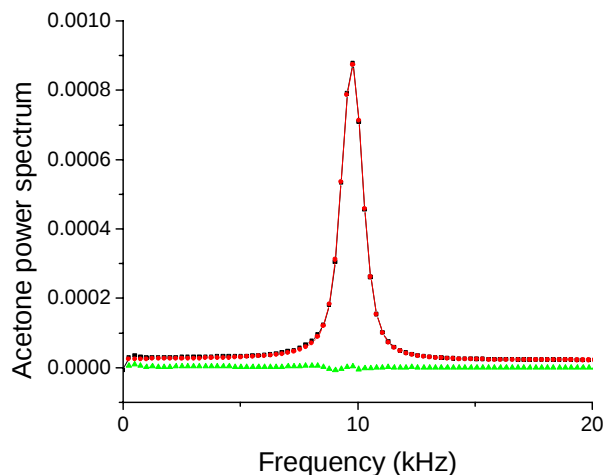


Fig. II-19. Acetone data taken with cross-correlation. Data fit with both the Mann and Meunier SRFs along with and the MGHQ instrument function. Identical results were obtained: surface tension, 23.270 dynes/cm (mN/m), S.E. 0.078 dynes/cm; viscosity, 0.31853 cP, S.E. 0.0210 cP; data, ■; fit, ●; residuals, ▲.

considerably better than a milliKelvin. Acetone (presented in Tables II-1 and II-2) is a challenging viscosity test because of its narrow linewidth and one can observe that the combination of a vibration-mitigating instrument design, a computationally viable instrument function, and a SRF provides good results. These fits to the data were made, except where noted otherwise in Table II-1, using a weighting function of unity.

There are several points apparent from the tables and figures:

- The surface tension is relatively insensitive to errors in the linewidth Γ .
- The instrument function corrects the bandwidth rather well so that viscosity is well-estimated.
- With this instrument design, only the beam cross section at the grating (impacted by surface curvature in some cases), the spatial frequency of the grating, and the magnification are required (along with index changes when entering a liquid before encountering the interface) for an accurate interpretation of the measurements. While these numbers can be determined by physical measurement, their values, to the accuracy needed, can be calibrated with simple liquids that are carefully controlled in temperature.
- Experimentally, the geometry of Figs. II-3 and II-4 and the cross-correlation detection systems of Fig. II-2 are effective in reducing contributions from slosh.

It should be noted that it is even easier to determine the viscosity of other fluids with greater linewidth. Since we have chosen the above data sets to support the points being made in the paper, we should remark that at times our autocorrelation measurements on other (more viscous) fluids and at other temperatures are of sufficient quality that only a small improvement is realized with the addition of cross correlation. The new cell geometry (or equivalent pinning edge geometry) offers considerable improvement in all cases (at times allowing us to make otherwise difficult measurements).

In our opinion, our data support the following observations:

1. The correlator produces Gaussian-distributed data that can be averaged to a very good estimate of the correlation function.
2. The use of Gaussian maximum likelihood fitting techniques is justified.
3. The Edwards weighting function may be useful in the time domain. It is not needed in the frequency domain, since the Fourier transform reduces channel-to-channel noise correlation to a single bin width in the frequency domain. The Edwards weighting function also adds confidence to the error analysis, for if one does not include all the independent variables and any significant weighting function when fitting data, the error analysis is at best incomplete. Please see Ref. [4] for a detailed discussion.
4. The Mann conjecture is a reasonable and practical approximation for including the instrument function in the fitting algorithm, for small N_{ca} (large Y).
5. The spectrum function for the surface response function has the combined advantages that it is accurate for underdamped, critically damped and overdamped systems, and it can provide computationally more accurate results and error analysis since it determines all the independent variables simultaneously.

Table II-1. Surface Tension and Viscosity, Exponentially Damped Cosines Fits

Temperature = 23.0475 °C, $N = 33.6271 = K_s \sigma_s$, $K_s = 505.401 \text{ cm}^{-1}$, $\sigma_s = 0.066535 \text{ cm}$, (High-pass roll-off filter set for -12 dB at 300 Hz)	Cross-correlation	Autocorrelation	Literature
	(acetone liquid – acetone vapor)		(acetone liquid – air vapor)
	Data file: Aceton11.dat	Data file: Aceton45.dat	Literature [54] (extrapolated)
Exponentially damped cosine algorithm with Mann-GHQ instrument function correction:			
Surface tension (time domain) [mN/m]	23.194 (6.01384×10^{-6}) [‡]	23.100 (2.33108×10^{-5}) [‡]	23.265
Surface tension (time domain, with the addition of the Edwards weighting function) [mN/m]	23.195 (5.61882×10^{-6}) [‡]	23.100 (2.15674×10^{-5}) [‡]	23.265
Surface tension (freq. domain) [mN/m]	23.194 (3.41266×10^{-6}) [‡]	23.098 (1.15624×10^{-5}) [‡]	23.265
Viscosity (time domain) [cP]	0.31703 (6.01384×10^{-6}) [‡]	0.36646 (2.33108×10^{-5}) [‡]	0.31345
Viscosity (time domain, with the addition of the Edwards weighting function) [cP]	0.31510 (5.61882×10^{-6}) [‡]	0.35479 (2.15674×10^{-5}) [‡]	0.31345
Viscosity (frequency domain) [cP]	0.31869 (3.41266×10^{-6}) [‡]	0.36639 (1.15624×10^{-5}) [‡]	0.31345
Exponentially damped cosine algorithm with no instrument function correction:			
Surface tension (time domain) [mN/m]	23.244 (1.26889×10^{-5}) [‡]	23.150 (1.09555×10^{-5}) [‡]	23.265
Surface tension (time domain, with the addition of the Edwards weighting function) [mN/m]	23.225 (1.20257×10^{-5}) [‡]	23.153 (1.9717×10^{-5}) [‡]	23.265
Surface tension (freq. domain) [mN/m]	23.244 (7.47483×10^{-6}) [‡]	23.150 (2.20838×10^{-5}) [‡]	23.265
Viscosity (time domain) [cP]	0.53082 (1.26889×10^{-5}) [‡]	0.56889 (2.20838×10^{-5}) [‡]	0.31345
Viscosity (time domain, with the addition of the Edwards weighting function) [mN/m]	0.53781 (1.20257×10^{-5}) [‡]	0.56616 (1.9717×10^{-5}) [‡]	0.31345
Viscosity (frequency domain) [cP]	0.53113 (7.47483×10^{-6}) [‡]	0.56879 (1.09555×10^{-5}) [‡]	0.31345
() [‡] = Std. dev. of all frequency fitting parameters. Please note that standard deviation (std. dev.) in Table II-1 above applies to the fits obtained using ω and Γ before applying the dispersion equation. This is somewhat different from the use of std. dev. in Table II-2, where the SRF is used for both fitting and analyzing the data.			

Table II-2. Surface Tension and Viscosity Using SRF Fits

Temperature = 23.0475 °C, $N = 33.6271 = K_s \sigma_s$, $K_s = 505.401 \text{ cm}^{-1}$, $\sigma_s = 0.066535 \text{ cm}$, (High-pass roll-off filter set for -12 dB at 300 Hz)	Cross-correlation	Autocorrelation	Literature
	(acetone liquid – acetone vapor)		(acetone liquid – air vapor)
	Data file: Aceton11.dat	Data file: Aceton45.dat	Literature [54] (extrapolated)
SRF algorithms with Mann-GHQ instrument function correction:			
Surface tension (Mann algorithm) [mN/m]	23.270 (2.07533×10^{-6}) [‡]	23.195 (1.108065×10^{-5}) [‡]	23.265
Surface tension (Meunier algorithm) [mN/m]	23.270 (2.07533×10^{-6}) [‡]	23.195 (1.108065×10^{-5}) [‡]	23.265
Viscosity (Mann algorithm) [cP]	0.31853 (2.07533×10^{-6}) [‡]	0.37842 (1.108065×10^{-5}) [‡]	0.31345
Viscosity (Meunier algorithm) [cP]	0.31853 (2.07533×10^{-6}) [‡]	0.37842 (1.108065×10^{-5}) [‡]	0.31345
SRF algorithms with no instrument function correction:			
Surface tension (Mann algorithm) [mN/m]	23.355 (7.57408×10^{-6}) [‡]	23.278 (9.88393×10^{-6}) [‡]	23.265
Surface tension (Meunier algorithm) [mN/m]	23.355 (7.57407×10^{-6}) [‡]	23.278 (9.88393×10^{-6}) [‡]	23.265
Viscosity (Mann algorithm) [cP]	0.52870 (7.57408×10^{-6}) [‡]	0.57521 (9.88393×10^{-6}) [‡]	0.31345
Viscosity (Meunier algorithm) [cP]	0.52870 (7.57407×10^{-6}) [‡]	0.57521 (9.88393×10^{-6}) [‡]	0.31345
() [‡] = Std. dev. of all SRF fitting parameters. Please note that standard deviation (std. dev.) in Table II-2 above applies to the final results obtained using the surface response function (SRF). This is somewhat different from the use of std. dev. in Table II-1. The std. error (Asymptotic SE) and confidence interval (CI) for all independent fitting parameters, along with the asymptotic correlation and covariance matrices, Hessian condition numbers, and other fitting details and plots are provided in the Data Analysis Results appendix (Appendix II-G) where available.			

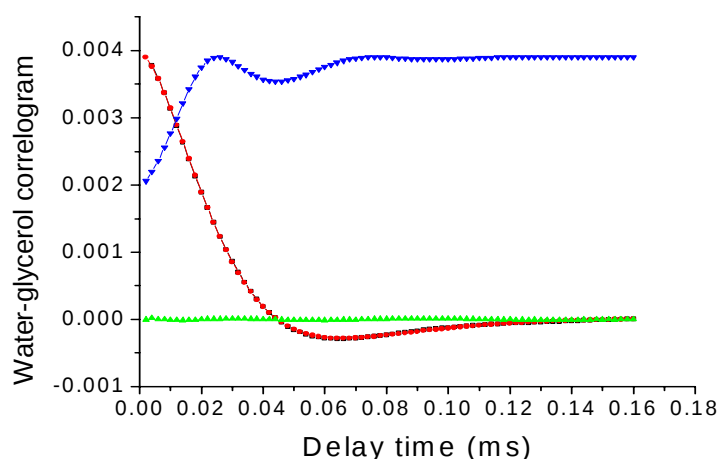


Fig. II-20. Water-glycerol data taken with cross correlation. Critically damped data fit with an exponentially damped cosine and sine model and the MGHQ instrument function: $\omega = 8790.580$ Hz, S.E. 14.806 Hz; $\Gamma = 5070.020$ Hz, S.E. 30.170 Hz; interfacial tension, 56.8451 dynes/cm (mN/m); viscosity, 13.5592 cP; data, $\blacksquare$; fit, $\bullet$; residuals, $\blacktriangle$; Edwards' correlation weighting function, $\blacktriangledown$. The dispersion equation, which provides values for surface tension and viscosity, does not work with the critically damped data values provided by Eq. (II.21).

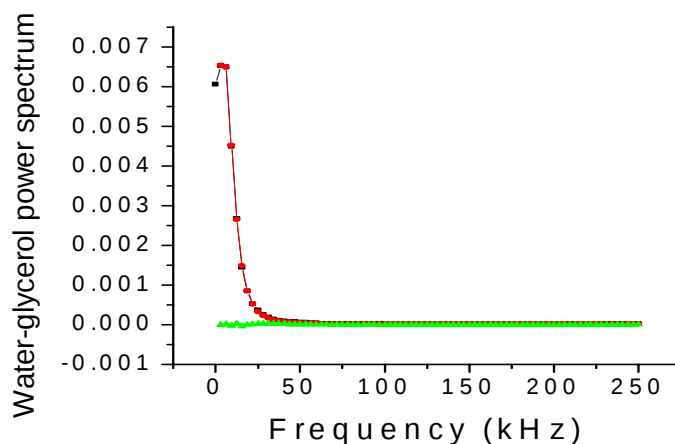


Fig. II-21. Water-glycerol data taken with cross correlation. Critically damped data fit with the Mann SRF using the MGHQ instrument function: surface tension, 60.171 dynes/cm (mN/m), S.E. 0.1683 dynes/cm; viscosity, 18.9835 cP, S.E. 0.0491 cP; data, $\blacksquare$; fit, $\bullet$; residuals, $\blacktriangle$. Accurate results are obtained using the Mann SRF, which (unlike the combination of Eq. (II.21) and the dispersion equation) accounts for the coupling of the bulk fluid into the interface.

Some of our work with a critically damped water-glycerol system is shown in Figs. II-20 and II-21. The water-glycerol system was chosen because it is well characterized and changing either or both the temperature and water to glycerol ratio allows us to move from underdamped to critically damped and then on to overdamped systems. Critically damped systems are known to require a surface response function for accurate data analysis and we have shown this to be the case. There are additional advantages of the water glycerol system. Glycerol is fully soluble in water and the viscosity can be changed over a wide range with small impact on the surface tension.

Langevin ([49], p. 93, Eq. 6 using the definition of peak (renormalized) frequency ω_m suggested at the top of p. 96) provides a fitting formula (II.20) for working in the time domain when the Y parameter, which in this case with

$Y_q = \left(\frac{\omega_q}{\Gamma_q} \right)^2 = 0.94$, indicates a critically damped system. While the simple Lorentzian fit (an

exponentially damped cosine in the time domain) is poor for this critically damped system, after the correction of a printing sign error in the formula (Ch. 7, Formula 6) for fitting critically damped systems in Langevin's book [49], we find that formula (II.21) below, which is intended to model a simple harmonic oscillator, fits the critically damped data in Fig. II-20 better than a simple Lorentzian model (when used in conjunction with the MGHQ instrument function, in this

case NOT substituting in $\omega \rightarrow \omega \left| \frac{q}{K_s} \right|^{3/2}$ and $\Gamma \rightarrow \Gamma \left| \frac{q}{K_s} \right|^2$, since the Kelvin equation portion of the Mann conjecture for applying the instrument function to underdamped systems is not intended and not appropriate for critically damped systems).

$$\begin{aligned} & \exp(-\Gamma_K \tau) \cos(\omega_0 \tau) + \frac{\Gamma_K \sin(\omega_0 \tau)}{\omega_0} \\ &= \exp(-\Gamma_K \tau) \cos\left(\sqrt{\omega_m^2 + \Gamma_K^2} \tau\right) + \frac{\Gamma_K \sin\left(\sqrt{\omega_m^2 + \Gamma_K^2} \tau\right)}{\sqrt{\omega_m^2 + \Gamma_K^2}} \end{aligned} \quad (\text{II.20})$$

$$\begin{aligned} R_i(K_s, \tau) = A \times \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{K_B T}{\gamma q^2 + g \Delta \rho} & \left(\exp(-\Gamma_q \tau) \cos\left(\sqrt{\omega_m^2 + \Gamma_q^2} \tau\right) + \frac{\Gamma_q \sin\left(\sqrt{\omega_m^2 + \Gamma_q^2} \tau\right)}{\sqrt{\omega_m^2 + \Gamma_q^2}} \right) \\ & \times F^2(q_{sx} - K_s, q_{sy}) dq_{sx} dq_{sy} + B \end{aligned} \quad (\text{II.21})$$

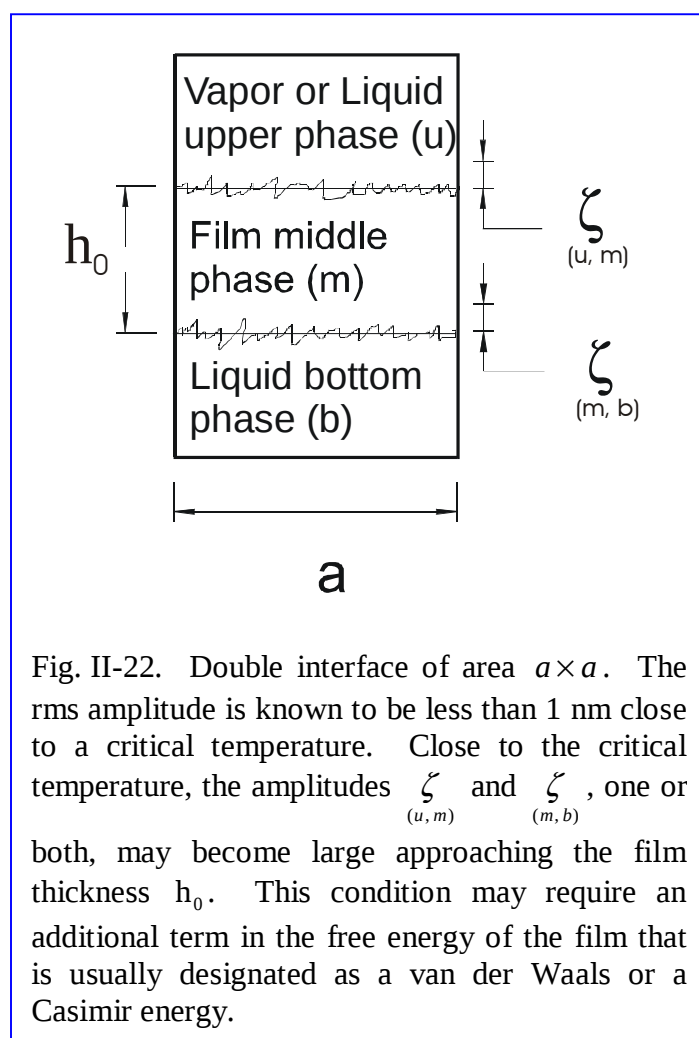
The fit for the values obtained with Eq. (II.21) for the oscillation frequency (8790.58 Hz, with an asymptotic standard error, S.E. 14.8059 Hz) and decay time (5070.02 Hz, S.E. 30.17 Hz) of this critically damped system has a standard deviation of 1.22558×10^{-5} . The data is the average of 94 data sets taken with a 60 °C critically damped mixture of glycerol (88.4013 % from n = 1.456) and water. Each individual data set looked clean and the resulting compilation had a nice Gaussian distribution in each correlation channel. This mixture is sufficiently viscous that

autocorrelation using a cylindrical cell (without needing to resort to cross-correlation) provided good vibration free data. For this temperature, the independent fitting parameters included values for: lower phase liquid density of 1.20522 g/ml; upper phase vapor density of 0.0014 g/ml; scattering angle, 32.4 °; a grating value of 532.333 cm⁻¹; and $\sigma = 0.00620$ cm. When using all these values in the same dispersion equation that we applied with excellent results to our underdamped acetone data above (Figs. II-16 and II-18 and in Table II-1), the dispersion equation no longer yields correct values for the surface (interfacial) tension and the lower phase viscosity. The value derived here with the dispersion equation for the surface tension is 56.8451 dynes/cm, and for the lower phase viscosity 13.5592 cP. The extrapolated literature values [54] for this water/glycerol system are 60.1684 dynes/cm for the surface tension and 18.9808 cP for the lower phase viscosity. While these values would likely improve if we had an equivalent of the Kelvin equation to use with the instrument function for critically damped systems, because the simple harmonic oscillator model ignores vorticity (the stream function) and only deals with the potential function; even with this improvement the results would still be poor for critically damped systems unless a surface response function is used. Note that the surface response function does not need the Kelvin equation corrections for ω and Γ . The surface response function will provide more accurate results for critically damped systems because it accounts for the coupling of the bulk fluid with the interface. When fitting this same critically damped data with the Mann surface response function, using the same independent fitting parameters, we obtain a value of 60.171 dynes/cm, S.E. 0.1466 dynes/cm for the surface tension and 18.9835 cP, S.E. 0.0448 cP for the lower phase viscosity with a standard deviation in the fit of 1.10191×10^{-5} . The goodness of fit of this SRF can be seen in Fig. II-21. Note that the zero-frequency bin in the power spectrum was given zero weighting when fitting the data since the zero-frequency bin stores the d.c. offset information of the correlation data.

We used the surface response function to fit the same mixture of water/glycerol at a different temperature inside the UvA microKelvin temperature controller. With the temperature controller equilibrated at 30.018 °C, we now have an essentially overdamped system. At 30.018 °C (using a lower phase density value of 1.22452 g/ml and an upper phase density value of 0.0014 g/ml), the fitting value provided by the SRF of 84.9117 cP for the viscosity, which has a extrapolated literature value [54] of 84.19201 cP, is obtained to within 0.47 %, but the fitting value for the interfacial tension, 54.5983 dynes/cm, whose extrapolated literature value is 60.5383 dynes/cm, is low by 9.8 %. This fit has a standard deviation of 1.82259×10^{-4} with the residuals in the fit becoming increasing worse as the zero-frequency in the power spectra is approached. If we were working in the time domain with an overdamped system, we would be able to fit for either the interfacial tension or linewidth. Here we have been able to fit for both when using the surface response function, but we need to revisit the overdamped case in future work to see if the fits can be improved or if this is perhaps a problem of ill conditioning. The condition number for the Hessian for the power spectrum of the critically damped system in Fig. II-21 is 6.410955×10^{10} , giving us a remaining base-10 hardware precision for the Compaq Pentium-4 based workstation used for this calculation of 131072 (okay if greater than zero). The condition number for the Hessian for the power spectrum of the overdamped system is 4.81655×10^{11} , leaving us a hardware precision of 16384. No hardware roll-off filters were used for either the critically damped or overdamped water/glycerol systems just described.

SLSS-4.5 Experiment Sample Preparation

All chemicals samples are from Aldrich and are spectroscopic grade. Alcohols: purity 99.8%, where the only significant contamination is water; alkanes: 99.99%, are distilled over alumina covered with silver nitrate to remove traces of unsaturated alkanes. The liquids are freed of dust by pressing them through Millipore filters with 0.5 or 0.1 micron pores. After that, they are heated to remove dissolved air and stored in clean sealed bottles until used. The cells are cleaned first with soap during the previous 24 hours, next they are put into an acoustic bath, rinsed thoroughly with distilled, dust free water (from a Millipore clean water station), next they are put into chromic acid, again thoroughly rinsed with distilled, dust free water, and then baked in a furnace at 100 degrees C, resulting in a cell surface that is clean, and has a surface with only OH-groups. At this stage the surface can be silanated to cover it with CH_3 groups, if needed. Into these clean cells the clean liquids are either distilled under vacuum or the liquids are brought into the cells via a syringe (which has also been cleaned). The cells are then flame sealed under vacuum. Care is taken that there is no contact with the surroundings between the filling and the sealing. The sealed samples have shown no change with time. This also holds for the samples in the silanated cells (which have all been stored at least a year).



SLSS-4.6 Theory for the Development of the Single and Asymmetric Double-Interface (Thin Film)

While the derivation for both the single-interface surface response function and its lengthy asymmetric double-interface SRF cousin are included in Appendices II-C and II-D, an outline of the underlying theory first presented in Mann *et al.* [5] will now be given. This theoretical foundation was used to derive the algorithms for the single and asymmetric double-interface and to obtain the surface response function results presented in this text.

SLSS-4.6.1 Outline of the Construction of the Spectrum Function

SLSS-4.6.1.1 Linearization: A Single-Component, Liquid-Vapor Interface

Consider a pure liquid and use the Gibbs convention so that the surface density

for the chemical species $\Gamma_1 = 0$. For the normal momentum balance, it is assumed that $|\zeta|$, where ζ , the fluctuation amplitude normal to the interface, is small compared with the wavelength of the fluctuations selected by the optical system (see Fig. II-22). For

$$\left[P^{ij} \right] n_j n_i = \gamma a^{\alpha\beta} b_{\alpha\beta} = 2 \gamma H, \quad (\text{II.22})$$

where $\mathbf{P}$ is the pressure tensor, γ is the interfacial tension, and H comes from the invariant $2H = c_1 + c_2$, where $c_\alpha = 1/R_\alpha$, Eq. (II.22) becomes

$$0 = \gamma \left(\frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right) - \left[P_{zz} \right]_0, \quad (\text{II.23})$$

$$P_{zz} = p - 2 \eta \frac{\partial v_z}{\partial z}, \quad (\text{II.24})$$

$$\frac{d\zeta}{dt} = v_z \Big|_{z \rightarrow 0}, \quad (\text{II.25})$$

where η is the viscosity and v_z is the velocity field in the z-direction.

For this same case [Eq. (II.22)] the tangent balance is

$$0 = \left[P_{zx} \right]_0 = \left[P_{zy} \right]_0, \quad (\text{II.26})$$

$$P_{zx} = \eta \left(\frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} \right). \quad (\text{II.27})$$

As the liquid is pure, $\nabla \sigma = 0$, no surface-tension gradients are possible in the hydrodynamic limit. Also, the pressure and the velocity fields must be determined for the volume phases. This is done in the next Subsection below (entitled *Solution Technique Using the Potential and the Stream Functions*). All these equations are linear but coupled.

The boundary-value problem to be solved is

$$0 = \gamma \left(\frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right) - [P] + 2 \left(\eta \frac{\partial v_z}{\partial z} \right), \quad (\text{II.28})$$

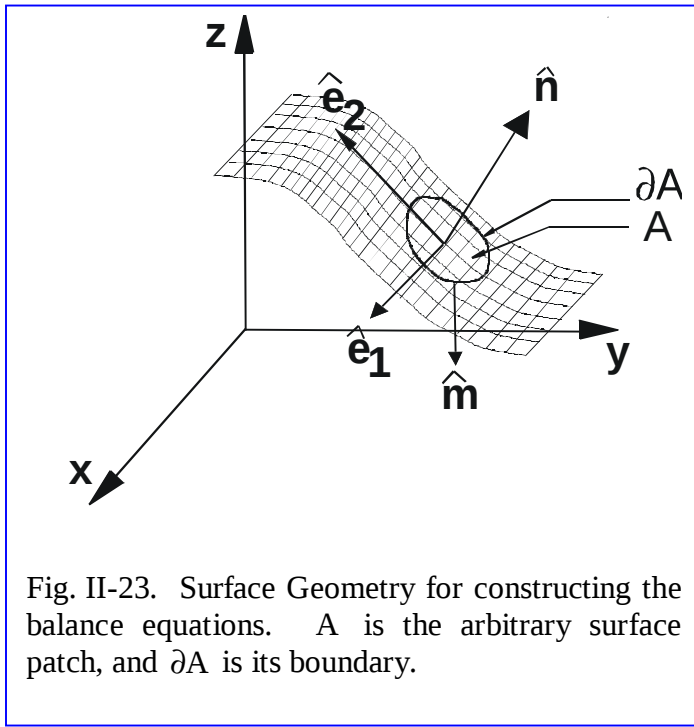
subject to $\zeta \rightarrow 0$ for $x, y \rightarrow \pm \infty$, and $\dot{\zeta} = v_z \Big|_{z \rightarrow 0}$, plus initial conditions.

The momentum balance in the tangent plane with an insoluble monolayer present gives

$$0 = \eta \left(\frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} \right) + k_e \frac{\partial^2 \xi_x}{\partial x^2} + k_v \frac{\partial^2 \dot{\xi}_x}{\partial x^2} \quad (\text{II.29})$$

where $k_e = \overline{G} + \overline{K}$, $k_v = \overline{\eta} + \overline{\zeta}$, ξ , the fluctuation amplitude tangential to the interface, and there is a similar equation for the y direction. The effect of adsorption is added below. The no-slip condition at the interface requires continuity of the tangent vector's time rate of change:

$$\frac{\partial \xi}{\partial t} = \mathbf{v} \cdot \mathbf{U}_n \Big|_{z \downarrow 0} = \mathbf{v} \cdot \mathbf{U}_n \Big|_{z \uparrow 0} \quad (\text{II.30})$$



Here $\mathbf{U}_n$ is the projector to the tangent plane and the grating orientation of the spectrometer determines $\hat{\mathbf{e}}_x$ (see Fig. II-23).

We need to recognize that we are assuming in Eq. (II.30) that the system is a pure liquid-fluid interface so that $\Gamma = 0$ by choice of convention with respect to the Gibbs surface. Moreover, the surface viscoelastic moduli are zero in this case. Note also that ζ and ξ are considered to be random variables. We are to compute $\langle \zeta_q(0) \zeta_q(t) \rangle$. When a monolayer is present, $\langle \xi_q(0) \xi_q(t) \rangle$ can be computed, but at this time the light-scattering instrument will not resolve these components.

SLSS-4.6.1.2 Solution Technique Using the Potential and the Stream Functions

It is well documented that a velocity field can be written as

$$\begin{aligned} \mathbf{v} &= \mathbf{v}_1(x, t) + \mathbf{v}_2(x, t) + \mathbf{u}(t), \\ \nabla \times \mathbf{v}_1 &= 0, \\ \nabla \cdot \mathbf{v}_2 &= 0 \end{aligned} \quad (\text{II.31})$$

so that

$$\mathbf{v}_1 = -\nabla\phi, \quad (\text{II.32})$$

$$\mathbf{v}_2 = \nabla \times \mathbf{A}, \quad (\text{II.33})$$

where ϕ is the scalar potential, $\mathbf{A}$ is the vector potential, and $\mathbf{u}(t)$ is arbitrary, does not depend on space variables and is usually set to zero. However, suppose the surface is set in motion by a steady velocity field. Even so, there will be fluctuations that are due to $K_B T$ excited pressure pulses. We can model this situation by making $\mathbf{u}$ represent the steady flow and letting $\mathbf{v}_1$ and $\mathbf{v}_2$ represent the fluctuations around the mean flow. In particle language the ripples will behave like seed particles in a laser anemometer experiment. The surface velocity field can be mapped out by use of surface-light-scattering spectroscopy.

The mass balance for incompressible media leads immediately to

$$0 = \nabla \cdot \mathbf{v} = -\nabla^2 \phi \quad (\text{II.34})$$

so that, along with boundary conditions, ϕ is uniquely determined. The momentum balance is more interesting so that for N_M (amplitude-to-wavelength ratio) sufficiently small

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla P + \eta \nabla^2 \mathbf{v}; \quad (\text{II.35})$$

Hence

$$\nabla \left(-\rho \frac{\partial \phi}{\partial t} + P \right) + \rho \dot{\mathbf{u}} = \nabla \times \left(-\rho \frac{\partial \mathbf{A}}{\partial t} + \eta \nabla^2 \mathbf{A} \right). \quad (\text{II.36})$$

However, the vector $\dot{\mathbf{u}}$ can always be represented by $\dot{\mathbf{u}} = \nabla(\dot{u}_1 x + \dot{u}_2 y + \dot{u}_3 z)$ so that incorporation into the gradient term only means that the potential is redefined. A solution to Eq. (II.36) is the set of equations

$$-\rho \frac{\partial \mathbf{v}}{\partial t} + P = 0, \quad (\text{II.37})$$

$$-\rho \frac{\partial \mathbf{A}}{\partial t} + \eta \nabla^2 \mathbf{A} = 0. \quad (\text{II.38})$$

Eqs. (II.34), (II.37), and (II.38) split the problem into one of potential flow and of flow of nonzero vorticity. The basis for splitting the velocity field in this way is kinematics alone;

dynamics is not an issue. The splitting of the velocity does induce a partitioning of the dynamic governing equations for both the volume and the surface equations of motion.

There are several ways to solve the surface-boundary–initial-value problem. However, because light scattering provides information about fluctuations that propagate in a selected direction, we make use of that information directly. Set the coordinate system so that the waves detected by the light-scattering spectrometer propagate in the x direction and the amplitude of the transverse wave is in the z direction. The formulas derived are based on this representation.

Define the stream function Ψ such that

$$\mathbf{v}_2 = \left(-\frac{\partial \Psi}{\partial z}, 0, \frac{\partial \Psi}{\partial x} \right) \quad (\text{II.39})$$

so that for this special case $\nabla \cdot \mathbf{v}_2 = 0$. From the properties of the vector potential, we have $A_y = \Psi$ for the two-dimensional case. Hence

$$-\rho \frac{\partial \Psi}{\partial t} + \eta \nabla^2 \Psi = 0.$$

Then one may use a velocity potential function ϕ and a velocity stream function Ψ to represent the velocity field so that

$$v_x = -\frac{\partial \phi}{\partial x} - \frac{\partial \Psi}{\partial z} + u_x(t), \quad (\text{II.40})$$

$$v_z = -\frac{\partial \phi}{\partial z} + \frac{\partial \Psi}{\partial x} + u_z(t), \quad (\text{II.41})$$

Note that the vorticity is $\zeta_{\text{vort}} = \nabla \times \mathbf{v} = \nabla \times \mathbf{v}_2$ in this representation, and indeed here

$$\zeta_{\text{vort}} = -\nabla^2 \Psi \hat{\mathbf{e}}_y, \quad (\text{II.42})$$

so that the total flow can be partitioned into potential flow along with vortex flow — both are needed for a complete description. Again, this is a point of kinematics.

With these definitions and under the assumptions of incompressible flow, the volume mass and the momentum equations of motion become

$$0 = \frac{\partial^2 \phi}{\partial x_2^2} + \frac{\partial^2 \phi}{\partial z_2^2}, \quad (\text{II.43})$$

$$\rho \frac{\partial \phi}{\partial t} = P, \quad (\text{II.44})$$

$$\frac{\rho}{\eta} \frac{\partial \Psi}{\partial t} = \nabla^2 \Psi. \quad (\text{II.45})$$

Note that $\rho \dot{\phi} = P$ is determined up to a constant, which is taken to be zero here. However, inclusion of a constant, the disjoining pressure, will be necessary in the case of thin films.

Consider the solution of Eq. (II.43), which is subject to boundary and initial conditions. The determination of the stream function follows the same pattern. First, do the space Fourier transform on $\nabla^2 \phi = 0$:

$$\frac{d^2 \phi_q}{dz^2} - q^2 \phi_q = 0 \quad (\text{II.46})$$

subject to $\phi_q \rightarrow 0$ as $z \rightarrow -\infty$. Hence

$$\phi_q = A(t) e^{-|q|z}, \text{ for } z > 0, \quad (\text{II.47})$$

$$\phi_q = A(t) e^{|q|z}, \text{ for } z < 0, \quad (\text{II.48})$$

However, note that, if a solid surface is of distance $-h$ from the surface at $z = 0$, the condition changes. Consider only potential flow. In this case, $v_z \rightarrow 0$ as $z \rightarrow -h$, and as a result $\frac{\partial \phi}{\partial z} \rightarrow 0$ as $z \rightarrow -h$ is a boundary condition. In this case

$$\phi_q = c \left\{ \exp[|q|(z+h)] + \exp[-|q|(z+h)] \right\}, \quad (\text{II.49})$$

which can be written as

$$\phi_q \big|_{z \rightarrow 0} = \phi_q(z=0, t) \cosh(|q|h). \quad (\text{II.50})$$

Eq. (II.50) adds terms to the dispersion equation that involve h . Adding the stream-function contribution leads to a more complicated formula for the velocity field throughout the fluid phase on the solid side of the interface. These functions are then used to provide the velocity and the pressure fields that appear in the jump conditions and the continuity conditions at the liquid interface.

It is important to recognize an assumption that is made by all who have studied this problem: The initial values of ϕ and Ψ obtained in the Laplace transform of Eqs. (II.44) and (II.45) are both taken to be zero everywhere; only the initial value of ζ is nonzero. This assumption is of questionable validity but leads to a spectrum function that fits data well. A qualitative discussion by Bouchiat [49] supports this assumption.

SLSS-4.6.1.3 *Solution by Fourier – Laplace Transformation in Space and Time*

The method of solution through the averaging of initial conditions that we develop for the surface transport problem is well described in the book by Berne and Pecora [7] for three-dimensional hypersonic wave motion. The governing equations are very different, and the methods of Berne and Pecora are used in what follows. An alternative is the construction that employs the fluctuation dissipation theorem. Bouchiat [49] showed that they are consistent.

In general, define for fluctuations moving in the x direction as determined by the optical system

$$\hat{\mathbf{T}}[f(x, t)](q, s) = \int_{-\infty}^{\infty} dx \int_0^{\infty} dt \exp(i q x - s t) f(x, t) \quad (\text{II.51})$$

Note that the kernel of the transform uses $(i q x - s t)$ so that, when $s \rightarrow i \omega$, the wave will propagate in the direction $\hat{\mathbf{e}}_x$. Experimentally, $\hat{\mathbf{e}}_x$ is selected simply by one's rotating the grating of Figs. II-3 or II-4. The operator $\hat{\mathbf{T}}$ when applied to the governing equations generates a set of linear equations of the form

$$\mathbf{M}(\mathbf{q}, s) \hat{\mathbf{x}} = \mathbf{L} \mathbf{x}(\mathbf{q}, 0), \quad (\text{II.52})$$

where $\hat{\mathbf{x}}(\mathbf{q}, s) = \hat{\mathbf{T}}[\mathbf{x}(\mathbf{x}, t)]$ and $\mathbf{x}(\mathbf{q}, t=0) = 0$ is the vector of initial values. Note that $\mathbf{x}(\mathbf{q}, 0)$ is *only* the Fourier transform of $\mathbf{x}(\mathbf{x}, t)$ at $t=0$. You can see that $\hat{\mathbf{x}}$ and $\mathbf{x}$ will be vectors of the dynamic variables ζ and ξ . The matrix $\mathbf{L}$ organizes the coefficients of the initial values. Solve Eq. (II.52) to get

$$\hat{\mathbf{x}}(\mathbf{q}, s) = \mathbf{M}^{-1} \mathbf{L} \mathbf{x}(\mathbf{q}, 0) \quad (\text{II.53})$$

There is an advantage to writing $\mathbf{M}^{-1}$ as

$$\mathbf{M}^{-1} = \frac{1}{\det(\mathbf{M})} \text{adj}(\mathbf{M}) \quad (\text{II.54})$$

where $\text{adj}(\mathbf{M})$ is the classical matrix adjoint (adjugate). We obtain the average, and thereby the spectrum, of the fluctuations by first multiplying through by $\mathbf{x}(\mathbf{q}, t=0)^t$ and computing $\langle \dots \rangle$

$$\begin{aligned} \mathbf{C}(s) &\stackrel{\text{def}}{=} \left\langle \hat{\mathbf{x}}(\mathbf{q}, s) \mathbf{x}(\mathbf{q}, 0)^t \right\rangle, \\ \mathbf{C}(s) &= \mathbf{M}^{-1} \mathbf{L} \left\langle \mathbf{x}(\mathbf{q}, 0) \mathbf{x}(\mathbf{q}, 0)^t \right\rangle. \end{aligned} \quad (\text{II.55})$$

Assume that $\left\langle \mathbf{x}(\mathbf{q}, 0) \mathbf{x}(\mathbf{q}, 0)^t \right\rangle$ is diagonal for the single-interface case (but not in general):

$$\mathbf{B} = \left\langle \mathbf{x}_i(\mathbf{q}, 0) \mathbf{x}_j(\mathbf{q}, 0) \right\rangle = \left\langle \left| \mathbf{x}_i(\mathbf{q}, 0) \right|^2 \right\rangle \delta_{ij}, \quad (\text{II.56})$$

$$\mathbf{C}(s) = \mathbf{M}^{-1} \mathbf{L} \mathbf{B}. \quad (\text{II.57})$$

Therefore for the amplitude correlation function

$$\mathbf{C}_{11}(s) = \frac{1}{\mathbf{D}(q, s)} \left(\left[\text{adj}(\mathbf{M}) \mathbf{L} \right]_{11} \right) \left\langle \left| \mathbf{x}_1(q, 0) \right|^2 \right\rangle, \quad (\text{II.58})$$

from which the spectrum function is computed. Note that $x_1 = \zeta_q$ and that the expectation must be calculated by use of the equipartition algorithm, as shown in Subsection 3.A, starting on page 4096 of Ref. [5]. However, the dispersion equation is, with $s \rightarrow i\omega$, the determinant set to zero

$$\mathbf{D}(q, i\omega) = 0. \quad (\text{II.59})$$

The spectrum function used to fit data is obtained as

$$\mathbf{G}(\omega) = \frac{1}{\pi} \text{Re} \left[\mathbf{C}_{11}(i\omega) \right]. \quad (\text{II.60})$$

Next, we apply this procedure first to the simple potential-flow problem as a simple but explicit example of the algorithm with an average over the distribution of possible initial conditions. The second application is to the isolated liquid–fluid interface that may be covered by a monolayer.

SLSS-4.6.2 Spectrum Function for the Single Interface

The harmonic-oscillator model for surface fluctuations has been popular, can be reasonably accurate for small N_{ca} , and is signaled by large γ/η ratios and also for overdamped ripples wherein N_{ca} is large, consistent with γ/η being small. However, as Bouchiat and Meunier showed (see, for example, Ref. [49]), the harmonic-oscillator model is flawed: The spectra deviate from the Lorentzian line shape, especially when $N_{\text{ca}} \approx 1$. We briefly show that the harmonic-oscillator model is obtained when vorticity is ignored, $\zeta_{\text{vort}} = 0$ [Eq. (II.42)], so that velocity fields are potential. The full spectrum function is then derived by use of the stream function to provide the vorticity contribution to the representation of the fluctuation dynamics.

SLSS-4.6.2.1 Potential-Flow Model and the Lorentzian Spectrum Function

Suppose that the flow is potential, a kinematic condition, so that at some initial time the velocity field was everywhere irrotational: $\nabla \times \mathbf{v} = 0$, thus $\Psi = 0$ everywhere and at all times. Use $\nabla^2 \phi = 0$ and $\rho \dot{\phi} = P$ for each phase and the continuity of the velocity field, which is $\dot{\zeta} = v_z|_{z \downarrow 0} = v_z|_{z \uparrow 0}$ (this is a requirement for a material surface connected to the surrounding phases), and the Laplace equation becomes

$$-q^2 \bar{\gamma} \zeta_q - [P_q] + 2 \left(\eta \frac{\partial v_{zq}}{\partial z} \right) = 0,$$

where $\bar{\gamma} = \gamma + (\Delta \rho g / q^2) + B_e q^2$ is the surface tension dressed by the gravity and the bending effects. Substitution and some algebra leads to

$$\frac{d^2 \zeta_q}{dt^2} + \bar{\omega}_q \frac{d \zeta_q}{dt} + \omega_q^2 \zeta_q = a_q(t), \quad (\text{II.61})$$

$$\bar{\omega}_q = 2 \frac{\left(\eta_u + \eta_b \right)}{\left(\rho_u + \rho_b \right)} q^2, \quad (\text{II.62})$$

$$\omega_q^2 = \frac{\bar{\gamma} q^2 |q|}{\left(\rho_u + \rho_b \right)}. \quad (\text{II.63})$$

Eqs. (II.62) and (II.63) are referred to hereafter as the Kelvin solution. Here we have added a stochastic term $a_q(t)$ that has units of acceleration but is a type of force, actually, the force over

the density. For this model, the tangential balance yields equations that depend on only the surface quality ξ_q , and there is no coupling between ς_q and ξ_q . This result is certainly wrong.

The limitation of this model is that, if the tangential pressure jump across the tangent plane is satisfied, then irrotational flow implies that $\dot{\varsigma}$ is a constant. Indeed, the tangent plane condition, $0 = \hat{n} \cdot [\mathbf{P}] \cdot \mathbf{U}_{\hat{n}}$, along with the irrotational condition, $\nabla \times \mathbf{v} = 0$, both satisfied for all z , imply that $\dot{\xi} = c$, independent of x and t so that there are no fluctuations at all! So, the general problem is not solved by the assertion that the flow is irrotational. However, from Eq. (II.61) a spectrum function is obtained that tracks the center frequency of experimental data through $\Im(\langle \varsigma_q^* \varsigma_q(t) \rangle)[\omega]$, but the width of the experimental spectrum is poorly represented.

After Fourier–Laplace transforming, Eq. (II.61) becomes

$$(s^2 + \bar{\omega}_q s + \omega_q^2) \hat{\varsigma}_q = \hat{a}(s) + \dot{\varsigma}_q(0) + (s + \bar{\omega}_q) \varsigma_q(0). \quad (\text{II.64})$$

Noting that $\langle \varsigma_q^*(0) \hat{a}(s) \rangle = 0$ and $\langle \varsigma_q^*(0) \dot{\varsigma}_q(0) \rangle = 0$ gives

$$\mathbf{C}(s) = \langle \varsigma_q^*(0) \hat{\varsigma}_q(s) \rangle = \frac{(s + \bar{\omega}_q)}{s^2 + \bar{\omega}_q s + \omega_q^2} \langle \varsigma_q^*(0) \varsigma_q(0) \rangle, \quad (\text{II.65})$$

so the spectrum is

$$G(\omega) = \frac{1}{\pi} \text{Re} \left(\frac{i \omega + \bar{\omega}_q}{-\omega^2 + i \bar{\omega}_q \omega + \omega_q^2} \right) \frac{K_B T}{\bar{\gamma} q^2} \quad (\text{II.66})$$

$$= \frac{K_B T}{\pi \bar{\gamma} q^2} \frac{\bar{\omega}_q \omega_q^2}{(\omega_q^2 - \omega^2)^2 + (\bar{\omega}_q \omega)^2}. \quad (\text{II.67})$$

This spectrum function can be put into a more familiar form in terms of a sum of Lorentzian-like functions:

$$G(\omega) = \frac{K_B T}{2\pi \bar{\gamma} q^2} \frac{\bar{\omega}_q \left[1 + (\bar{\omega}_q / \omega_q)^2 \right]}{(\omega_q - \omega)^2 + \bar{\omega}_q^2} + \frac{\bar{\omega}_q \left[1 + (\bar{\omega}_q / \omega_q)^2 \right]}{(\omega_q + \omega)^2 + \bar{\omega}_q^2} \quad (\text{II.68})$$

Eq. (II.68) is another example (Refs. [43, 47, 49, 56, 57]) of the utility of defining $Y = (\omega_q / \bar{\omega}_q)^2$ as it is clear that $G(\omega)$ is a double Lorentzian when Y is sufficiently large. The dimensionless group Y is directly related to the capillary number:

$$Y = \frac{1}{(2N_{ca})^2}. \quad (\text{II.69})$$

The capillary number is standard in the engineering literature, but Y is convenient for designing light scattering experiments. Also, note that Y , or N_{ca} , is calculated in terms of thermal-physical properties including the surface tension, the density and the viscosity sums for the surrounding phases, and the wave number characteristic of the experiment. The optical arrangement fixes the value of the wave number of the capillary ripples detected so that the dimensionless group Y , or N_{ca} , is known for that experiment.

The spectrum function Eq. (II.68) is often used in applications because of its simplicity. Occasionally, the Kelvin solution Eq. (II.63) is used and will provide a reasonable estimate of the surface tension, usually within 5 % to 10 % of the actual value. However, the estimate of the volume viscosity from Eq. (II.62) is very much in error, even when the instrument function correction is applied.

When $Y \gg 1$, the spectrum function Eq. (II.68), corrected for the instrument function, can be used effectively to determine $\bar{\omega}_q$ and ω_q . Then any two parameters can be computed from the *full* dispersion equation by one's finding its zero numerically. Explicitly, the dispersion equation is complex and in general is $\hat{\mathbf{D}}\left(q, \bar{\omega}_q, \omega_q, \rho_u, \rho_b, \eta_u, \eta_b, \gamma, \gamma_v, K_e, K_v, B_e, B_v\right) = 0$. See Eq. (II.96) for the construction of this function for the single, isolated interface case. The experimentalist must decide which two parameters are to be determined. For monolayer work, usually γ_v , B_e , and B_v are set to zero so that K_e and K_v are studied. When a pure fluid is being studied, γ and η_b , the surface tension and the major phase viscosity coefficients, respectively, are determined; γ_v, K_e, K_v, B_e , and B_v are taken to be zero and with reasonable justification (see Ref. [58] for additional comments framed with experimental data). However, there are obvious difficulties in determining the surface tension along with two volume viscosities for liquid-liquid interfaces. The computer power available allows the fitting of data to the full spectrum function, which carries all the parameters considered to be relevant to the experimental spectra. There is no longer a need to limit the fit to a Lorentzian model.

Keep in mind that the spectrum function for $Y > 10$ is still fairly close to being Lorentzian, so fitting to more than two or three parameters may lead to ill-conditioned, nonlinear least-squares problems and thereby to uncertainty in the values found by the fit. It is well worth the time and effort to use statistical design methods as part of the planning process for doing surface light-scattering spectroscopy.

SLSS-4.6.2.2 Derivation of the Spectrum Function for the Insoluble Monolayer

The governing equation for the normal balance is transformed according to Eq. (II.51) to obtain

$$-q^2 \bar{\gamma} \hat{\xi}_q - q^2 \bar{\gamma}_v \varsigma_q - \left[\rho \hat{\phi}_q \right] + 2 \left(\eta \frac{\partial \hat{v}_{zq}}{\partial z} \right) = 0, \quad (\text{II.70})$$

where $\bar{\gamma} = \gamma + (\Delta \rho g / q^2) + B_e q^2$ and $\bar{\gamma}_v = \gamma_v + B_v q^2$. The notation $\hat{\xi}_q = -\varsigma_q(t=0) + s \varsigma_q(s)$ is used to keep track of the initial condition. Such terms will be expanded before assembling the response matrix. The notation for dynamic variables such as $\hat{\phi}_q = s \phi_q$ take into account that the nonzero initial conditions will be in only the surface-displacement variables, $\hat{\xi}_q$ and $\hat{\xi}_q$. The velocity field in each phase must include both potential flow and vorticity. The vorticity is included through the transformed stream function [Eq. (II.45)]

$$\Psi_u = B_u \exp(-m_u z) \quad \text{and} \quad \Psi_b = B_b \exp(m_b z), \quad (\text{II.71})$$

$$m_u = \sqrt{q^2 + s \frac{\rho_u}{\eta_u}} \quad \text{and} \quad m_b = \sqrt{q^2 + s \frac{\rho_b}{\eta_b}} \quad (\text{II.72})$$

and are written for the isolated interface for which $\Psi_u \rightarrow 0$, $\Psi_b \rightarrow 0$, and $z \rightarrow \pm \infty$.

Note that the real part of m_u and m_b must be positive. Also, because q may be negative, the potential function is always taken as $\hat{\phi}_u = A_u \exp(-|q|z)$ and $\hat{\phi}_b = A_b \exp(|q|z)$. Failure to observe this protocol leads to a spectrum function that is not symmetric, as it must be, for $q \rightarrow -q$.

The tangent plane balance is

$$-q^2 K_e \hat{\xi}_q - q^2 K_v \hat{\xi}_q + \left[\eta \left(\frac{\partial \hat{v}_x}{\partial z} \Big|_q + \frac{\partial \hat{v}_z}{\partial x} \Big|_q \right) \right] = 0, \quad (\text{II.73})$$

where care is required to transform $\frac{\partial \hat{v}_z}{\partial x}$.

Additional relations are found through the four mathematical conditions of continuity of the velocity fields at the surface, where $[v_x] = 0$ is the no-slip condition and also $[v_z] = 0$. Because the surface is connected to each phase, we have

$$\hat{\zeta}_q = \lim_{z \downarrow 0} \hat{v}_z|_q, \quad (\text{II.74})$$

$$\hat{\zeta}_q = \lim_{z \uparrow 0} \hat{v}_z|_q, \quad (\text{II.75})$$

$$\hat{\xi}_q = \lim_{z \downarrow 0} \hat{v}_x|_q, \quad (\text{II.76})$$

$$\hat{\xi}_q = \lim_{z \uparrow 0} \hat{v}_x|_q. \quad (\text{II.77})$$

Eqs. (II.74) – (II.77) thus specified provide a response matrix after some tedious algebra that is involved in deriving the jump condition, which is now given.

Computation of $[\rho \hat{\phi}_q]$. The pressure jump is $[\rho \dot{\phi}_q] = \rho_u \dot{\phi}_q - \rho_b \dot{\phi}_q$ so that

$$[\rho \hat{\phi}_q] = \left(\frac{m_u}{|q|m - q^2} \rho_u + \frac{m_b}{|q|m - q^2} \rho_b \right) s \hat{\zeta}_q + \left(\frac{i q}{|q|m - q^2} \rho_u - \frac{i q}{|q|m - q^2} \rho_b \right) s \hat{\xi}_q \quad (\text{II.78})$$

where the limit

$$\lim_{\eta_u \rightarrow 0} [\rho \hat{\phi}_q] = \frac{\rho_u + \rho_b}{|q|} s \hat{\zeta}_q \quad \text{and} \quad \lim_{\eta_b \rightarrow 0} [\rho \hat{\phi}_q] = \frac{\rho_u + \rho_b}{|q|} s \hat{\zeta}_q$$

is as expected. A point of notation is that $s \hat{\zeta}_q = \hat{\zeta}_q$ since the initial condition is assumed to be $\dot{\zeta}_q(t=0) = 0$, and $s \hat{\xi}_q = \hat{\xi}_q$ since again the initial condition is assumed to be $\dot{\xi}_q(t=0) = 0$.

Computation of $\left[\eta \frac{\partial \hat{v}_{zq}}{\partial z} \right]$. The evaluation of this jump is most interesting for two reasons.

First, it couples the tangential displacement field into the governing equation for the displacement field along the normal. Second, it depends on only the tangential displacement field; nothing analogous to the second term in Eq. (II.61) appears. The simple harmonic-oscillator model does not emerge in the limit of small volume viscosities. This fact is a consequence of one's assuming nonzero vorticity. This is also the reason that it is incorrect to think of the spectrum as some perturbation of the harmonic-oscillator problem; the terms that allow that possibility cancel out to zero.

The result is

$$\left[\eta \frac{\partial \hat{v}_{zq}}{\partial z} \right] = \left\{ i q |q| \left(\frac{m_u}{|q| m_u - q^2} \eta_u - \frac{m_b}{|q| m_b - q^2} \eta_b \right) s \hat{\xi}_q - q^2 \left(\frac{i q}{|q| m_u - q^2} \eta_u - \frac{i q}{|q| m_b - q^2} \eta_b \right) \right\} \hat{\xi}_q \quad (\text{II.79})$$

and the limit, as the viscosity of the phases vanishes, is

$$\lim_{\eta_u \rightarrow 0} \left[\eta \frac{\partial \hat{v}_{zq}}{\partial z} \right] \rightarrow i q \left[\eta_u - \eta_b \right] \hat{\xi}_q \quad \text{and} \quad \lim_{\eta_b \rightarrow 0} \left[\eta \frac{\partial \hat{v}_{zq}}{\partial z} \right] \rightarrow i q \left[\eta_u - \eta_b \right] \hat{\xi}_q$$

and this does not depend on $\hat{\xi}_q$, as is required by the harmonic-oscillator model.

Computation of $\left[\eta \left(\frac{\partial \hat{v}_{xq}}{\partial z} + \frac{\partial \hat{v}_z}{\partial x} \right) \right]_q$. The tangential balance couples both the normal and the tangent plane displacements to give

$$\left[\eta \left(\frac{\partial \hat{v}_{xq}}{\partial z} + \frac{\partial \hat{v}_z}{\partial x} \right) \right]_q = \frac{i q}{|q|} \left\{ \left(m_u - |q| \right) \eta_u - \left(m_b - |q| \right) \eta_b \right\} \hat{\xi}_q - \left\{ \left(m_u + |q| \right) \eta_u + \left(m_b - |q| \right) \eta_b \right\} \hat{\xi}_q \quad (\text{II.80})$$

Again, note that we carefully distinguished between q that emerged from the Fourier transform of a derivative with respect to x and the derivative of the potential function with respect to z , which results in a factor $|q|$. The reason for attention to this detail is to retain the proper symmetry of the spectrum function.

Assembly of the response matrix. It is revealing to rewrite Eq. (II.70) in a form as close to the harmonic-oscillator approximation as possible by the redefinition of the center frequency ω_q and the damping frequency Γ_q as

$$\omega_q^2 = \frac{\bar{\gamma} q^2 |q|}{\frac{m_u}{m_u - |q|} \rho_u + \frac{m_b}{m_b - |q|} \rho_b}, \quad (\text{II.81})$$

which reduces to Eq. (II.63) in the limit of small viscosity. However,

$$\Gamma_q = \frac{\bar{\gamma}_v q^2 |q|}{\frac{m_u}{m-|q|} \rho_u + \frac{m_b}{m-|q|} \rho_b} \quad (\text{II.82})$$

which does not reduce to $\bar{\omega}_q$, [Eq. (II.62)], but rather accounts for the effect of the renormalized transverse viscosity $\bar{\gamma}_v$.

For the purpose of building the response matrix, define the auxiliary functions

$$a_1 = \frac{\frac{\rho_u}{m-|q|} + \frac{\rho_b}{m-|q|}}{\frac{m_u}{m-|q|} \rho_u + \frac{m_b}{m-|q|} \rho_b}, \quad (\text{II.83})$$

$$a_2 = \frac{2 i q |q| \left(\eta_u - \eta_b \right)}{\frac{m_u}{m-|q|} \rho_u + \frac{m_b}{m-|q|} \rho_b} \quad (\text{II.84})$$

for the normal balance so that

$$\omega_q^2 \hat{\xi}_q + \Gamma_q \hat{\xi}_q + \hat{\xi}_q + a_1 \hat{\xi}_q - a_2 \hat{\xi}_q = 0, \quad (\text{II.85})$$

where, when the viscosities are small, the harmonic-oscillator function

$$\omega_q^2 \hat{\xi}_q + \Gamma_q \hat{\xi}_q + \hat{\xi}_q = 0 \quad (\text{II.86})$$

holds, but the spectral width is determined by $\bar{\gamma}_v |q|$ and not by $\left(\eta_u + \eta_b \right)$.

Define the functions

$$b_1 = -\frac{i q}{|q|} \left\{ \left(\frac{m_u}{m-|q|} \right) \eta_u - \left(\frac{m_b}{m-|q|} \right) \eta_b \right\}, \quad (\text{II.87})$$

$$b_2 = \left\{ \left(\frac{m_u}{m+|q|} \right) \eta_u + \left(\frac{m_b}{m+|q|} \right) \eta_b \right\}. \quad (\text{II.88})$$

For the tangent plane, we find

$$K_e q^2 \hat{\xi}_q + (K_\nu q^2 + b_2) \hat{\xi}_q + b_1 \hat{\xi}_q = 0. \quad (\text{II.89})$$

Define $\hat{K} = K_e + s K_\nu$ and expand the derivative terms in Eqs. (II.85) and (II.89) to find the linear equations

$$(\omega_q^2 + \Gamma_q s + s^2) \hat{\xi}_q + (a_1 s^2 - a_2 s) \hat{\xi}_q = (\Gamma_q + s) \zeta_q(0) + (a_1 s - a_2) \xi_q(0), \quad (\text{II.90})$$

$$(s b_1) \hat{\xi}_q + (\hat{K} q^2 + s b_2) \hat{\xi}_q = (b_1) \zeta_q(0) + (K_\nu q^2 + b_2) \xi_q(0), \quad (\text{II.91})$$

so the linear response matrix is

$$\begin{bmatrix} \omega_q^2 + \Gamma_q s + s^2 & a_1 s^2 - a_2 s \\ s b_1 & \hat{K} q^2 + s b_2 \end{bmatrix} \begin{bmatrix} \hat{\xi}_q \\ \hat{\xi}_q \end{bmatrix} = \begin{bmatrix} \Gamma_q + s & a_1 s - a_2 \\ b_1 & K_\nu q^2 + b_2 \end{bmatrix} \begin{bmatrix} \zeta_q(0) \\ \xi_q(0) \end{bmatrix}. \quad (\text{II.92})$$

It follows that

$$\mathbf{M} = \begin{bmatrix} \omega_q^2 + \Gamma_q s + s^2 & a_1 s^2 - a_2 s \\ s b_1 & \hat{K} q^2 + s b_2 \end{bmatrix}, \quad (\text{II.93})$$

$$\mathbf{L} = \begin{bmatrix} \Gamma_q + s & a_1 s - a_2 \\ b_1 & K_\nu q^2 + b_2 \end{bmatrix}. \quad (\text{II.94})$$

The spectrum function for the elevation function then follows from the application of Eqs. (II.54), (II.58), and (II.60). Note that, with the addition of the bending coefficient [see Eq. 86 in Ref. [5]] and $\bar{\gamma} = \gamma + (g \Delta\rho/q^2) + B_e q^2$, the mean-squared elevation computed for Eq. 29 in Ref. [5], which is

$$\langle \zeta_q \zeta_q^* \rangle = \frac{K_B T}{(\gamma q^2 + \Delta\rho g) A_0},$$

generalizes to

$$\langle \zeta_q \zeta_q^* \rangle = \frac{K_B T}{(\gamma q^2 + \Delta\rho g + B_e q^4) A_0}. \quad (\text{II.95})$$

Note that the dispersion equation is

$$\det(\mathbf{M}) = 0, \quad (\text{II.96})$$

which, after the substitution $s \rightarrow i\omega$ [see Eq. (II.59)], is of use in interpreting the center frequency and the decay constant numbers estimated from a fit of the experimental correlogram to the Lorentzian model. However, we advocate use of the full spectrum function in the fitting algorithm along with the instrument function for the most accurate estimation of the parameters γ , K_e , K_v , and so on.

It is evident that the spectrum of the tangent plane displacement vector is easy to compute, as are the cross spectra between ς and ξ . These spectra are not observable with the surface light scattering instrument described in this text. Because $\langle \hat{\xi}_q(s) \xi_q(0) \rangle$ is dominated by the surface elastic modulus and not by the surface tension, a considerable enhancement of the resolution of the surface viscoelastic moduli is possible. It is doubtful that light scattering can be used for this purpose. $\langle \hat{\xi}_q(s) \xi_q(0) \rangle$ is calculated from the free energy

$F_e = G \left[u_{xx} u_{xx} - 1/2 (u_{xx})^2 \right] + K (u_{xx})^2$, which goes to the functional

$$R_e = \frac{\bar{G} + \bar{K}}{2} \int_{A_0} \left(\frac{\partial \xi}{\partial x} \right)^2 \sqrt{a} \, dx \, dy, \quad (\text{II.97})$$

where any coupling to ς must come from the metric and will be through $\sqrt{a} \approx 1 + \left(\frac{\partial \xi}{\partial x} \right)^2 / 2$.

Therefore

$$\langle \xi_q(0) \xi_q^*(0) \rangle = \frac{K_B T}{K_e q^2} \quad (\text{II.98})$$

$$\langle \xi_q(0) \varsigma_q^*(0) \rangle = 0. \quad (\text{II.99})$$

This completes the construction of the linear response theory for a single interface. Additional details are given in Ref. [5] and the full derivation is provided in Appendix II-C. The double interface development follows the same procedure as was used here for the single interface, but is a much longer calculation whose results are provided immediately below. The lengthy full derivation for the double interface is provided in Appendix II-D.

SLSS-4.6.3 Surface Response Function Algorithm for an Asymmetric Double-Interface (Thin Film)

After indulging in a fair amount of mathematics (provided in Appendix II-D), Meyer obtained the following general solutions for the mMatrix and nMatrix formulation of the normal and tangential governing equations for the asymmetric double-interface (thin-film) problem [3].

Examples showing results obtained with this SRF, whose theoretical underpinnings are outlined in Mann *et al.* [5], are plotted in Figs. II-25 – II-29. Experimental data [48, 59] taken with a thin film of pentane on water (as a function of temperature, *i.e.*, film thickness) are plotted in Fig. II-24 and support the formulation of the asymmetric double-interface SRF that follows. A summary of key analytical results follows:

$$\begin{pmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{pmatrix} \begin{pmatrix} \zeta_{q,u,m}[s] \\ \hat{\xi}_{q,u,m}[s] \\ \zeta_{q,m,b}[s] \\ \hat{\xi}_{q,m,b}[s] \end{pmatrix} = \begin{pmatrix} n_{11} & n_{12} & n_{13} & n_{14} \\ n_{21} & n_{22} & n_{23} & n_{24} \\ n_{31} & n_{32} & n_{33} & n_{34} \\ n_{41} & n_{42} & n_{43} & n_{44} \end{pmatrix} \begin{pmatrix} \zeta_{q,u,m}[0] \\ \xi_{q,u,m}[0] \\ \zeta_{q,m,b}[0] \\ \xi_{q,m,b}[0] \end{pmatrix}$$

Multiplying both sides by $\begin{pmatrix} \zeta_{q,u,m}^*[0] & \xi_{q,u,m}^*[0] & \zeta_{q,m,b}^*[0] & \xi_{q,m,b}^*[0] \end{pmatrix}$, we obtain:

$$\begin{aligned}
& \begin{pmatrix} \left\langle \zeta_q^*[0] \zeta_q[s] \right\rangle_{u,m} & \left\langle \xi_q^*[0] \zeta_q[s] \right\rangle_{u,m} & \left\langle \zeta_q^*[0] \zeta_q[s] \right\rangle_{m,b} & \left\langle \xi_q^*[0] \zeta_q[s] \right\rangle_{m,b} \\ \left\langle \zeta_q^*[0] \hat{\xi}_q[s] \right\rangle_{u,m} & \left\langle \xi_q^*[0] \hat{\xi}_q[s] \right\rangle_{u,m} & \left\langle \zeta_q^*[0] \hat{\xi}_q[s] \right\rangle_{m,b} & \left\langle \xi_q^*[0] \hat{\xi}_q[s] \right\rangle_{m,b} \\ \left\langle \zeta_q^*[0] \zeta_q[s] \right\rangle_{u,m} & \left\langle \xi_q^*[0] \zeta_q[s] \right\rangle_{u,m} & \left\langle \zeta_q^*[0] \zeta_q[s] \right\rangle_{m,b} & \left\langle \xi_q^*[0] \zeta_q[s] \right\rangle_{m,b} \\ \left\langle \zeta_q^*[0] \hat{\xi}_q[s] \right\rangle_{u,m} & \left\langle \xi_q^*[0] \hat{\xi}_q[s] \right\rangle_{u,m} & \left\langle \zeta_q^*[0] \hat{\xi}_q[s] \right\rangle_{m,b} & \left\langle \xi_q^*[0] \hat{\xi}_q[s] \right\rangle_{m,b} \end{pmatrix} \\
& = \text{Inverse} \begin{bmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix} \begin{pmatrix} n_{11} & n_{12} & n_{13} & n_{14} \\ n_{21} & n_{22} & n_{23} & n_{24} \\ n_{31} & n_{32} & n_{33} & n_{34} \\ n_{41} & n_{42} & n_{43} & n_{44} \end{pmatrix} \\
& \begin{pmatrix} \left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{u,m} & \left\langle \xi_q^*[0] \zeta_q[0] \right\rangle_{u,m} & \left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{m,b} & \left\langle \xi_q^*[0] \zeta_q[0] \right\rangle_{m,b} \\ \left\langle \zeta_q^*[0] \xi_q[0] \right\rangle_{u,m} & \left\langle \xi_q^*[0] \xi_q[0] \right\rangle_{u,m} & \left\langle \zeta_q^*[0] \xi_q[0] \right\rangle_{m,b} & \left\langle \xi_q^*[0] \xi_q[0] \right\rangle_{m,b} \\ \left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{u,m} & \left\langle \xi_q^*[0] \zeta_q[0] \right\rangle_{u,m} & \left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{m,b} & \left\langle \xi_q^*[0] \zeta_q[0] \right\rangle_{m,b} \\ \left\langle \zeta_q^*[0] \xi_q[0] \right\rangle_{u,m} & \left\langle \xi_q^*[0] \xi_q[0] \right\rangle_{u,m} & \left\langle \zeta_q^*[0] \xi_q[0] \right\rangle_{m,b} & \left\langle \xi_q^*[0] \xi_q[0] \right\rangle_{m,b} \end{pmatrix}
\end{aligned}$$

Here

$$denom001 = \left[2 q^2 \begin{pmatrix} -2 \left\{ \begin{aligned} & 1 + \exp(2 |q| h_0) + \exp(2 m h_0) - 4 \exp\left[\left(|q| + m\right) h_0\right] \\ & + \exp\left[2 \left(|q| + m\right) h_0\right] \end{aligned} \right\} |q| m \\ + \left[-1 + \exp(2 |q| h_0)\right] \left[-1 + \exp(2 m h_0)\right] (q^2 + m^2) \end{pmatrix} \right]$$

$$m_{11}(*zetaQHatUMUpperNormalCoef2*) = -q^2 \bar{\gamma}_{u,m} + s n_{11}$$

$$m12 (* xiQHatUMUpperNormalCoef 2 *) = s \ n12$$

$$m13 (* zetaQHatMBUpperNormalCoef 2 *) = vanDerWaalsTerm + s \ n13$$

$$m14 (* xiQHatMBUpperNormalCoef 2 *) = s \ n14$$

$$n11 (* zetaQUMUpperNormalCoef 2 *)$$

$$= - \left(\frac{2 s \ m \left\{ \begin{array}{l} \left[-1 + \exp(2 |q| h_0) \right] \left[1 + \exp(2 \ m \ h_0) \right] q^2 \\ - \left[1 + \exp(2 |q| h_0) \right] \left[-1 + \exp(2 \ m \ h_0) \right] |q| \ m \end{array} \right\} \rho}{denom001} - \frac{s \ \rho \ m}{q^2 - |q| \ m} + q^2 \ \bar{\gamma}_{u,m} \right)$$

$$n12 (* xiQUMUpperNormalCoef 2 *)$$

$$= i \ q \left\{ \begin{array}{l} \frac{-2 \ \eta_m + 2 \ \eta_u}{denom001} \\ \times \left[\begin{array}{l} \left[-1 + \exp(2 |q| h_0) \right] \left[-1 + \exp(2 \ m \ h_0) \right] q^2 \\ + \left\{ \begin{array}{l} 1 + \exp(2 |q| h_0) + \exp(2 \ m \ h_0) - 4 \exp \left[\left(|q| + m \right) h_0 \right] \\ + \exp \left[2 \left(|q| + m \right) h_0 \right] \end{array} \right\} |q| \ m \end{array} \right\} \rho_m \end{array} \right] + \left(\frac{s \ \rho_u}{q^2 - |q| \ m} \right) \end{array} \right\}$$

$$n13 (* zetaQMBUpperNormalCoef 2 *) =$$

$$\left\{ \frac{8 \exp \left[\left(|q| + m \right) h_0 \right] s \ |q| \ m \left[-q \sinh(q \ h_0) + m \sinh(m \ h_0) \right] \rho}{denom001} \right\}$$

$$n14 (* xiQMBUpperNormalCoef 2 *) =$$

$$\left(\frac{4 \ i \left\{ \exp(|q| \ h_0) - \exp(m \ h_0) - \exp \left[\left(2 |q| + m \right) h_0 \right] + \exp \left[\left(|q| + 2 \ m \right) h_0 \right] \right\} s \ m \ |q| \ q \ \rho}{denom001} \right)$$

$$m21 (* zetaQHatUMLowerNormalCoef 2 *)$$

$$= vanDerWaalsTerm + s \ n21 = vanDerWaalsTerm + s \ n13$$

$$m22 (* xiQHatUMLowerNormalCoef 2 *) = s \ n22 = -s \ n14$$

$$m23(*zetaQHatMBLowerNormalCoef\ 2\ *) = -q^2_{m,b} \bar{\gamma} + s\ n23$$

$$m24(*xiQHatMBLowerNormalCoef\ 2\ *) = s\ n24$$

$$n21(*zetaQUMLowerNormalCoef\ 2\ *) = n13$$

$$n22(*xiQUMLowerNormalCoef\ 2\ *) = -n14$$

$$n23(*zetaQMBLowerNormalCoef\ 2\ *) =$$

$$- \left(\frac{2\ s\ m_b \left\{ \begin{array}{l} \left[-1 + \exp(2\ |q|\ h_0) \right] \left[1 + \exp\left(2\ \frac{m}{m}\ h_0\right) \right] q^2 \\ - \left[1 + \exp(2\ |q|\ h_0) \right] \left[-1 + \exp\left(2\ \frac{m}{m}\ h_0\right) \right] |q|\ \frac{m}{m} \end{array} \right\} \rho_m}{denom001} - \frac{s\ \rho_b\ m_b}{q^2 - |q|\ \frac{m}{m_b}} + q^2\ \bar{\gamma}_{m,b} \right)$$

$$n24(*xiQMBLowerNormalCoef\ 2\ *)$$

$$= i\ q \left[\begin{array}{l} \frac{-2\ \eta_b + 2\ \eta_m}{denom001} \\ \times\ 2\ s \left\{ \begin{array}{l} \left[-1 + \exp(2\ |q|\ h_0) \right] \left[-1 + \exp\left(2\ \frac{m}{m}\ h_0\right) \right] q^2 \\ - \left(1 + \exp(2\ |q|\ h_0) + \exp\left(2\ \frac{m}{m}\ h_0\right) - 4\ \exp\left[\left(|q| + \frac{m}{m}\right) h_0\right] \right. \\ \left. + \exp\left[2\ \left(|q| + \frac{m}{m}\right) h_0\right] \right) |q|\ \frac{m}{m} \end{array} \right\} \rho_m - \left(\frac{s\ \rho_b}{q^2 - |q|\ \frac{m}{m_b}} \right) \end{array} \right]$$

$$m31(*zetaQHatUMUpperTangentCoef\ 2\ *) = s\ n31$$

$$m32(*xiQHatUMUpperTangentCoef\ 2\ *) = -q^2\ K_e + s\ n32$$

$$m33(*zetaQHatMBUpperTangentCoef\ 2\ *) = s\ n33$$

$$m34(*xiQHatMBUpperTangentCoef\ 2\ *) = s\ n34$$

n31 (* zetaQUMUpperTangentCoef 2 *)

$$= -\frac{1}{|q|} \left\{ i q \left[\begin{aligned} & -2 |q| \eta_m + \frac{1}{denom001} \\ & \times \left[\begin{aligned} & \left[-1 + \exp(2 |q| h_0) \right] \left[-1 + \exp\left(2 \frac{m}{m} h_0\right) \right] |q| \\ & 2 q^2 \left\{ \begin{aligned} & 1 + \exp(2 |q| h_0) + \exp\left(2 \frac{m}{m} h_0\right) \\ & -4 \exp\left[\left(|q| + \frac{m}{m}\right) h_0\right] + \exp\left[2 \left(|q| + \frac{m}{m}\right) h_0\right] \end{aligned} \right\} \frac{m}{m} \\ & \times \left(q^2 - \frac{m^2}{m}\right) \eta_m \end{aligned} \right] \right\} + |q| \eta_u - \eta_u \frac{m}{m} \end{aligned} \right\}$$

n32 (* xiQUMUpperTangentCoef 2 *)

$$= - \left(q^2 K_v + \frac{1}{denom001 |q|} \left\{ 8 \exp\left[\left(|q| + \frac{m}{m}\right) h_0\right] q^3 \left(q^2 - \frac{m^2}{m}\right) \left[\begin{aligned} & -\cosh\left(\frac{m}{m} h_0\right) \frac{m}{m} \sinh(q h_0) + \\ & q \cosh(q h_0) \sinh\left(\frac{m}{m} h_0\right) \end{aligned} \right] \eta_m \right\} \right. \\ \left. + \eta_u \left(|q| + \frac{m}{m}\right) \right)$$

n33 (* zetaQMBUpperTangentCoef 2 *)

$$= \frac{8 i \exp\left[\left(|q| + \frac{m}{m}\right) h_0\right] q |q| \left[\cosh(q h_0) - \cosh\left(\frac{m}{m} h_0\right) \right] \frac{m}{m} \left(q^2 - \frac{m^2}{m}\right) \eta_m}{denom001}$$

n34 (* xiQMBUpperTangentCoef 2 *)

$$= \frac{8 \exp\left[\left(|q| + \frac{m}{m}\right) h_0\right] q^3 \left(q^2 - \frac{m^2}{m}\right) \left[-\frac{m}{m} \sinh(q h_0) + q \sinh\left(\frac{m}{m} h_0\right) \right] \eta_m}{denom001 |q|}$$

m41 (* zetaQHatUMLowerTangentCoef 2 *) = s n41 = - s n33

m42 (* xiQHatUMLowerTangentCoef 2 *) = s n42 = s n34

m43 (* zetaQHatMBLowerTangentCoef 2 *) = s n43

m44 (* xiQHatMBLowerTangentCoef 2 *) = -q^2 K_e + s n44

n41 (* zetaQUMLowerTangentCoef 2 *) = - n33

n42 (* xiQUMLowerTangentCoef 2 *) = n34

n43 (* zetaQMBLowerTangentCoef 2 *)

$$= -i q \left\{ \left[\eta_m + \eta_b \left(-1 + \frac{m}{|q|} \right) + \frac{1}{denom001} \right] \times \left[2 m \eta_m \left(\begin{aligned} & 2 \left[-1 + \exp \left(2 \frac{m}{m} h_0 \right) \right] \left[-1 + \exp \left(2 |q| h_0 \right) \right] \frac{m}{m} q^2 \\ & - \left\{ \begin{aligned} & 1 + \exp \left(2 \frac{m}{m} h_0 \right) + \exp \left(2 |q| h_0 \right) \\ & - 4 \exp \left[\left(|q| + \frac{m}{m} \right) h_0 \right] + \exp \left[2 \left(|q| + \frac{m}{m} \right) h_0 \right] \end{aligned} \right\} \left(\frac{m^2}{m} + q^2 \right) |q| \end{aligned} \right] \right\}$$

n44 (* xiQMBLowerTangentCoef 2 *)

$$= - \left(q^2 K_v + \frac{1}{denom001 |q|} \left\{ 8 \exp \left[\left(|q| + \frac{m}{m} \right) h_0 \right] q^3 \left(q^2 - \frac{m^2}{m} \right) \left[\begin{aligned} & - \cosh \left(\frac{m}{m} h_0 \right) \frac{m}{m} \sinh (q h_0) + \\ & q \cosh (q h_0) \sinh \left(\frac{m}{m} h_0 \right) \end{aligned} \right] \eta_m \right\} + \eta_b \left(|q| + \frac{m}{b} \right) \right)$$

We simplify this by keeping its $\left\langle \zeta_{q,u,m}^* [0] \zeta_{q,m,b} [0] \right\rangle$ and $\left\langle \zeta_{q,u,m}^* [0] \zeta_{q,u,m} [0] \right\rangle$ components and dropping

its $\left\langle \zeta_{q,u,m}^* [0] \zeta_{q,m,b} [0] \right\rangle$ and $\left\langle \zeta_{q,u,m}^* [0] \zeta_{q,u,m} [0] \right\rangle$ components (where we assume the later two terms are

small since the components are nearly orthogonal for low amplitudes). We obtain the following intermediate form, which can be further simplified (begin by replacing the mMatrix components with their nMatrix forms and using the nMatrix equalities provided above). Because we are using TIR from the upper interface (see Fig. II-4) to collect the data shown in Fig. II-24, we only

need to consider the $\left\langle \zeta_{q,u,m}^* [0] \zeta_{q,u,m} [s] \right\rangle$ upper interface term when plotting the theoretical results shown in Fig. II-26 for comparison with our experimental data:

$$\begin{aligned}
& \left\langle \zeta_{u,m}^*[0] \zeta_{u,m}[s] \right\rangle \\
& = \text{Re} \left[\begin{aligned}
& \left((m_{22} m_{34} m_{43} n_{13} - m_{22} m_{33} m_{44} n_{13} - m_{14} m_{33} m_{42} n_{23} + m_{14} m_{32} m_{43} n_{23} - m_{12} m_{34} m_{43} n_{23} - m_{13} m_{32} m_{44} n_{23} + m_{12} m_{22} m_{43} n_{33} + m_{13} m_{22} m_{44} n_{33} + m_{14} m_{22} m_{33} n_{43} - m_{12} m_{34} n_{43} + m_{13} m_{32} n_{43} - m_{12} m_{33} n_{43}) + m_{23} (-m_{34} m_{42} n_{13} + m_{32} m_{44} n_{13} + m_{14} m_{42} n_{33} - m_{12} m_{44} n_{33} - m_{14} m_{32} n_{43} + m_{12} m_{34} n_{43}) \right) \left\langle \zeta_{u,m}^*[0] \zeta_{m,b}[0] \right\rangle + \\
& (m_{22} m_{34} m_{43} n_{11} - m_{22} m_{33} m_{44} n_{11} - m_{14} m_{33} m_{42} n_{21} + m_{14} m_{32} m_{43} n_{21} - m_{12} m_{34} m_{43} n_{21} - m_{13} m_{32} m_{44} n_{21} + m_{12} m_{22} m_{43} n_{31} + m_{13} m_{22} m_{44} n_{31} + m_{14} m_{22} m_{33} n_{41} - m_{12} m_{34} n_{41} + m_{13} m_{32} n_{41} - m_{12} m_{33} n_{41}) + m_{23} (-m_{34} m_{42} n_{11} + m_{32} m_{44} n_{11} + m_{14} m_{42} n_{31} - m_{12} m_{44} n_{31} - m_{14} m_{32} n_{41} + m_{12} m_{34} n_{41}) \right) \left\langle \zeta_{u,m}^*[0] \zeta_{u,m}[0] \right\rangle \\
& (-m_{12} m_{24} m_{33} m_{41} + m_{12} m_{23} m_{34} m_{41} + m_{11} m_{24} m_{33} m_{42} - m_{11} m_{23} m_{34} m_{42} + m_{12} m_{24} m_{31} m_{43} - m_{11} m_{24} m_{32} m_{43} - m_{12} m_{21} m_{34} m_{43} + m_{11} m_{22} m_{34} m_{43} + m_{14} (-m_{23} m_{32} m_{41} + m_{22} m_{33} m_{41} + m_{23} m_{31} m_{42} - m_{21} m_{33} m_{42} - m_{22} m_{31} m_{43} + m_{21} m_{32} m_{43}) - m_{12} m_{23} m_{31} m_{44} + m_{11} m_{23} m_{32} m_{44} + m_{12} m_{21} m_{33} m_{44} - m_{11} m_{22} m_{33} m_{44} + m_{13} (m_{24} m_{32} m_{41} - m_{22} m_{34} m_{41} - m_{24} m_{31} m_{42} + m_{21} m_{34} m_{42} + m_{22} m_{31} m_{44} - m_{21} m_{32} m_{44}))
\end{aligned} \right]
\end{aligned}$$

Noting that

$$\begin{aligned}
& \left\langle \zeta_{u,m}^*[0] \zeta_{u,m}[0] \right\rangle \\
& = \frac{k_B \text{ temperature} \left(\gamma_{m,b} q^2 + \left| \rho - \rho \right|_{m,b} g + B_e q^4 + \text{vanDerWaalsTerm} \right)}{\left[\left(\gamma_{u,m} q^2 + \left| \rho - \rho \right|_{u,m} g + B_e q^4 + \text{vanDerWaalsTerm} \right) \right.} \\
& \quad \left. \times \left(\gamma_{m,b} q^2 + \left| \rho - \rho \right|_{m,b} g + B_e q^4 + \text{vanDerWaalsTerm} \right) - \text{vanDerWaalsTerm}^2 \right],
\end{aligned}$$

this can be succinctly written as

$$\begin{aligned}
& \left\langle \xi_{u,m}^*[0] \xi_{u,m}[0] \right\rangle \\
&= \frac{k_B \text{ temperature} \left(\bar{\gamma}_{m,b} q^2 + \text{vanDerWaalsTerm} \right)}{\left(\bar{\gamma}_{u,m} q^2 + \text{vanDerWaalsTerm} \right) \left(\bar{\gamma}_{m,b} q^2 + \text{vanDerWaalsTerm} \right) - \text{vanDerWaalsTerm}^2}.
\end{aligned}$$

$$\begin{aligned}
&= \frac{k_B \text{ temperature} \left(\bar{\gamma}_{m,b} q^2 + \text{vanDerWaalsTerm} \right)}{\left(\bar{\gamma}_{m,b} q^2 \text{ vanDerWaalsTerm} \right) + \bar{\gamma}_{u,m} q^2 \left(\bar{\gamma}_{m,b} q^2 + \text{vanDerWaalsTerm} \right)}
\end{aligned}$$

Noting that

$$\begin{aligned}
& \left\langle \xi_{u,m}^*[0] \xi_{m,b}[0] \right\rangle = \left\langle \xi_{u,m}[0] \xi_{m,b}^*[0] \right\rangle \\
&= \frac{k_B \text{ temperature} \times \text{vanDerWaalsTerm}}{\left(\bar{\gamma}_{m,b} q^2 \text{ vanDerWaalsTerm} \right) + \bar{\gamma}_{u,m} q^2 \left(\bar{\gamma}_{m,b} q^2 + \text{vanDerWaalsTerm} \right)},
\end{aligned}$$

where

$$\bar{\gamma}_{u,m} \rightarrow \gamma_{u,m} + \frac{\left| \rho_u - \rho_m \right| g}{q^2} + B_{e,u,m} q^2 \quad \text{and} \quad \bar{\gamma}_{m,b} \rightarrow \gamma_{m,b} + \frac{\left| \rho_m - \rho_b \right| g}{q^2} + B_{e,m,b} q^2$$

and

$$\left\langle \xi_{m,b}^*[0] \xi_{m,b}[0] \right\rangle = \frac{k_B \text{ temperature} \left(\bar{\gamma}_{u,m} q^2 + \text{vanDerWaalsTerm} \right)}{\left(\bar{\gamma}_{m,b} q^2 \text{ vanDerWaalsTerm} \right) + \bar{\gamma}_{u,m} q^2 \left(\bar{\gamma}_{m,b} q^2 + \text{vanDerWaalsTerm} \right)}.$$

Additionally,

$$\left\langle \xi_{u,m}^*[0] \xi_{u,m}[0] \right\rangle = 0 \text{ when no monolayer is present}$$

and

$$\left\langle \xi_{u,m}^*[0] \xi_{u,m}[0] \right\rangle \neq 0 \text{ when a monolayer is present.}$$

When TIR from below the interface is not used for simply determining the power spectrum of the upper interface [such as when the middle fluid has an index of refraction that is greater than that of the bottom fluid and hence TIR results at the bottom interface at the angle of interest; or when the difference in the indices of refraction of the bottom and middle fluids is not small compared to the liquid – vapor (upper – middle) interface], the lower interface component

$\left\langle \zeta_{q, b}^*[0] \zeta_{q, b}[s] \right\rangle$, shown in Fig. II-28, may be added by using the approach and information provided above to obtain:

$$\begin{aligned}
 & \left\langle \zeta_{q, b}^*[0] \zeta_{q, b}[s] \right\rangle \\
 = \text{Re} & \left[\begin{aligned}
 & \left(-(\text{mm21 mm34 mm43 nn12} - \text{mm21 mm33 mm44 nn12} - \text{mm14 mm33 mm41 nn22} + \right. \\
 & \quad \text{mm13 mm34 mm41 nn22} + \text{mm14 mm31 mm43 nn22} - \text{mm11 mm34 mm43 nn22} - \\
 & \quad \text{mm13 mm31 mm44 nn22} + \text{mm11 mm33 mm44 nn22} - \text{mm14 mm21 mm43 nn32} + \\
 & \quad \text{mm13 mm21 mm44 nn32} + \text{mm14 mm21 mm33 nn42} - \text{mm13 mm21 mm34 nn42} + \\
 & \quad \text{mm24 (mm33 mm41 nn12} - \text{mm31 mm43 nn12} - \text{mm13 mm41 nn32} + \\
 & \quad \quad \text{mm11 mm43 nn32} + \text{mm13 mm31 nn42} - \text{mm11 mm33 nn42}) + \\
 & \quad \text{mm23 (-mm34 mm41 nn12} + \text{mm31 mm44 nn12} + \text{mm14 mm41 nn32} - \\
 & \quad \quad \text{mm11 mm44 nn32} - \text{mm14 mm31 nn42} + \text{mm11 mm34 nn42})) \left\langle \zeta_{q, b}^*[0] \zeta_{q, b}[0] \right\rangle \\
 & -(\text{mm21 mm34 mm43 nn11} - \text{mm21 mm33 mm44 nn11} - \text{mm14 mm33 mm41 nn21} + \\
 & \quad \text{mm13 mm34 mm41 nn21} + \text{mm14 mm31 mm43 nn21} - \text{mm11 mm34 mm43 nn21} - \\
 & \quad \text{mm13 mm31 mm44 nn21} + \text{mm11 mm33 mm44 nn21} - \text{mm14 mm21 mm43 nn31} + \\
 & \quad \text{mm13 mm21 mm44 nn31} + \text{mm14 mm21 mm33 nn41} - \text{mm13 mm21 mm34 nn41} + \\
 & \quad \text{mm24 (mm33 mm41 nn11} - \text{mm31 mm43 nn11} - \text{mm13 mm41 nn31} + \\
 & \quad \quad \text{mm11 mm43 nn31} + \text{mm13 mm31 nn41} - \text{mm11 mm33 nn41}) + \\
 & \quad \text{mm23 (-mm34 mm41 nn11} + \text{mm31 mm44 nn11} + \text{mm14 mm41 nn31} - \\
 & \quad \quad \text{mm11 mm44 nn31} - \text{mm14 mm31 nn41} + \text{mm11 mm34 nn41})) \left\langle \zeta_{q, b}^*[0] \zeta_{q, u, m}[0] \right\rangle \\
 & \left. \begin{aligned}
 & (-\text{m12 m24 m33 m41} + \text{m12 m23 m34 m41} + \text{m11 m24 m33 m42} - \text{m11 m23 m34 m42} + \\
 & \quad \text{m12 m24 m31 m43} - \text{m11 m24 m32 m43} - \text{m12 m21 m34 m43} + \text{m11 m22 m34 m43} + \\
 & \quad \text{m14 (-m23 m32 m41} + \text{m22 m33 m41} + \text{m23 m31 m42} - \text{m21 m33 m42} - \text{m22 m31 m43} + \\
 & \quad \text{m21 m32 m43})} - \text{m12 m23 m31 m44} + \text{m11 m23 m32 m44} + \text{m12 m21 m33 m44} - \\
 & \quad \text{m11 m22 m33 m44} + \text{m13 (m24 m32 m41} - \text{m22 m34 m41} - \text{m24 m31 m42} + \\
 & \quad \text{m21 m34 m42} + \text{m22 m31 m44} - \text{m21 m32 m44})) \right) \right]
 \end{aligned}
 \right.
 \end{aligned}$$

Fig. II-29 shows the upper and lower interface intensity components plotted on top of each other without regard to the impact on the intensity of the scattered light that results from the relative refractive indices of the liquids, which would make the comparison even more dramatic. When both the upper and lower interface scattered light information is available, their intensities need to be combined in a ratio that is related to the relative refractive indices of refraction of the upper and lower interfaces (which may not consist of sharp boundaries formed by two distinct indices of refraction). The use of total internal reflection and the possibility of evanescent coupling can have additional intensity ratio impacts.

Definitions for the symbols used for the asymmetric double-interface solution follow:

$$\left\{ \begin{array}{l} \text{vanDerWaalsTerm} = -\frac{\partial^2}{\partial h_0^2} \left(\frac{\text{HamakerConstant}}{12 \pi h_0^2} \right) \quad (* \text{ The vanDerWaalsTerm} \\ \text{function has more sophisticated forms, which are easily accomodated.} *) \end{array} \right\}$$

$$\left\{ \begin{array}{l} (* \text{ Note that an Under-script "u, m" denotes the} \\ \text{upper-middle interface and that an Under-script "m, b" denotes the} \\ \text{middle-bottom interface throughout this manuscript.} *) \\ \bar{\gamma}_{u,m} \rightarrow \gamma_{u,m} + \frac{\left| \rho_u - \rho_m \right| g}{q^2} + B_{e,u,m} q^2, \quad \bar{\gamma}_{m,b} \rightarrow \gamma_{m,b} + \frac{\left| \rho_m - \rho_b \right| g}{q^2} + B_{e,m,b} q^2, \\ \bar{\gamma}_v \rightarrow \gamma_v + B_v q^2, \quad \bar{\gamma}_v \rightarrow \gamma_v + B_v q^2, \\ m_b \rightarrow \text{positiveRealRoot} \left[q^2 + \frac{i \omega \rho_b}{\eta_b} \right], \quad m_m \rightarrow \text{positiveRealRoot} \left[q^2 + \frac{i \omega \rho_m}{\eta_m} \right], \\ m_u \rightarrow \text{positiveRealRoot} \left[q^2 + \frac{i \omega \rho_u}{\eta_u} \right] \end{array} \right\}$$

$$\left\{ \begin{array}{l}
(* \text{ Comment: The viscoelastic coefficients we take to be zero. } *) \\
s \rightarrow i \omega, B_{e,u,m} (* \text{ bending modulus } *) \rightarrow 0, B_{e,m,b} (* \text{ bending modulus } *) \rightarrow 0, \\
B_{v,u,m} (* \text{ bending viscosity } *) \rightarrow 0, B_{v,m,b} (* \text{ bending viscosity } *) \rightarrow 0, \\
\gamma_{v,u,m} (* \text{ transverse surface viscosity } *) \rightarrow 0, \gamma_{v,m,b} (* \text{ transverse surface viscosity } *) \rightarrow 0, \\
K_e (* = \bar{G} + \bar{K}, \text{ surface shear plus dilational elastic modulus } *) \rightarrow 0, \\
K_v (* = \bar{\eta} + \bar{\zeta}, \text{ surface shear plus dilational viscosity modulus } *) \rightarrow 0, \\
q \rightarrow \text{surfaceWaveNumber}, h_0 \rightarrow \text{interfacialThickness}, \\
\rho_u \rightarrow \text{densityUpperPhase}, \rho_m \rightarrow \text{densityMiddlePhase}, \rho_b \rightarrow \text{densityBottomPhase}, \\
\eta_u \rightarrow \text{viscosityUpperPhase}, \eta_m \rightarrow \text{viscosityMiddlePhase}, \eta_b \rightarrow \text{viscosityBottomPhase}, \\
\gamma_{u,m} \rightarrow \text{interfacialTensionUpperMiddleInterface}, \\
\gamma_{m,b} \rightarrow \text{interfacialTensionMiddleBottomInterface}, \\
g \rightarrow \text{gravitationalAcceleraton}, k_B \rightarrow 1 (* \text{ Drop Boltzmann constant scalefactor. } *), \\
\omega \rightarrow 2 \pi \text{ selectedFrequencyValuesForPowerSpectrumAxis}
\end{array} \right\}$$

SLSS-4.7 Asymmetric Double-Interface (Thin Film) Algorithm Results and their Comparison with Experimental Data

The following figures show and describe both experimental and theoretical power spectra plots for a thin-film of pentane on water. As the temperature of the sample cell and its contents are raised the pentane film thins. This allows us to study the coupling of the lower interface into the upper interface. The analytical solution we derived to solve this problem is provided in Appendix II-D and analytically summarized in the text above and in the figures that follow. This solution is supported by the experimental data in Fig. II-24, indicating that the essential pieces are now in hand for using surface light scattering spectroscopy to characterize thin films (including the measure and study Casimir-Polder forces, *i.e.*, vacuum fluctuations).

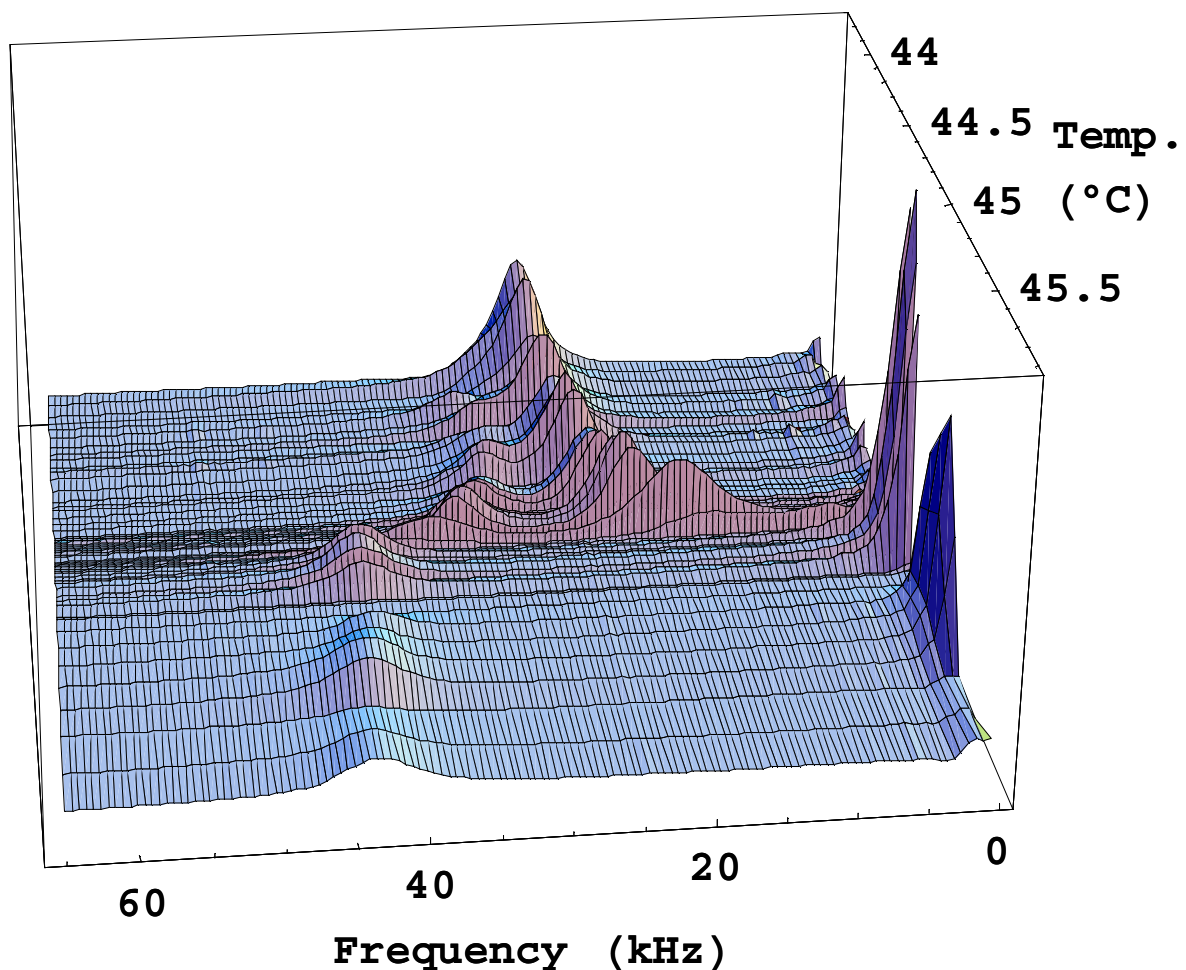


Fig. II-24. Power spectra measurements of a thin film of pentane on water, where the film thickness changes with temperature. These data were taken using TIR (see Fig. II-4) and plotted parametrically as functions of frequency and temperature, with the temperature axis being plotted nonlinearly. Compare with the theory plot shown in Fig. II-25, noting that Fig. II-25 does not include instrument function broadening. Gaps in the experimentally measured power spectra are visible where one expects a large low frequency contribution, *e.g.*, at 45 °C. Where gaps in the power spectrum exist across a complete frequency spectrum, this is likely a result of the application of cross correlation (which rejects otherwise corrupted data). Roll-off filters were set for – 6dB at 100 Hz and 1 MHz.

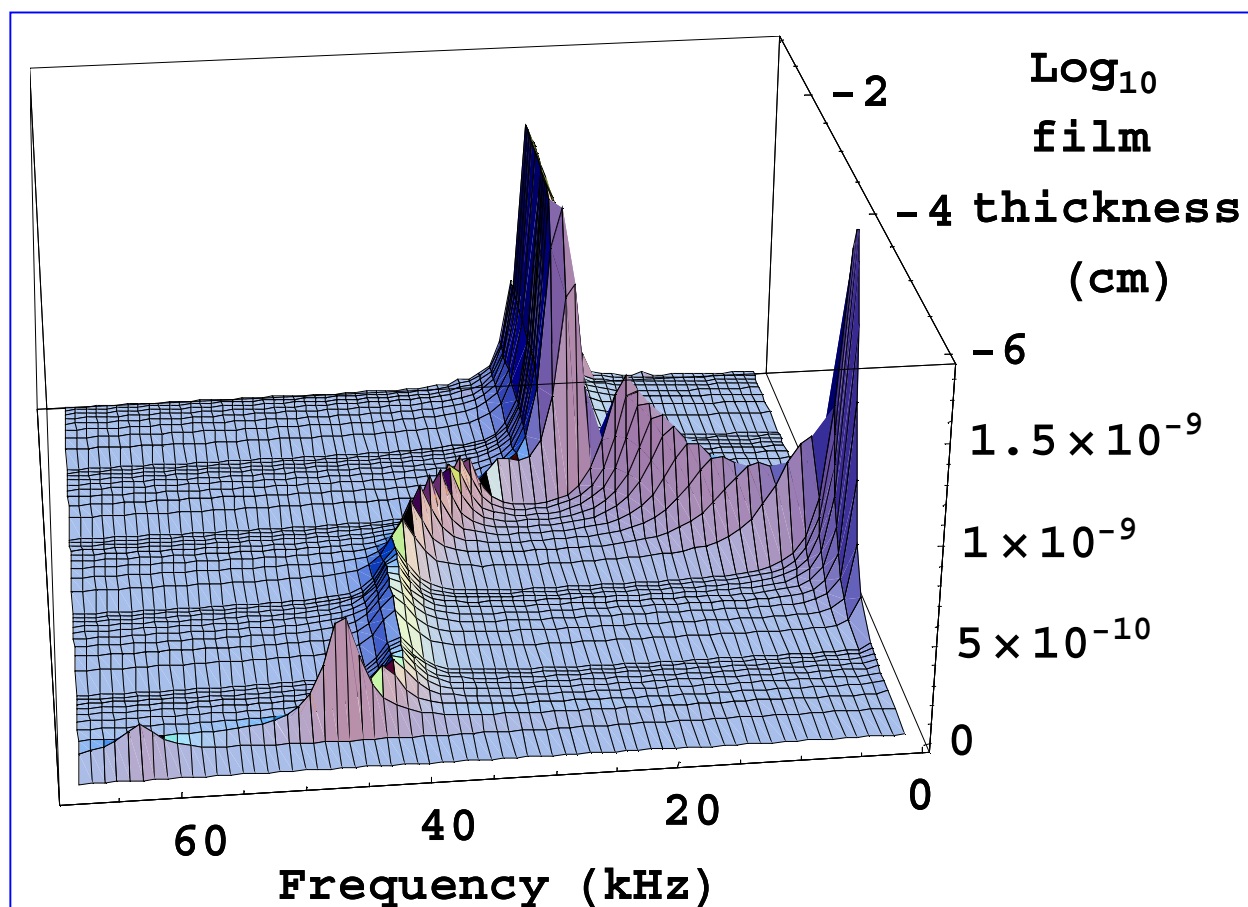


Fig. II-25. Theoretical power spectra measured at the liquid-vapor interface for a thin film of pentane on water. These power spectra are calculated without free parameters and given as a function of interfacial thickness for a fixed computational temperature of 45 °C, a Hamaker coefficient of 1.1×10^{-21} J, and a grating value of $K = 1000 \text{ cm}^{-1}$. Roll-off filters were not used in the computation. When comparing the figure above to Fig. II-24, note that the zero frequency is not plotted in Fig. II-25. The addition of ellipsometry data (not available at this time) should allow us to correlate the change in temperature with interfacial thickness, along with allowing us to adjust for the thermal-physical effects of temperature on the plot of the power spectra. All of this is included in the complete analytical formulation we provide in Appendix II-D and support in our Refs. (see Meyer *et al.* [3] and Mann *et al.* [5]).

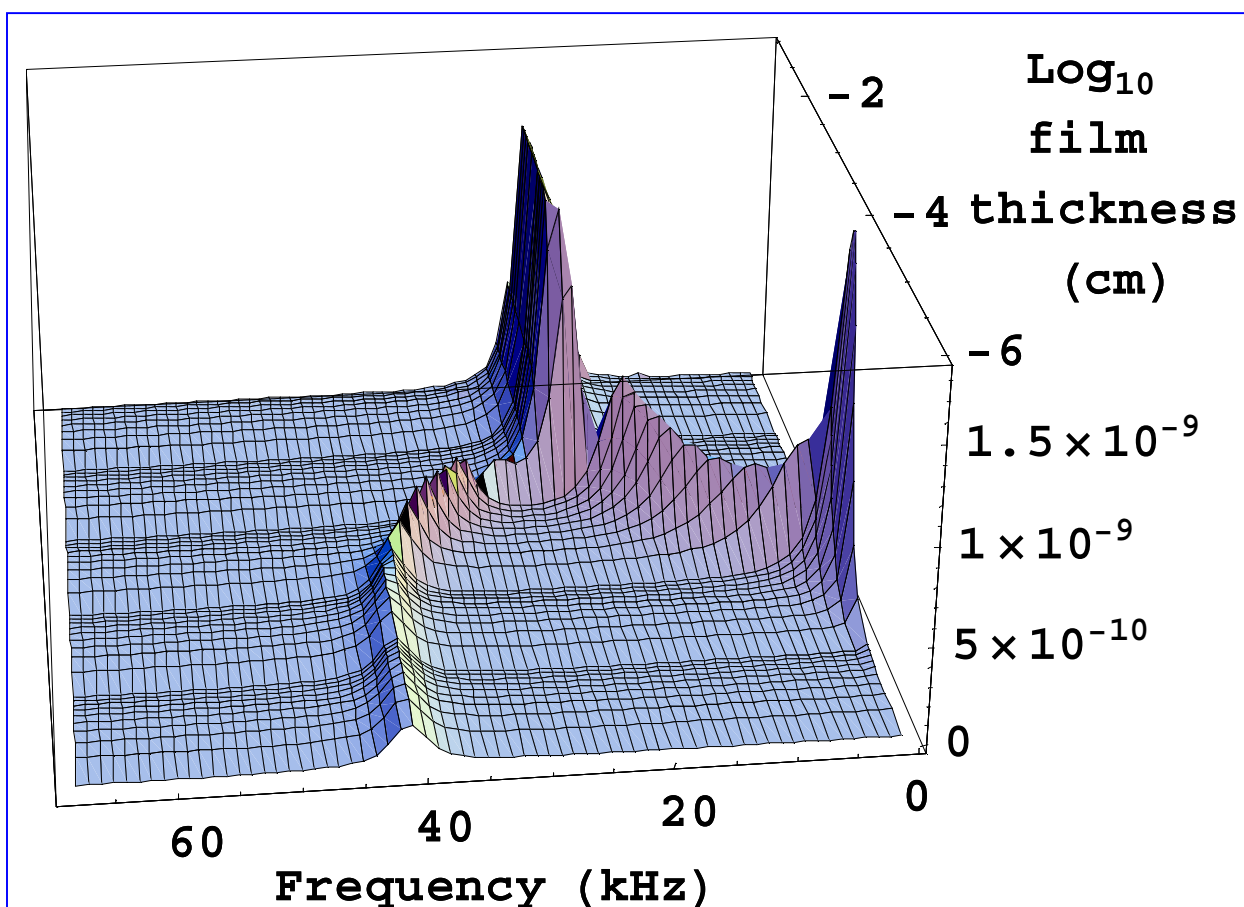


Fig. II-26. Theoretical power spectra measured at the liquid-vapor interface for a thin film of pentane on water. These power spectra are calculated without free parameters and given as a function of interfacial thickness for a fixed computational temperature of 45 °C, a Hamaker coefficient of zero J (*i.e.*, no Hamaker coefficient, Casimir-Polder force, included in the calculation), and a grating value of $K = 1000 \text{ cm}^{-1}$. Roll-off filters were not used in the computation. When comparing the figure above to Fig. II-24, note that the zero frequency is not plotted in Fig. II-26. Compare with Fig. II-25, which includes a Casimir-Polder force term for the upper interface that manifests itself as the film thins.

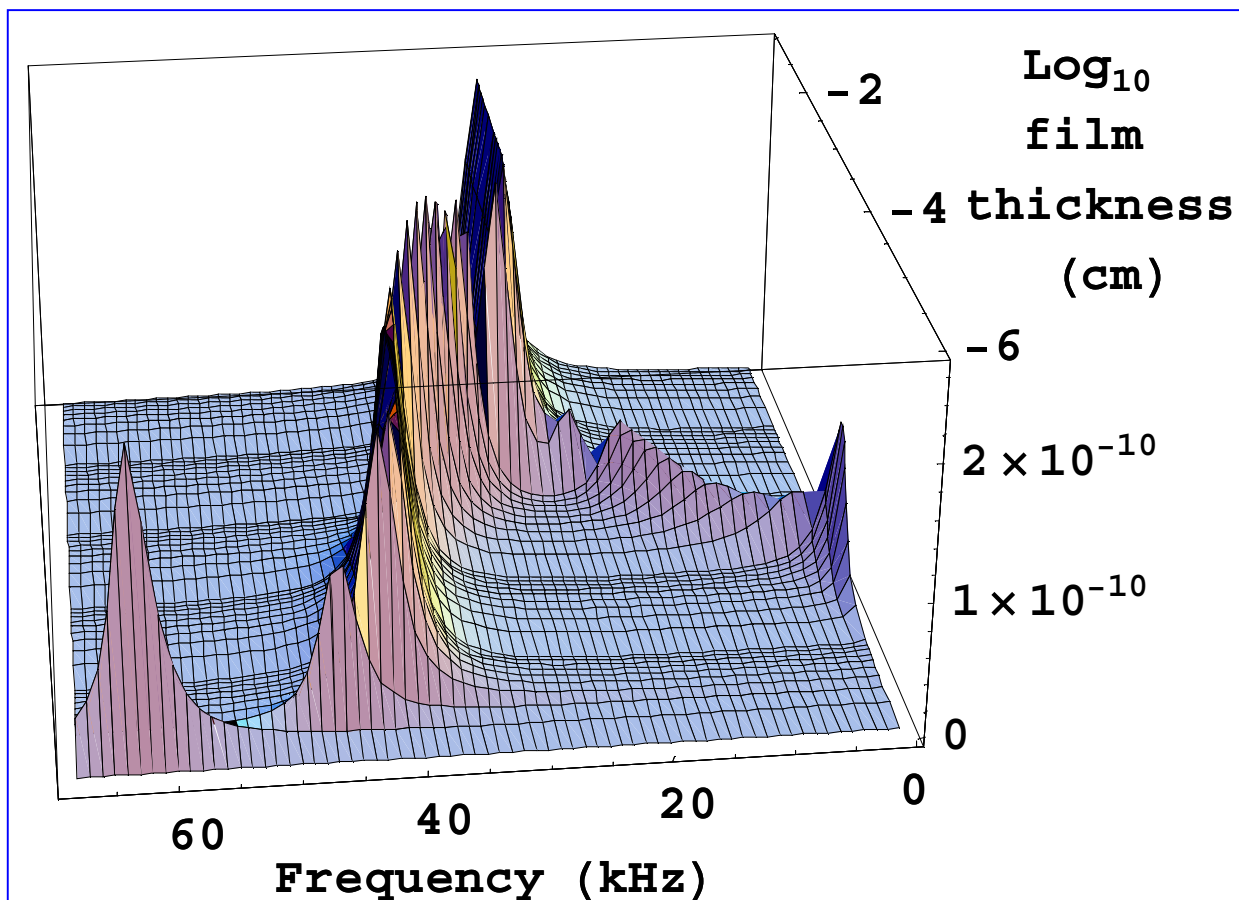


Fig. II-27. Theoretical power spectra for a thin film of pentane on water for light scattered from the lower (liquid-liquid) interface. These power spectra are calculated without free parameters and given as a function of interfacial thickness for a fixed computational temperature of 45 °C, a Hamaker coefficient of 1.1×10^{-21} J, and a grating value of $K = 1000 \text{ cm}^{-1}$. The same thermal-physical parameters are used, as in the previous 3-D power spectra plot in Fig. II-25 for the upper interface. While the use of total internal reflection in the present optical geometry ensures that the lower interface is not directly seen by the detector(s), the possibility of evanescent coupling or a different optical geometry might lead one to ask how the power spectrum plot of light scattered by the lower interface would look.

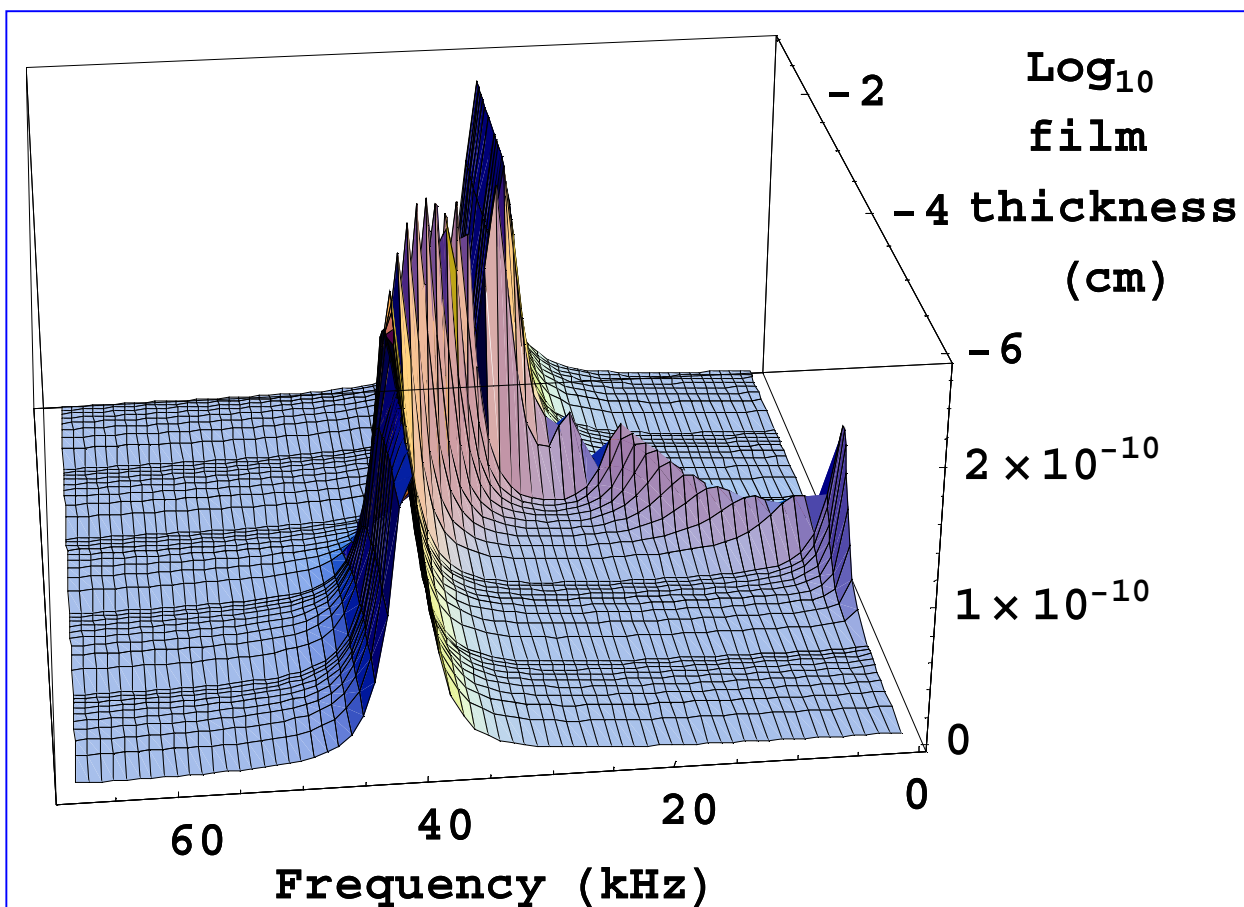


Fig. II-28. Theoretical power spectra for a thin film of pentane on water for light scattered from the lower (liquid-liquid) interface. The same thermal-physical parameters are used, as in the previous 3-D power spectra plot in Fig. II-26 for the upper interface (no Casimir-Polder force term has been included, *i.e.*, a Hamaker coefficient of zero J was used). Compare with Fig. II-27, which includes a Casimir-Polder force term for the lower interface that manifests itself as the film thins.

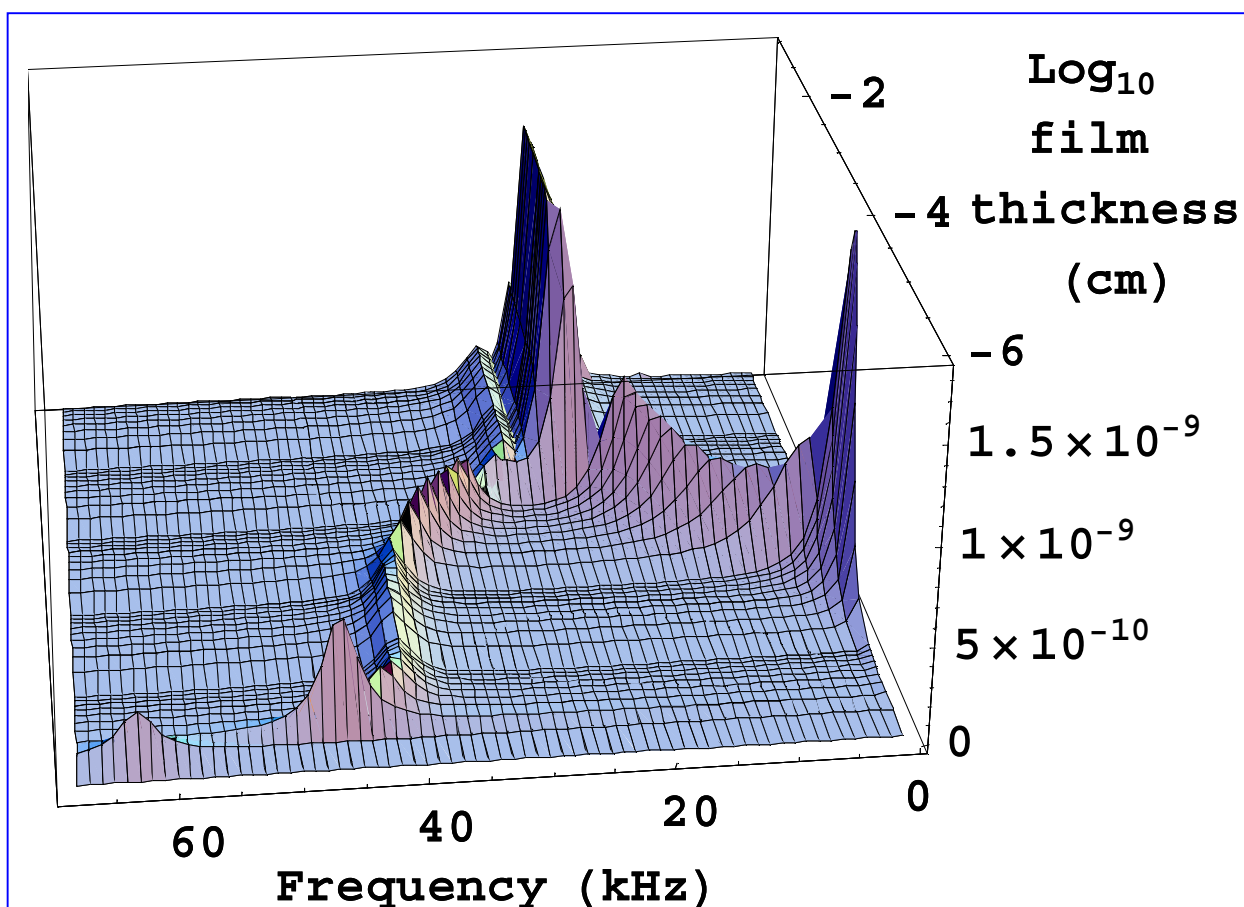


Fig. II-29. This figure shows the combined theoretical power spectra of Figs. II-25 and II-27, which displays the power spectra of both the upper interface and lower interface (including the Casimir-Polder force term) for a thin film of pentane on water. Note that the power spectra for the lower interface are about an order of magnitude lower in amplitude than the power spectra for the upper interface. This model does not account for the difference in the amount of light scattered from each interface due to the relative indices of refraction of the fluids or the use of total internal reflection (TIR). If evanescent coupling for very thin films exists, its contribution, for fluids in general, will be impacted by the above observations. Additionally, the possibility of TIR occurring at either the upper or lower interface (depending upon the relative indices of refraction of the two liquids and the entrance surface chosen for the laser beam) will impact the intensity ratio of the two sets of spectra seen at the detectors.

SLSS-5. Discussion and Conclusions

We have devised and demonstrated a new and easy to use method for mitigating the unwanted effects of external vibrations when using surface light scattering to non-invasively measure surface tension and viscosity at a fluid–fluid interface. This approach effectively suppresses normal vibration effects and allows our instrument to be used in a regular environment, rather

than in a more traditional environment that requires careful vibration isolation (as extreme as floating portions of the building). This instrument design can accommodate a total internal reflection (TIR) implementation, which acquires data much faster than when working in a non-TIR mode (since all the light is from the upper interface is reflected); and because the grating is oriented perpendicular to the cylindrical scattering cell, the scattering angle does not change when the index of refraction of the fluid is changed (but with a cylindrical cell and the grating oriented as we've discussed this index should be included in the instrument function, since it may shorten the grating lines at the interface; and flat entrance and exit windows for the laser beam entering and exiting the cylindrical cell may be used to address lensing affects of the cell). TIR also simplifies the power spectrum computation since very little light, in comparison, is scattered from the bottom interface when the wetting layer has an index of refraction comparable to that of the bottom fluid (the middle fluid index should be greater than the bottom fluid index to avoid TIR from the bottom interface for a particular angular range). We have found and implemented a practical algorithm for instrument function effects; these effects must be accounted for in order to obtain accurate results with typical instruments. We have demonstrated that the experimental correlograms follow Gaussian statistics, and we have shown the efficacy of including our instrument function algorithm in a maximum likelihood fit of experimental data acquired with a correlator. Our results have allowed us to empirically verify the correlation weighting function derived by Edwards. We have derived and computationally implemented SRFs for both the simple interface and the asymmetric thin-film interface based on the theory of Mann *et al.* [5] and the derivations of Meyer *et al.* [3]. Appendices II-C and II-D contains the full derivations and they are included on the accompanying CD ROM. Whereas the damped cosine model in combination with the full dispersion equation is limited to large or small values of Y , the SRF is more accurate and covers the full range of Y (including critically damped data). Our results for the simple fluid-vapor interface (confirmed computationally and with experimental data) provide the same results as Meunier's SRF. We have found that our theoretical results for the asymmetric thin-film interface are supported by experimental data (see Figs. II-26, II-28 and II-24, Appendix II-D, and Refs. [3], [48] and [5]). These advances, when combined, provide an accurate and non-invasive way to measure surface tension, viscosity, and many other interfacial parameters.

We note that we have developed and now have all the experimental and analytical tools needed allow surface light scattering spectroscopy to measure vacuum fluctuations by measuring the spectrum of thin films like those referenced experimentally and analytically in Figs. II-24, II-26 and II-28. The full analytical power spectrum plot shows that the experimental data taken to date are very close to having recorded vacuum fluctuations. We did not complete the theoretical calculation shown in Fig. II-26 until the data in Fig. II-24 was already acquired. The acquired data and theory agree over the range of recorded film thicknesses. The theoretical work in this text (detailed in Appendix II-D and plotted in Fig. II-26 and Fig. II-28) indicates that a change occurs (in both the position and height) in the power spectrums because of the Casimir-Polder forces in asymmetric thin films, when the films are only slightly thinner than in our experimental data shown in Fig. II-24. Compare Fig. II-25 with Fig. II-26 to see the effects of the Casimir-Polder force in the theoretical plots on the upper interface of the thin film and compare Fig. II-27 with Fig. II-28 to see the effects of the Casimir-Polder force on the theoretical plots of the lower interface of the thin film.

In conclusion, in Section II of this work we have added instrumental and analytical capabilities, along with ease of use to surface light scattering spectroscopy. Our improved instrument design, data analysis routines, instrument function, and theoretical derivations allow us to measure the interfacial properties of both simple fluids and of asymmetric thin films of a liquid-liquid-vapor interface.

SLSS-6. Appendices for Section II (large appendices found on CD ROM)

SLSS-6.1 Appendix II-A: Fourier Optics Derivation of Instrument Function

This derivation of the surface light scattering instrument function allows for both the traditional Edwards instrument function grating orientation and the rotated grating orientation discussed in this text. The derivation is provided as a *Mathematica* notebook of approximately 70 pages, which is included on the accompanying CD ROM. All of the *Mathematica* notebooks on this CD ROM can be either run in Mathematica or viewed with the *MathReader* program that is included on the CD ROM in Appendix II-I. . The latest version of the *MathReader* program, which can be downloaded for free and used for viewing *Mathematica* notebooks, may be found on the World Wide Web at <http://www.wolfram.com> .

SLSS-6.2 Appendix II-B: Using the NonlinearRegress Routine in Mathematica

In order for *Mathematica*'s NonlinearRegress data fitting routine to function at all with the SRFs, one must help *Mathematica* define the gradients it will find and use. Otherwise, when *Mathematica* 4.1 (and earlier versions) encounters the derivatives Re', Im', and Abs', it does not know how to proceed. Re' [] results from taking the derivative of Re [], which surrounds the Mann SRF. Im' [] results from taking the derivative of Im [], which surrounds the Meunier SRF. Whenever using the NonlinearRegress routine in *Mathematica* with the Mann and Meunier SRFs, add the following type of replacement rules to the gradient definition in the NonlinearRegress routine (here eqn_ stands for any equation):

```
Gradient → {Re [δinterfacialTensionSought powerSpectrumFitUsingMannSRF /. {Re' [eqn_ ] → 1,
Im' [eqn_ ] → - i, Abs' [eqn_ ] → 1}],
Re[δviscosityLowerPhaseSought powerSpectrumFitUsingMannSRF /. {Re' [eqn_ ] → 1,
Im' [eqn_ ] → - i, Abs' [eqn_ ] → 1}], etc.}
```

The - i is needed in the computer software for the Meunier SRF because *Mathematica* needs real numbers for its gradients and the Meunier SRF is set up so that the power spectrum is the imaginary part of the SRF. The - i multiplication factor takes the Im' [] that results from the Im [] function that surrounds the entire Meunier SRF and replaces it with - i to convert all the derived gradients to real values with an appropriate sign, since the negative sign flips the resulting minus sign that arises from ($i \times i$). Abs' [eqn_] → 1 is needed if you decide to computationally back-calculate K_s and σ_s using fluid standards, since Abs [K_s] is found throughout the SRFs. While W. Meyer derived and tested the algorithms in this work using *Mathematica* 4.1, we are working towards being able to provide a version of this *Mathematica* code or a related C programming language version (being developed by P. D. Crouser and S. M.

Grasson). Both programs contain bulk- and surface-light-scattering data analysis routines. The C programming language version of our software has both analysis routines and data acquisition capabilities and scripting for select correlators.

SLSS-6.3 Appendix II-C: Derivation of the Single Interface Surface Response Function Algorithm

This is about a 35-page derivation in a *Mathematica* notebook and is included on an accompanying CD ROM. This can be viewed using the MathReader program in Appendix II-I.

SLSS-6.4 Appendix II-D: Derivation of the Asymmetric Double-Interface (Thin Film) Surface Response Function Algorithm

This is about a 300-page derivation in a *Mathematica* notebook included on an accompanying CD ROM. This can be viewed using the MathReader program in Appendix II-I.

SLSS-6.5 Appendix II-E: Mathematica Notebook for generating 3-D Power Spectra of an Asymmetric Double-Interface (Thin Film) Using the Surface Response Function Algorithm

This contains two approximately 200-page *Mathematica* notebooks (when including graphics and 3-D plot values) and is included on an accompanying CD ROM. It contains both the generating routines for creating the 3-D power spectra of thin films as a function of film thickness (with and without Casimir-Polder forces) and plots for the **m** and **n** elements of the surface response function. The **m** and **n** element plots allow comparisons to be made when moving the *Mathematica* routines into other computing languages, thus significantly easing the effort required to find typing errors in portions of the large equations associated with the surface response function of the asymmetrical (thin-film) interface.

SLSS-6.6 Appendix II-F: Laser Light Scattering and Surface Light Scattering Data Analysis Program

This is a 10-megabyte program written by W. Meyer using *Mathematica*. It is included on an accompanying CD ROM. This program was used extensively for the surface light scattering and volume scattering data analysis in this work. This *Mathematica* program was often used in conjunction with the *Mathematica Link* (sequencer) tool of *Origin*® for obtaining many of the *Origin* data plots provided in this text. This program includes the ability to load single or multiple correlation functions and fit the correlograms and their Fourier transforms (power spectra) using any of several kinds of fitting routines with a selection of fitting parameters and weighting functions. Detailed fitting results and graphs are provided in Appendix II-G. Plots for statistical analyses can be generated, including plots of the variance, covariance matrices and

their inverses (e.g. – the correlation weighting function), correlation matrices, cumulative distribution functions, etc. The *Mathematica* program is required to run this software package.

SLSS-6.7 Appendix II-G: Data and Analysis Results

Found on the accompanying CD ROM.

SLSS-6.8 Appendix II-H: Vitae for W. V. Meyer

SLSS-6.8.1 Publications:

1. "Proceedings NASA Laser Light Scattering Advanced Technology Development Workshop, 1988," CP10033, published August 1989, edited by W.V. Meyer (meeting organizer).
2. W. V. Meyer and R. R. Ansari, "A Preview of a Microgravity Laser Light Scattering Instrument," 29th Aerospace Sciences Meeting, Reno, NV, January 9, 1991, American Institute of Aeronautics and Astronautics (AIAA 91-0779).
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4. R. R. Ansari, Harbans S. Dhadwal, Michael Cheung, and W. V. Meyer, "Particle sizing of concentrated suspensions using a back scatter fiber optic probe," paper #92, 65th Colloid and Surface Science Symposium, June 17-19 (1991), Norman, Oklahoma.
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11. Harbans S. Dhadwal, William Wilson, Rafat Ansari, and William V. Meyer, "Dynamic light scattering studies of BSA and Lysozyme using a backscatter fiber optic system", *Proceeding of the International Society of Optical Engineering: Fiber Optic Medical and Fluorescent Sensors and Applications*, Los Angeles, 19-24 January 1993.
12. W. V. Meyer, P. Tin, J. A. Mann, Jr., H. M. Cheung, R. B. Rogers, L. Lading, "A preview of a modular surface light scattering instrument with autotracking optics," *International Symposium on Space Optics*, April 18-22, 1994, Garmisch-Partenkirchen, FRG, EOS/SPIE Joint Venture, paper 2210-29.
13. W. V. Meyer, W. W. Tscharnuter, A. D. MacGregor, H. Dautet, P. Deschamps, F. Boucher, J. Zhu, P. Tin, R. B. Rogers, R. R. Ansari, "Laser Light Scattering, From an Advanced Technology Development Program to Experiments in a Reduced Gravity Environment," *International Symposium on Space Optics*, April 18-22, 1994, Garmisch-Partenkirchen, FRG, EOS/SPIE Joint Venture, paper 2210-21.
14. R. R. Ansari, H. S. Dhadwal, W. V. Meyer, "Method and Apparatus for Determining the Physical Properties of Materials Using Dynamic Light Scattering Techniques," *NASA Tech Briefs*, Vol. 19, Issue 9, p. 86, Sept. 1995.
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SLSS-6.8.2 Special Awards:

1. NASA's Silver Snoopy Award: (November 1, 2001, presented by NASA Astronaut Lee Morin), given by the NASA astronauts for significant contributions.

2. Special Achievement Award: LMM HCR/RDR team achievement award (June 27, 2001 – from Donald J. Campbell, NASA Glenn Research Center Director).

SLSS-6.8.3 Patent Applications (awarded or pending):

1. William V. Meyer, Padetha Tin, J. Adin Mann, Jr., James A. Lock, Anthony E. Smart, David S. Cannell, H. Michael Cheung, Thomas W. Taylor, Jixiang Zhu, “Cross-Correlation Apparatus and Method For Laser Light Scattering,” LEW-16517-1, U.S. patent filing 08/905-536 (awarded as patent # 5,956,139), foreign filing 98/114631.
2. William V. Meyer, David S. Cannell, Anthony E. Smart, Dynamic Light Scattering Homodyne Probe (U.S. Patent Pending, Docket No. 32188). 2001, OAI Patent Disclosure 98-01 (Pearne & Gordon LLP), UC Case 2001-295-1.
3. William V. Meyer, Anthony E. Smart, “Optical Device for Measuring a Surface Characteristic of an Object by Multi-Color Interferometry,” (OAI-1925-1) awarded January 30, 2001, U.S. patent number 6,181,430 B1.

SLSS-6.8.4 Patent Disclosures (held by OAI):

William V. Meyer, Padetha Tin, Thomas W. Taylor, “High Amplitude Power Spectrum Analyzer,” LEW-1639-1.

William V. Meyer, Padetha Tin, J. Adin Mann, Jr., “Diffractive Optical Elements (DOE) for Surface Light Scattering,” LEW-16360-1.

William V. Meyer, J. Adin Mann, Jr., Padetha Tin, James A. Lock, Thomas W. Taylor, H. Michael Cheung, “Cross Correlation For Surface Light Scattering,” LEW-16361-1.

William V. Meyer, Padetha Tin, J. Adin Mann, Jr., James A. Lock, Thomas W. Taylor, H. Michael Cheung, “Anti-Slosh Optical Train,” LEW-16362-1.

J. Adin Mann, Jr., Padetha Tin, William V. Meyer, “Fiber Optic Surface Light Scattering Instrument,” LEW-16363-1.

William V. Meyer, Gerard H. Wegdam, “Improved Signal Collection (higher K-sigma) Optics and Anti-Slosh Sample Cell for Surface Light Scattering Spectrometers,” LEW-16518-1, OAI-96-09.

SLSS-6.9 Appendix II-I: MathReader program for viewing Mathematica notebooks

The latest version of MathReader is available as a set of free downloadable files that can be run on multiple computer operating systems. It can be downloaded at <http://www.wolfram.com/products/mathreader/>. Found on the accompanying CD ROM.

SLSS-6.10 Appendix II-J: Table of Symbols and Acronyms

a	Hydrodynamic particle radius.
A	Intercept fitting parameter for correlation fitting function.
A	Vector potential.
APL	A Programming Language.
α	$= \frac{g \Delta \rho}{\gamma (K_g / M)^2}$
B	Baseline fitting parameter for correlation fitting function.
$B_{e_{m,b}}$	Bending modulus at the middle-bottom interface.
$B_{v_{m,b}}$	Bending viscosity at the middle-bottom interface.
$B_{e_{u,m}}$	Bending modulus at the upper-middle interface.
$B_{v_{u,m}}$	Bending viscosity at the upper-middle interface.
cm ⁻¹	Reciprocal (inverse) centimeters, i.e., lines/cm for a grating.
cP	centiPoise 10 ⁻² Poise (cm · g · second unit of viscosity equivalent to 10 ⁻³ Pa · s).
C(τ)	Correlation function. When measured we refer to this as a correlogram, which is an empirical approximation of a mathematical correlation function.
CI	Confidence interval.
d_{beam}	Illuminating diameter of the laser beam.
d_{fibers}	Separation distance between fiber optic pickups, $\xi_{\text{multiple}} < d_{\text{fibers}} < \xi_{\text{single}}$.
D	$= \frac{k_B T}{6\pi \eta a}$, diffusion coefficient in volume light scattering.
$\hat{\mathbf{D}}$	The eigenvalue matrix for the dispersion equation.

$\Delta\rho$	The density jump across the fluid-fluid interface.
ε_x	The cosine of the angle between the surface normal and the incoming laser beam for a flat interface (experimentally, it also accounts the ellipticity of the beam spot at the interface, which can be affected by surface curvature which elongates the grating lines when using geometries like Fig. II-3).
η	Viscosity.
η_b	Viscosity of the bottom phase.
η_m	Viscosity of the middle phase.
η_u	Viscosity of the upper phase.
f	Focus formed by index matching vat for scattering from a single scattering angle where $f = R \frac{n}{n-1}$, R is the radius of the index matching vat and n is the index of refraction of the liquid.
$f(t)$	Detected signal.
F	The surface light scattering instrument function kernel.
F_e	$= G \left[u_{xx} u_{xx} - 1/2 (u_{xx})^2 \right] + K (u_{xx})^2$, free energy.
FFT	Fast Fourier transform.
g	Gravitational acceleration.
$G(\tau)$	$= \langle n(t+\tau) n(t) \rangle$, auto-correlation function.
$G_{AB}(\tau)$	$= \langle n_A(t+\tau) n_B(t) \rangle = \langle n_B(t+\tau) n_A(t) \rangle$, temporal cross-correlation function.
$G(\omega)$	Power spectrum function.
GHQ	Gauss-Hermite Quadrature.
γ	Interfacial tension.

$\gamma_{m,b}$ Interfacial tension between the middle and bottom interface.

$\gamma_{u,m}$ Interfacial tension between the upper and middle interface.

$\gamma_v_{m,b}$ Transverse surface viscosity at the middle-bottom interface.

$\gamma_v_{u,m}$ Transverse surface viscosity at the upper-middle interface.

$\bar{\gamma}_{m,b} = \gamma_{m,b} + \frac{\left| \rho_m - \rho_b \right| g}{q^2} + B_{e,m,b} q^2$, dressed interfacial tension for middle-bottom interface.

$\bar{\gamma}_{u,m} = \gamma_{u,m} + \frac{\left| \rho_u - \rho_m \right| g}{q^2} + B_{e,u,m} q^2$, dressed interfacial tension for upper-middle interface.

$\bar{\gamma}_v_{m,b} = \gamma_v_{m,b} + B_v_{m,b} q^2$, dressed transverse surface viscosity at the middle-bottom interface.

$\bar{\gamma}_v_{u,m} = \gamma_v_{u,m} + B_v_{u,m} q^2$, dressed transverse surface viscosity at the upper-middle interface.

$$\Gamma_0 = 2 q^2 \left(\frac{\eta_u + \eta_b}{\rho_u + \rho_b} \right).$$

Γ_1 Chemical species.

$$\Gamma_K = 2 K_s^2 \left(\frac{\eta_u + \eta_b}{\rho_u + \rho_b} \right).$$

$$\Gamma_q \approx \Gamma_K \left(\frac{q}{K_s} \right)^2, \text{ decay coefficient.}$$

h_0 Interfacial thickness.

H Comes from the invariant $2H = c_1 + c_2$, where $c_\alpha = 1/R_\alpha$, where R_α is the radius of curvature of surface α .

HP	High-pass roll-off filters.
$i_A(t)$	Signal from detector A which arises from both single and multiple scattering contributions.
$i_B(t)$	Signal from detector B which arises from both single and multiple scattering contributions.
I_I	Incident light intensity used to calculate the Rayleigh ratio.
I_S	Scattered light intensity used to calculate the Rayleigh ratio.
I_{VH}	Intensity of horizontally (H) polarized scattered light that was vertically (V) polarized before scattering.
I_{VV}	Intensity of vertically (V) polarized scattered light that was vertically (V) polarized before scattering.
Im	The Imaginary part of a number or expression.
k_B	Boltzmann's constant.
K_e	$= \bar{G} + \bar{K}$, surface shear plus dilational elastic modulus.
K_v	$= \bar{\eta} + \bar{\zeta}$, surface shear plus dilational viscosity modulus.
$\hat{K}$	$= K_e + s K_v$
K_s	The wave number of the grating in the plane of the fluid interface.
K_1	First cumulant.
K_2	Second cumulant.
l_{photon}	Illuminating diameter of multiply scattered light surrounding the laser beam.
L	Matrix that organizes the coefficients of the initial values for the SRF.
LP	Low-pass roll-off filters.
λ	Vacuum wavelength of the laser light used in experiment.

- λ_0 Vacuum wavelength of the laser light used in experiment.
- $\Lambda_n = 1 / \sigma_n^2$, vector of Edwards weighting factor for n^{th} correlation channel.
- mN/m milliNewtons / meter, 10^{-3} Newtons per meter (unit for interfacial tension equivalent to dynes / cm).
- m_b = the positive real root of $\sqrt[+]{q^2 + s \frac{\rho_b}{\eta_b}}$
- m_m = the positive real root of $\sqrt[+]{q^2 + s \frac{\rho_m}{\eta_m}}$
- m_u = the positive real root of $\sqrt[+]{q^2 + s \frac{\rho_u}{\eta_u}}$
- M A magnification factor for the grating that determines the ripplon wave numbers K_s detected by the optical system. This may include misfocusing effects.
- MGHQ Use of Gauss-Hermite Quadrature approach proposed by Mann for computationally applying the instrument function in surface light scattering spectroscopy.
- n Refractive index of the media.
- n Number of terms in the Gauss-Hermite quadrature expansion. This must be an odd number of terms to include the zero-channel, i.e., $n = 11$.
- $n(t)$ Number of counts received during each interval $(t, t + T)$.
- $n_A(t)$ Resulting pulse stream from detector A.
- $n_B(t)$ Resulting pulse stream from detector B.
- N = $K_s \sigma_s$, a dimensionless group that essentially represents the number of grating lines seen by the ripples capillary waves) on the fluid interface.

$$N_{ca} = \frac{\omega_q}{|q|} \left(\frac{\gamma}{\eta_u + \eta_b} \right)^{-1}, \text{ capillary number.}$$

N_M Mach number or amplitude-to-wavelength ratio.

$\mathbf{P}$ Pressure tensor.

$P(\omega)$ Power spectrum.

$P_i(K_s, \omega)$ Model of power spectrum with instrument function F^2 .

$P_\zeta[q, \omega]$ Model of power spectrum without instrument function F^2 .

$$\text{positiveRealRoot } [z_] := \frac{\sqrt{x + |x + i y|} + i \text{Sign}[y] \sqrt{-x + |x + i y|}}{\sqrt{2}}$$

and we use the following replacement rules

$$\{x \rightarrow \text{Re}[z], y \rightarrow \text{Im}[z]\}.$$

PDF Probability Distribution Function.

Ψ Velocity stream function, which along with the velocity potential function ϕ represents the velocity field.

ϕ Velocity potential function, which along with the velocity stream function Ψ represents the velocity field.

ϕ_g Orientation of grating lines with respect to scattering plane.

$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$, where $\mathbf{k}_i$ is the wave vector of the incident light, $\mathbf{k}_s$ is that of the scattered light, and $\mathbf{q}$ is the scattered wave vector.

q_{sx} The surface wave number in the x direction always taken in the plane of the interface perpendicular to the grating lines.

q_{sy} The surface wave number in the y direction taken in the plane of the interface parallel to the grating lines.

Q An instrument scaling factor that includes factors such as the quantum efficiency of the detector. Q can be set equal to 1 for our purposes.

- r Distance detector is from detected scattering volume.
- R Pathlength of light used to calculate the Rayleigh ratio.
- $R_i(K_s, \tau)$ Model of correlation function with instrument function F^2 .
- $\langle R_i \rangle$ Average value for R_i .
- $R_\zeta(q, \tau)$ Model of correlation function without instrument function F^2 .
- Re The Real part of a number or expression.
- $\Re = \frac{I_s}{I_i} \frac{R^2}{V}$, Rayleigh ratio.
- ρ_b Density of the bottom phase.
- ρ_m Density of the middle phase.
- ρ_u Density of the upper phase.
- $s = i\omega$, where $i = \sqrt{-1}$.
- S.E. Asymptotic Standard Error $= \frac{\sigma}{\sqrt{2 \times (\text{number of samples})}}$, where σ is the standard deviation.
- SLSS Surface Light Scattering Spectroscopy.
- SRF Surface Response Function.
- σ Standard deviation (Std. dev.).
- σ_{gMag} The magnified beam width just before the surface, normal to the magnified beam propagation direction.
- $\sigma^2 = \left\langle \left(R_i - \langle R_i \rangle \right)^2 \right\rangle$ is the variance, where σ is the standard deviation.
- σ_s Spot size measured perpendicular to the laser beam, i.e., $\sigma_s = 0.066535$ cm (intensity measured at the $1/e^2$ points $= 4 \sigma_s$).

$$\sigma_{sx} = \frac{\sigma_{gMag}}{\varepsilon_x}.$$

t Time.

τ Lag-time between channels in the correlation function $C(\tau)$.

τ^* Turbidity.

T Temperature.

θ Scattering angle.

$\mathbf{U}_n$ The projector to the tangent plane and the grating orientation of the spectrometer.

v_z The velocity field in the z-direction.

V The scattering volume), by the integration of $\Re$ over the whole solid angle:

$$\tau^* = \int_{\Omega} \Re \, d\Omega(\theta, \phi).$$

VLS Volume Light Scattering.

ω $2\pi \times$ selected frequency values for the power spectrum axis (radians / second unless noted otherwise).

$$\omega_0 = \left(\frac{\gamma q^2 |q|}{\rho_u + \rho_b} \right)^{1/2}.$$

$$\omega_K = \left(\frac{\gamma K_s^2 |K_s|}{\rho_u + \rho_b} \right)^{1/2}.$$

ω_m $\sqrt{\omega_q^2 + \Gamma_q^2}$, renormalized (peak) frequency for simple harmonic oscillator.

$$\omega_q \approx \left(\frac{\gamma K_s^2 |K_s|}{\rho_u + \rho_b} \right)^{1/2} \left(\frac{q}{K_s} \right)^{3/2} = \omega_K \left(\frac{q}{K_s} \right)^{3/2}, \text{ center frequency.}$$

$\omega_i^{(n)}$ Weights used in Gauss-Hermite quadrature.

ξ The fluctuation amplitude tangential to the fluid-fluid interface.

$\xi_{\text{multiple}} \sim \frac{\lambda r}{l_{\text{photon}}} \sim 1 \text{ mm}$, multiple scattering speckle.

$\xi_{\text{single}} \sim \frac{\lambda r}{d_{\text{beam}}} \sim 1 \text{ mm}$, single scattering speckle.

$Y = 1 / (2 N_{\text{ca}})^2 = (\omega_0 / \Gamma_0)^2$.

ζ The fluctuation amplitude normal to the fluid-fluid interface.

$\mathbf{S}_{\text{vort}} = \nabla \times \mathbf{v} = \nabla \times \mathbf{v}_2$, vorticity.

$\zeta_{(m,b)}$ The fluctuation amplitude normal to the middle-bottom fluid-fluid interface.

$\zeta_{(u,m)}$ The fluctuation amplitude normal to the upper-middle fluid-fluid interface.

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Prof. Dr. Rens Waters	University of Amsterdam
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Yevick software, with its denser computational mesh spacing, is included in Appendix I-A on the accompanying CD ROM and was utilized to create Fig. I-10.

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VLS and SLSS-8. References for all Sections

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