Volume and Interface Studies of Complex Liquid Media

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Citation for published version (APA):

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ADVANCES IN INSTRUMENTATION AND ANALYSIS FOR NON-INVASIVELY MEASURING SURFACE TENSION, VISCOSITY, AND OTHER INTERFACIAL PARAMETERS IN 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 [6] 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 [6], 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 corregrogram to an accurate approximation of the spectrogram. Here, we use the terminology that the corregrogram is a point-wise, experimental representation of the theoretical correlation function.

The corregrogram that is measured is a finite approximation of the correlation function; the corregrogram 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. \cite{5}. The results of applying the FFT to the corregrogram to obtain a power spectrum is not exact and can be subject to errors, due in part to the finite length of the corregrogram. This concern with the FFT and our approach for mitigating this concern is discussed below and is addressed in more detail in Ref. \cite{5} 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 \cite{6}. Surface-light-scattering spectroscopy reports the dynamics that can be analyzed in terms of this more general surface property \cite{6}. This paper will deal analytically with both simple and complex interfaces; the generalization to complex interfaces has been written about by several authors \cite{43}, \cite{6}, \cite{49}, \cite{51}, \cite{50}. While the stream and potential function approach was first used in Ref. \cite{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. \cite{6} (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

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.
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.

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 (ripplons) 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 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 (Fig. II-2). 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. 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 rippons 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 ripplons; 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 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.

![Schematic diagram](image-url)

**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.
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 \( R_r = \int q R(q, r) dq \). The beam is Gaussian so that when \( \lambda_s \) 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 \( \phi_g \), where \( \phi_g = 90^\circ \) 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]:

\[
F^2 = Q^2 \exp \left[ -\left( \frac{\sigma_{g\text{Mag}}}{\varepsilon_x} \right)^2 (Q_s - q_{ss})^2 \right] \exp \left[ -\left( \sigma_{g\text{Mag}} \right)^2 \left( q_{sy} \right)^2 \right], \tag{II.1}
\]

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), \( q_{ss} \) 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, \( \varepsilon_x^2 = \cos^2 \theta_x \), where \( \varepsilon_x \) 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), \( \sigma_{g\text{Mag}} \) 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:

\[
F^2 = Q^2 \exp \left[ -\left( \frac{\sigma_{gMag}}{\varepsilon_s} \right)^2 \left( (q_{ss} - K_s)^2 + (\varepsilon_s q_{ss} + \varepsilon_s K_s)^2 \right) \right].
\] (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 \textit{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 \( \varepsilon_s K_{sy} \) 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 \( \varepsilon_s K_{sy} \) term in Eq. (II.3)), an enhanced instrument function is written as:

\[
F^2 = Q^2 \exp \left[ -\left( \frac{\sigma_{gMag}}{\varepsilon_s} \right)^2 \left( (q_{ss} - \varepsilon_s K_s)^2 + \left( \varepsilon_s q_{ss} + \varepsilon_s K_s \right)^2 \right) \right] + \exp \left[ -\left( \frac{\sigma_{gMag}}{\varepsilon_s} \right)^2 \left( (q_{sy} + \varepsilon_s K_s)^2 + \left( \varepsilon_s q_{sy} + \varepsilon_s K_s \right)^2 \right) \right].
\] (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:

$$F^2 = Q^2 \exp \left[ -\left( \frac{\sigma_{g\text{Mag}}}{\varepsilon_s} \right)^2 \left( (q_{sx} - \varepsilon_s K_{sx})^2 + (\varepsilon_s q_{sy} - K_{sy})^2 \right) \right]. \quad (\text{II.4})$$

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-versa. The $\varepsilon_s$ term in $\varepsilon_s K_{sx}$, in Eq. (II.3) above, disappears when we define $K_s$ to be the projection of $K_{sx}$ in the interface ($\varepsilon_s K_{sx} = K_s$ and $K_{sy} = 0$). This accounts for the remaining difference in the two instrument function formulations when we include the rotated grating orientation term $\varepsilon_s K_{sx}$. The $\varepsilon_s$ in the equations accounts for the ellipticity of the grating spot at the fluid interface; this impacts the value of $K_s$, 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 $\sigma_{sx} = \frac{\sigma_{g\text{Mag}}}{\varepsilon_s}$ 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 $\varepsilon_s$ when projected onto the surface at an angle. $\sigma_{sy}$, 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 $\phi_f$ 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:

$$F^2 = Q^2 \exp \left[ -\left( \frac{\sigma_{g\text{Mag}}}{\varepsilon_s} \right)^2 \left( (q_{sx} - K_s \cos[\phi_f])^2 + (\varepsilon_s q_{sy} - K_s \sin[\phi_f])^2 \right) \right]. \quad (\text{II.5})$$

We need to take the absolute value of the $\cos[\phi_f]$ and $\sin[\phi_f]$ 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 $q_{xx}$ and $q_{yy}$ 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, $K_y = K_y / M$ and $\sigma_y = M \sigma_y$, where $M$ is a magnification factor that may include misfocusing effects, and that for our grating orientation $N = K_y \sigma_y = K_y \sigma_z$. 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 $K_y$ 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 $\sigma$ ellipticity parameter, $\varepsilon_z$, during data analysis) can affect the relationship for $N$ between $\sigma_y$ and $\sigma_z$. 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 $\sigma_y$. 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., $\sigma_y$ 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 $\sigma_z$ 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
\[ R(K_s, \tau) = (1/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R_2[q, \tau] \ F^2[q_s - K_s, q_v] \ dq_s \ dq_v \]
when the grating lines are oriented perpendicular to the plane containing the incident and scattered light, and
\[ R(K_s, \tau) = (1/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R_2[q, \tau] \ F^2[q_s, q_v - K_s] \ dq_s \ dq_v \]
when the grating lines are oriented parallel to the plane containing the incident and scattered light,

and in the frequency domain this becomes a power spectrum that can be obtained by a Fourier transform on \( \tau \):
\[ P_s(K_s, \omega) = (1/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_2[q, \omega] \ F^2[q_s - K_s, q_v] \ dq_s \ dq_v \]
when the grating lines are oriented perpendicular to the plane containing the incident and scattered light, and
\[ P_s(K_s, \omega) = (1/2) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_2[q, \omega] \ F^2[q_s, q_v - K_s] \ dq_s \ dq_v \]
when the grating lines are oriented parallel to the plane containing the incident and scattered light,

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 correlation function. The correlation function for thermal fluctuations in surface elevation is required to complete Eqs. (II.6) and (II.7). The response function formalism [6, 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 (\( \omega_c \)) and decay coefficient (\( \Gamma_c \)), assuming a Lorentzian spectrum. Langevin [49] clearly points out the limits of this approximation through the use of a type of capillary number, \( Y=\frac{1}{(2 \ N_{ca})^2} \), where
\[ Y = \left( \frac{\omega_c}{\Gamma_0} \right)^2 \text{ and } N_{ca} \text{ is the capillary number, with } N_{ca} = \frac{\omega_q}{\sqrt{\left( \frac{\eta}{\eta + \eta_b} \right)}} \] which is a ratio of velocities. Here \( \Gamma_0 \) and \( \omega_c \) are defined in terms of the properties of each liquid phase as
\[ \Gamma_0 = 2 q^2 \left( \frac{\eta + \eta_b}{\rho_a + \rho_b} \right)^2 \text{ and } \omega_c = \left[ \gamma q^2 \left( \frac{\rho_a + \rho_b}{\rho_a + \rho_b} \right)^2 \right]^{1/2} \] where \( \gamma \) is the interfacial tension.
tension, $\rho_u, \rho_b, \eta_u$, and $\eta_b$ are the density and viscosity numbers for the upper and bottom phases. If $Y > 100$, the ripplons 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 ripplons 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

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

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, $\Gamma_q$ and $\omega_q$, are solutions of the dispersion equation that has the form

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

where $\hat{D}$ is the eigenvalue matrix, giving the complex eigenvalues of the problem. For more complicated interfaces other parameters are required. See Refs. [6, 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)

$$ R_s(K_s, \tau) = \frac{1}{2} \int \int K_g T \exp \left( -\Gamma_q \tau \right) \cos \left( \omega_q \tau \right) F^2 \left( q_{\alpha} - K_s, q_{\alpha} \right) dq_{\alpha} dq_{\gamma_s}. \quad (II.10) $$

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 $q_{\alpha}$ 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 $\omega_q$ and $\Gamma_q$.  

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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

$$\omega_n \approx \left( \frac{\gamma K_s^2 |K_s|}{\rho + \rho_b} \right)^{1/2} \left( \frac{q}{K_s} \right)^{3/2} = \omega_K \left( \frac{q}{K_s} \right)^{3/2}$$  \hspace{0.5cm} (II.11)

$$\Gamma_q \approx \Gamma_K \left( \frac{q}{K_s} \right)^{3/2},$$  \hspace{0.5cm} (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 $q_{ny}$, 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 $\omega_K$ and $\Gamma_K$ computed with formula (II.13), and values for $\rho, \rho_b$, and $\eta$ are input into the full dispersion equation(s), good estimates of $\gamma$ and $\eta$ 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

$$R_k(A, B, N, \Gamma_K, \omega_K, \tau)$$

$$= A \int_{-\infty}^{\infty} \exp\left(-x^2\right) \frac{\exp\left(-\Gamma_K \left(1 - \frac{x}{N}\right)^2 \tau\right)}{\left(1 - \frac{x}{N}\right)^2 + \alpha} \cos\left(\omega_K \left[1 - \frac{x}{N}\right]^{3/2} \tau\right) + B \right) \, dx.$$  \hspace{0.5cm} (II.13)

Here, $\alpha = \frac{g \Delta \rho}{\gamma \left(K_g / M\right)}$, 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 $\gamma$ 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).
\[ \int_{-\infty}^{\infty} \exp(-u^2) f(u) \, du = \sum_{i=-n}^{n} \omega_i \, \exp(i \int_{-\infty}^{\infty} f(u) \, du) + R_n \quad \text{(II.14)} \]

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 \( u^{13} = 0 \) 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 change in the fourth decimal place and the precision limit of the Yaws standards tables [54] \(^\dagger\) 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 [5] and comparing center frequencies and linewidths, rather than results obtained after applying a dispersion equation or SRF.

\(^*\) Note that formula 4.5.9 in Ref. 52. W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C. The Art of Scientific Computing.* 1999, Cambridge, United Kingdom: Cambridge University Press. for determining the weights \( \omega_i^{\text{(iii)}} \) is missing a factor of 2 in the numerator. This can be confirmed by comparing \( \int_{-\infty}^{\infty} \exp[-x^2] x^5 \, dx = \pi^{3/2} / 2 \) to \( \sum_{i=-n}^{n} \omega_i^{\text{(iv)}} f(u_i^{\text{(iv)}}) \); other even powers of \( u \) in \( f(x) = x^u \) will also show this. Moreover, \( \pi^{3/2} = \sum_{i=-n}^{n} \omega_i^{\text{(iv)}} / 10 \) to 13 significant figures.

\(^\dagger\) 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. C. L. Yaws, in *Handbook of Viscosity.* 1997, Gulf Publishing Company: Houston, TX.: surfaceTensionLitValue = surfaceTensionAtRefTempInKelvin

\[
\times \left( \frac{\text{criticalTempInKelvin} - \text{tempInKelvin}}{\text{criticalTempInKelvin} - \text{refTempInKelvin}} \right)^{1.4728} .
\]
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, 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 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 \( \tau \). 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:

\[
\text{Minimize} \left\{ \sum_{n=1}^{z} \Lambda_n \left[ R_i(n) - \langle R_i \rangle_{A,B,N,Y,\omega,\tau_n} \right]^2 \right\},
\]

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 [5, 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 \( \sigma_n^2 \) 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. [6]. The full derivations for both 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 \( \left\{ \frac{\mathcal{R}_n}{\bar{\mathcal{R}}_n} \right\}_{n} \) 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 \( -q^2 \bar{\mathcal{R}} \) term. So the Mann surface response function for a single interface that follows can be written in the form:

![Graphs showing weight factor and correlogram](image)

**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.
\[
\left< \xi^*_{u,b} [0] \hat{\xi}_q [s] \right> = \frac{\text{Term01} \left( - q^2 \bar{\eta} + s (\text{Term02}) \right) + s \left( \text{Term03} \right)}{\text{Term01} \left( - q^2 \bar{\eta} + s \bar{\eta} \right) + s^2 \left( \text{Term02} \right) + s^2 \left( \text{Term03} \right)} + B,
\]
which in full form is:

\[
powerSpectrumFitUsingMannSRF = P_c [q, \omega] = \left< \xi^*_{u,b} [0] \hat{\xi}_q [s] \right>
\]

\[
= \left( \frac{1}{\pi} \right) \Re \left[ \left( \frac{\text{powerSpectrumAmplitude}_{k_b} \text{ temperature}}{q^2 \bar{\eta}} \right) \times \left\{ \begin{aligned}
&\left( - q^2 (K_e + s K_v) - s \left( m \eta + m \eta + |q| (\eta + \eta) \right) \right) \\
&\times \left( - q^2 \bar{\eta} + s \left( \frac{m \rho}{q^2 - |q| m} + \frac{m \rho}{q^2 - |q| m} \right) \right) \\
&+ s \left( q \left( - m \eta + m \eta \right) - q^2 \left( - \eta + \eta \right) \right) \\
&\times \left( 2 \left( - \eta + \eta \right) + s \left( - \frac{\rho}{q^2 - |q| m} + \frac{\rho}{q^2 - |q| m} \right) \right)
\end{aligned} \right\} + \text{powerSpectrumBaselineOffset} \right]
\]

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 \Re[z], y \rightarrow \Im[z]\}.

46
\[
\begin{align*}
\bar{y} & \rightarrow \gamma + \frac{\rho - \rho}{q^2} g/B, \quad \bar{y}_v \rightarrow \gamma_v + B_v q^2, \\
\rho & \rightarrow \text{positiveRealRoot} \left[ q^2 + \frac{i \omega \rho}{\eta} \right], \quad \rho_0 \rightarrow \text{positiveRealRoot} \left[ q^2 + \frac{i \omega \rho}{\eta} \right]
\end{align*}
\]

\((\ast \text{ Comment: For a monolayer free interface, we take the surface viscoelastic coefficients to be zero. \ast})\)

\(s \rightarrow i \omega, B_v (\ast \text{ bending modulus } \ast) \rightarrow 0, B_v (\ast \text{ bending viscosity } \ast) \rightarrow 0,\)

\(\gamma_v (\ast \text{ transverse surface viscosity } \ast) \rightarrow 0,\)

\(K_v (\ast = G + K_v, \text{ surface shear and dilational elastic modulus } \ast) \rightarrow 0,\)

\(K_v (\ast = \bar{\eta} + \bar{\zeta}, \text{ surface shear and dilational viscosity modulus } \ast) \rightarrow 0,\)

\(q \rightarrow \text{surfaceWaveNumber},\)

\(\rho \rightarrow \text{densityUpperPhase}, \rho_0 \rightarrow \text{densityBottomPhase},\)

\(\eta \rightarrow \text{viscosityUpperPhase}, \eta_0 \rightarrow \text{viscosityBottomPhaseSought},\)

\(\gamma \rightarrow \text{interfacialTensionSought}, g \rightarrow \text{gravitationalAcceleration},\)

\(k_\rho \rightarrow 1 (\ast \text{ Drop Boltzmann constant scalefactor. \ast}),\)

\(\omega \rightarrow 2 \pi \text{ selectedFrequencyValuesForPowerSpectrumAxis}\)

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. [4] 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.

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 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
Fig. II-10. Wiener-Khintchine relationship showing the association between the detected signal, f(t); the correlation function C(τ); and the power spectrum P(ω). 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.

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 domains using increasing lengths of the correlogram from one decay time up to the eight decay times available from the synthetic data [5]. Estimates are shown for the analytic data without correlated errors and the synthetic data generated as explained by Smart et al. in Ref. [5]. 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. 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.

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 [5].
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 [5], 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

![Fig. II-13. Measured hardware roll-off filter affects for the EG&G 5113 preamplifier. Using the sigmoidal model provided in the text, Eqs. (II.16) – (II.19), we can analytically invert gentle roll-off affects in both the low-pass, LP, and high-pass, HP, roll-off filters with our data analysis software, before fitting our data analytically. This can be useful when the significant portions of the acquired signal are distorted by the use of high-pass filters.](image)
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, where the SRF is applied.

\[
\begin{align*}
\text{filterInitialValue} & \quad \text{filterFinalValue} \\
\text{lowpass filter} & \quad 1.0 & 0.0 & \quad \text{(II.16)} \\
\text{highpass filter} & \quad 0.0 & 1.0
\end{align*}
\]

\[
\text{filterPower} = \sqrt{\frac{\text{filterRollOffSetting}}{3.0}}, \quad \text{(II.17)}
\]

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

\[
\text{hardwareFilterSettings} = \frac{\text{filterInitialValue} - \text{filterFinalValue}}{1.0 + \left(\frac{\text{freqAxisValues}}{\text{filterCenterFreq}}\right)^{\text{filterPower}}} + \text{filterFinalValue}, \quad \text{(II.19)}
\]

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 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 = 0.000663 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 $\sigma_s = 0.065535 \text{ cm}$ (intensity measured at the $1/e^2$ points $= 4 \sigma_s$). We have also used this approach for determining values for $K_s$ and $\sigma_s$ 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

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

![Acetone data taken with cross-correlation. Data fit with a Mann GHQ (MGHQ) instrument function: $\omega = 9780.510 \text{ Hz}$, S.E. 1.645 Hz; $\Gamma = 304.265 \text{ Hz}$, S.E. 2.577 Hz; surface tension, 23.194 dynes/cm (mN/m); viscosity, 0.31703 cP; data, ■; fit, ●; residuals, ▲.](image)
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 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 [6] 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

---

**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, ▲.
Fig. II-18. Acetone data taken with autocorrelation. Data fit with a Lorentzian model and the MGHQ instrument function: \( \omega = 9753.070 \text{ Hz}, \text{ S.E.} 10.615 \text{ Hz}; \Gamma = 347.622 \text{ Hz}, \text{ S.E.} 16.275 \text{ Hz}; \) 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, ▲.

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 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 \( \Gamma \).
- 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. [5] 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

<table>
<thead>
<tr>
<th>Temperature = 23.0475 °C, N = 33.6271 - K, σ, K, = 505.401 cm⁻¹, σ, = 0.066535 cm, (High-pass roll-off filter set for -12 dB at 300 Hz)</th>
<th>Cross-correlation</th>
<th>Autocorrelation</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(acetone liquid – acetone vapor)</td>
<td>(acetone liquid – air vapor)</td>
<td></td>
</tr>
<tr>
<td>Data file: Aceton11.dat</td>
<td>Data file: Aceton45.dat</td>
<td>Literature [54] (extrapolated)</td>
<td></td>
</tr>
</tbody>
</table>

Exponentially damped cosine algorithm with Mann-GHQ instrument function correction:

<table>
<thead>
<tr>
<th></th>
<th>Cross-correlation</th>
<th>Autocorrelation</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension (time domain) [mN/m]</td>
<td>23.194 (6.01384 x 10⁻⁵)⁻¹</td>
<td>23.100 (2.33108 x 10⁻⁵)⁻¹</td>
<td>23.265</td>
</tr>
<tr>
<td>Surface tension (time domain, with the addition of the Edwards weighting function) [mN/m]</td>
<td>23.195 (5.61882 x 10⁻⁵)⁻¹</td>
<td>23.100 (2.15674 x 10⁻⁵)⁻¹</td>
<td>23.265</td>
</tr>
<tr>
<td>Surface tension (freq. domain) [mN/m]</td>
<td>23.194 (3.41266 x 10⁻⁶)⁻¹</td>
<td>23.098 (1.15624 x 10⁻⁶)⁻¹</td>
<td>23.265</td>
</tr>
<tr>
<td>Viscosity (time domain) [cP]</td>
<td>0.31703 (6.01384 x 10⁻⁵)⁻¹</td>
<td>0.36646 (2.33108 x 10⁻⁵)⁻¹</td>
<td>0.31345</td>
</tr>
<tr>
<td>Viscosity (time domain, with the addition of the Edwards weighting function) [cP]</td>
<td>0.31510 (5.61882 x 10⁻⁵)⁻¹</td>
<td>0.35479 (2.15674 x 10⁻⁵)⁻¹</td>
<td>0.31345</td>
</tr>
<tr>
<td>Viscosity (frequency domain) [cP]</td>
<td>0.31869 (3.41266 x 10⁻⁶)⁻¹</td>
<td>0.36639 (1.15624 x 10⁻⁶)⁻¹</td>
<td>0.31345</td>
</tr>
</tbody>
</table>

Exponentially damped cosine algorithm with no instrument function correction:

<table>
<thead>
<tr>
<th></th>
<th>Cross-correlation</th>
<th>Autocorrelation</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension (time domain) [mN/m]</td>
<td>23.244 (1.26889 x 10⁻⁵)⁻¹</td>
<td>23.150 (1.09555 x 10⁻⁵)⁻¹</td>
<td>23.265</td>
</tr>
<tr>
<td>Surface tension (time domain, with the addition of the Edwards weighting function) [mN/m]</td>
<td>23.225 (1.20257 x 10⁻⁵)⁻¹</td>
<td>23.153 (1.9717 x 10⁻⁵)⁻¹</td>
<td>23.265</td>
</tr>
<tr>
<td>Surface tension (freq. domain) [mN/m]</td>
<td>23.244 (7.47483 x 10⁻⁶)⁻¹</td>
<td>23.150 (2.20838 x 10⁻⁶)⁻¹</td>
<td>23.265</td>
</tr>
<tr>
<td>Viscosity (time domain) [cP]</td>
<td>0.53082 (1.26889 x 10⁻⁵)⁻¹</td>
<td>0.56889 (2.20838 x 10⁻⁵)⁻¹</td>
<td>0.31345</td>
</tr>
<tr>
<td>Viscosity (time domain, with the addition of the Edwards weighting function) [mN/m]</td>
<td>0.53781 (1.20257 x 10⁻⁵)⁻¹</td>
<td>0.56616 (1.9717 x 10⁻⁵)⁻¹</td>
<td>0.31345</td>
</tr>
<tr>
<td>Viscosity (frequency domain) [cP]</td>
<td>0.53113 (7.47483 x 10⁻⁶)⁻¹</td>
<td>0.56879 (1.09555 x 10⁻⁶)⁻¹</td>
<td>0.31345</td>
</tr>
</tbody>
</table>

( )⁻¹ = 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

<table>
<thead>
<tr>
<th>Temperature = 23.0475 °C, N = 33.6271 = K, σ, Ks = 505.401 cm⁻¹, σs = 0.066535 cm, (High-pass roll-off filter set for -12 dB at 300 Hz)</th>
<th>Cross-correlation</th>
<th>Autocorrelation</th>
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#### SRF algorithms with Mann-GHQ instrument function correction:

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<tr>
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<th>Cross-correlation</th>
<th>Autocorrelation</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension (Mann algorithm) [mN/m]</td>
<td>23.270 ( (2.07533 \times 10^{-6}) )</td>
<td>23.195 ( (1.108065 \times 10^{-5}) )</td>
<td>23.265</td>
</tr>
<tr>
<td>Surface tension (Meunier algorithm) [mN/m]</td>
<td>23.270 ( (2.07533 \times 10^{-6}) )</td>
<td>23.195 ( (1.108065 \times 10^{-5}) )</td>
<td>23.265</td>
</tr>
<tr>
<td>Viscosity (Mann algorithm) [cP]</td>
<td>0.31853 ( (2.07533 \times 10^{-8}) )</td>
<td>0.37842 ( (1.108065 \times 10^{-5}) )</td>
<td>0.31345</td>
</tr>
<tr>
<td>Viscosity (Meunier algorithm) [cP]</td>
<td>0.31853 ( (2.07533 \times 10^{-8}) )</td>
<td>0.37842 ( (1.108065 \times 10^{-5}) )</td>
<td>0.31345</td>
</tr>
</tbody>
</table>

#### SRF algorithms with no instrument function correction:

<table>
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<th></th>
<th>Cross-correlation</th>
<th>Autocorrelation</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension (Mann algorithm) [mN/m]</td>
<td>23.355 ( (7.57408 \times 10^{-6}) )</td>
<td>23.278 ( (9.88393 \times 10^{-5}) )</td>
<td>23.265</td>
</tr>
<tr>
<td>Surface tension (Meunier algorithm) [mN/m]</td>
<td>23.355 ( (7.57407 \times 10^{-6}) )</td>
<td>23.278 ( (9.88393 \times 10^{-5}) )</td>
<td>23.265</td>
</tr>
<tr>
<td>Viscosity (Mann algorithm) [cP]</td>
<td>0.52870 ( (7.57408 \times 10^{-9}) )</td>
<td>0.57521 ( (9.88393 \times 10^{-8}) )</td>
<td>0.31345</td>
</tr>
<tr>
<td>Viscosity (Meunier algorithm) [cP]</td>
<td>0.52870 ( (7.57407 \times 10^{-9}) )</td>
<td>0.57521 ( (9.88393 \times 10^{-8}) )</td>
<td>0.31345</td>
</tr>
</tbody>
</table>

\( (\cdot) \) = 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.

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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 $\omega_m$ 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 $\omega \rightarrow \omega \left| q \right|^{1/2}$ and $\Gamma \rightarrow \Gamma \left| K \right|$, 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).

$$\exp(-\Gamma K \tau) \left[ \cos\left(\omega_q \tau\right) + \frac{\Gamma K \sin\left(\omega_q \tau\right)}{\omega_q} \right]$$

$$= \exp(-\Gamma K \tau) \left[ \cos\left(\sqrt{\omega_m^2 + \Gamma_k^2} \tau\right) + \frac{\Gamma K \sin\left(\sqrt{\omega_m^2 + \Gamma_k^2} \tau\right)}{\sqrt{\omega_m^2 + \Gamma_k^2}} \right]$$

$$R_q(K_q, \tau)$$

$$= A \times \frac{1}{\tau} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} K \frac{\Gamma}{\tau} \left[ \exp\left(-\Gamma_q \tau\right) \left[ \cos\left(\sqrt{\omega_m^2 + \Gamma_q^2} \tau\right) + \frac{\Gamma_q \sin\left(\sqrt{\omega_m^2 + \Gamma_q^2} \tau\right)}{\sqrt{\omega_m^2 + \Gamma_q^2}} \right] \right]$$

$$\times F^2(q_m - K_q, q_q) dq_m dq_q + B$$
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, •; fit, ●; residuals, ▲; Edwards' correlation weighting function, ▼. 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, ■; fit, ●; residuals, ▲. 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.
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 σ = 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 84.1901 cP, is obtained to within 0.47 %, but the fitting value for the interfacial tension, 54.5935 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 $4.81655 \times 10^{11}$, 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).
Vapor or Liquid upper phase (u)
Film middle phase (m)
Liquid bottom phase (b)

Fig. II-22. Double interface of area $a \times a$. The rms amplitude is known to be less than 1 nm close to a critical temperature. Close to the critical temperature, the amplitudes $\zeta$ and $\zeta'$, one or both, may become large approaching the film thickness $h_0$. This condition may require an additional term in the free energy of the film that is usually designated as a van der Waals or a Casimir energy.

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. [6] 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 $\zeta'$, 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
\[
\left[ P^{ij} \right] n_j n_i = \gamma \, a^\alpha b_{\alpha \beta} = 2 \gamma \, H,
\]

where \( P \) is the pressure tensor, \( \gamma \) is the interfacial tension, and \( H \) comes from the invariant \( 2H = c_1 + c_2 \), where \( c_\alpha = 1/\Lambda_\alpha \), Eq. (II.22) becomes

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

\[
P_{zz} = p - 2 \eta \frac{\partial v_z}{\partial z},
\]

\[
\frac{d\zeta}{dt} = v_z \big|_{z=0},
\]

where \( \eta \) 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

\[
0 = \left[ P_{xx} \right]_0 = \left[ P_{yy} \right]_0 \quad (\text{II.26})
\]

\[
P_{xx} = \eta \left( \frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} \right),
\]

As the liquid is pure, \( \nabla \cdot \sigma = 0 \), 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

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

subject to \( \zeta \to 0 \) for \( x, y \to \pm \infty \), and \( \zeta = v_z \big|_{z=0} \), plus initial conditions.

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

\[
0 = \eta \left( \frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} \right) + k_e \frac{\partial^2 \zeta}{\partial x^2} + k_v \frac{\partial^2 \zeta}{\partial x^2}
\]

(II.29)
where \( k_e = \bar{G} + \bar{K}, k_i = \bar{n} + \bar{\xi}, \xi, \) 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:

\[
\frac{\partial \xi}{\partial t} = \mathbf{v} \cdot \mathbf{U}_n \bigg|_{z = 0} = \mathbf{v} \cdot \mathbf{U}_n \bigg|_{z = 0}
\]  

(II.30)

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

![Surface Geometry for constructing the balance equations. A is the arbitrary surface patch, and \( \partial A \) is its boundary.](image)

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 \( \xi \) and \( \xi \) are considered to be random variables. We are to compute \( \langle \xi_\theta (0) \xi_\theta (t) \rangle \). When a monolayer is present, \( \langle \xi_\theta (0) \xi_\theta (t) \rangle \) 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

\[ \mathbf{v} = v_1(x,t) + v_2(x,t) + \mathbf{u}(t) \],

\[ \nabla \times v_1 = 0, \]
\[ \nabla \cdot v_2 = 0 \]  \hspace{1cm} (II.31)

so that

\[ v_1 = -\nabla \phi, \]  \hspace{1cm} (II.32)
\[ v_2 = \nabla \times \mathbf{A}, \]  \hspace{1cm} (II.33)

where \( \phi \) 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 \( \mathbf{K} \) excited pressure pulses. We can model this situation by making \( \mathbf{u} \) represent the steady flow and letting \( v_1 \) and \( v_2 \) represent the fluctuations around the mean flow. In particle language the ripplons 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

\[ 0 = \nabla \cdot \mathbf{v} = -\nabla^2 \phi \]  \hspace{1cm} (II.34)

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

\[ \rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla P + \eta \nabla^2 \mathbf{v}; \]  \hspace{1cm} (II.35)

Hence

\[ \nabla \left( -\rho \frac{\partial \phi}{\partial t} + P \right) + \rho \frac{\partial}{\partial t} \mathbf{u} = \nabla \times \left( -\rho \frac{\partial \mathbf{A}}{\partial t} + \eta \nabla^2 \mathbf{A} \right) \]  \hspace{1cm} (II.36)

However, the vector \( \mathbf{u} \) can always be represented by \( \mathbf{u} = \nabla (\dot{u}_1 x + \dot{u}_2 y + \dot{u}_3 z) \) 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.
Eqs. (11.34), (11.37), and (11.38) 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 $\Psi$ such that

$$v_z = \left(-\frac{\partial \Psi}{\partial z}, 0, \frac{\partial \Psi}{\partial x}\right)$$

so that for this special case $\nabla \cdot v_z = 0$. From the properties of the vector potential, we have $A_z = \Psi$ 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 $\phi$ and a velocity stream function $\Psi$ to represent the velocity field so that

$$v_x = -\frac{\partial \phi}{\partial x} - \frac{\partial \Psi}{\partial z} + u_x(t),$$

$$v_z = -\frac{\partial \phi}{\partial z} + \frac{\partial \Psi}{\partial x} + u_z(t).$$

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

$$\zeta_{vort} = -\nabla^2 \Psi \hat{e}_z.$$
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

\[
0 = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial z^2}, \quad (\text{II.43})
\]

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

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

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 \( \nabla^2 \phi = 0 \):

\[
\frac{d^2 \phi_u}{dz^2} - q^2 \phi_u = 0 \quad (\text{II.46})
\]

subject to \( \phi_u \rightarrow 0 \) as \( z \rightarrow -\infty \). Hence

\[
\phi_u = A(t) e^{-|z|}, \text{ for } z > 0, \quad (\text{II.47})
\]

\[
\phi_b = A(t) e^{|z|}, \text{ for } z < 0, \quad (\text{II.48})
\]

However, note that, if a solid surface is of distance \(-h\) form 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

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

which can be written as
\[
\phi_{h} \bigg|_{z=0} = \phi_{z} (z=0, t) \cosh \left( |q| h \right). \tag{II.50}
\]

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 \( \phi \) and \( \Psi \) obtained in the Laplace transform of Eqs. (II.44) and (II.45) are both taken to be zero everywhere; only the initial value of \( \zeta \) 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 [8] 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

\[
\hat{T} \left[ f(x,t) \right] (q,s) = \int_{-\infty}^{\infty} dx \int_{0}^{\infty} dt \exp \left( i q x - s t \right) f(x,t) \tag{II.51}
\]

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 \( \hat{e}_r \). Experimentally, \( \hat{e}_r \) is selected simply by one's rotating the grating of Figs. II-3 or II-4. The operator \( \hat{T} \) when applied to the governing equations generates a set of linear equations of the form

\[
M(q,s) \hat{x} = L \cdot x(q,0), \tag{II.52}
\]

where \( \hat{x}(q,s) = \hat{T} \left[ x(x,t) \right] \) and \( x(q,t=0) = 0 \) is the vector of initial values. Note that \( x(q,0) \) is only the Fourier transform of \( x(x,t) \) at \( t=0 \). You can see that \( \hat{x} \) and \( x \) will be vectors of the dynamic variables \( \zeta \) and \( \xi \). The matrix \( L \) organizes the coefficients of the initial values. Solve Eq. (II.52) to get
\( \dot{x}(q, t) = M^{-1} \cdot L \cdot x(q, 0) \) \hspace{1cm} (II.53)

There is an advantage to writing \( M^{-1} \) as

\[
M^{-1} = \frac{1}{\det(M)} \cdot \text{adj}(M) \tag{II.54}
\]

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

\[
C(s) = \langle \dot{x}(q, s) \cdot x(q, 0) \rangle, \quad C(s) = M^{-1} \cdot L \langle x(q, 0) \cdot x(q, 0) \rangle. \tag{II.55}
\]

Assume that \( \langle x(q, 0) \cdot x(q, 0) \rangle \) is diagonal for the single-interface case (but not in general):

\[
B = \langle x_i(q, 0) \cdot x_j(q, 0) \rangle = \langle |x_i(q, 0)|^2 \rangle \delta_{ij}, \tag{II.56}
\]

\[
C(s) = M^{-1} \cdot L \cdot B. \tag{II.57}
\]

Therefore for the amplitude correlation function

\[
C_{11}(s) = \frac{1}{D(q, s)} \left( \text{adj}(M) \cdot L \right)_{11} \langle |x_1(q, 0)|^2 \rangle, \tag{II.58}
\]

from which the spectrum function is computed. Note that \( x_i = \xi_i \) 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. [6]. However, the dispersion equation is, with \( s \to i \omega \), the determinant set to zero

\[
D(q, i \omega) = 0. \tag{II.59}
\]

The spectrum function used to fit data is obtained as

\[
G(\omega) = \frac{1}{\pi} \text{Re} \left[ C_{11}(i \omega) \right]. \tag{II.60}
\]

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 $N_{oa}$, and is signaled by large $\gamma/\eta$ ratios and also for overdamped ripples wherein $N_{oa}$ is large, consistent with $\gamma/\eta$ 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 $N_{oa} \approx 1$. 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: $\nabla \times v = 0$, thus $\Psi = 0$ everywhere and at all times. Use $\nabla^2 \phi = 0$ and $\rho \phi = P$ for each phase and the continuity of the velocity field, which is $\hat{\epsilon} = v_{|_{t=0}} = v |_{t=0}$ (this is a requirement for a material surface connected to the surrounding phases), and the Laplace equation becomes

$$-q^2 \nabla \cdot \zeta_q - \left[ P_i \right] + 2 \left( \eta \frac{\partial v_{x,y}}{\partial z} \right) = 0,$$

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

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

$$\bar{\omega}_q = 2 \left( \frac{\eta + \eta}{\rho + \rho} \right) q^2, \quad \text{(II.62)}$$

$$\omega_q = \frac{\nabla q^2 |q|}{\rho + \rho}. \quad \text{(II.63)}$$

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 \( \xi \), and there is no coupling between \( \zeta_q \) and \( \zeta_q \). 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 \( \zeta = c \) is a constant. Indeed, the tangent plane condition, \( 0 = \mathbf{n} \cdot [\mathbf{P}] \cdot \mathbf{U}_s \), along with the irrotational condition, \( \nabla \times \mathbf{v} = 0 \), both satisfied for all \( z \), imply that \( \xi = c \), 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 \( \Delta \left( \langle \zeta_q^* \zeta_q(t) \rangle \right) \), but the width of the experimental spectrum is poorly represented.

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

\[
(s^2 + \bar{\omega}_q s + \omega_q^2) \zeta_q = \hat{a}(s) + \xi_q(0) + (s + \bar{\omega}_q) \xi_q(0).
\]

Noting that \( \langle \zeta_q^* (0) \hat{a}(s) \rangle = 0 \) and \( \langle \zeta_q^* (0) \xi_q(0) \rangle = 0 \) gives

\[
C(s) = \langle \zeta_q^* (0) \xi_q(s) \rangle = \frac{(s + \bar{\omega}_q)}{s^2 + \bar{\omega}_q} \langle \zeta_q^* (0) \xi_q(0) \rangle,
\]

so the spectrum is

\[
G(\omega) = \frac{1}{\pi} \text{Re} \left( \frac{i \omega + \bar{\omega}_q}{-\omega^2 + i \bar{\omega}_q \omega + \omega_q^2} \right) \frac{K_B T}{\gamma q^2}
\]

\[
= \frac{K_B T}{\pi \bar{\omega}_q \omega_q^2} \left( \frac{\bar{\omega}_q}{(\omega_q - \omega)^2 + (\bar{\omega}_q \omega)^2} \right).
\]

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

\[
G(\omega) = \frac{K_B T}{2\pi \bar{\omega}_q q^2} \frac{1 + (\bar{\omega}_q / \omega_q)^2}{(\omega_q - \omega)^2 + \bar{\omega}_q^2} \left( 1 + (\bar{\omega}_q / \omega_q)^2 \right)
\]

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:
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 $\omega_q$. 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

$$ D(q, \bar{\omega}_q, \omega_q, \rho, \rho, \eta, \eta, \gamma, \gamma, K_c, K_v, B_v, B_v) = 0. $$

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 $\gamma_v, B_v$, and $B_v$ are set to zero so that $K_c$ and $K_v$ are studied. When a pure fluid is being studied, $\gamma$ and $\eta$, the surface tension and the major phase viscosity coefficients, respectively, are determined; $\gamma_v, K_c, K_v, B_v, B_v$ 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.

$$ Y = \frac{1}{(2N_{ca})^2}. $$

(II.69)
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

$$-q^2 \bar{\gamma} \ddot{\xi}_q - q^2 \bar{\gamma}_v \xi_q - \left[ \rho \dot{\phi}_q \right] + 2 \left( \eta \frac{\partial \hat{\psi}_q}{\partial z} \right) = 0,$$

(II.70)

where $\bar{\gamma} = \gamma + (\Delta \rho \, g / q^2) + B_v \, q^2$ and $\bar{\gamma}_v = \gamma_v + B_v \, q^2$. The notation $\ddot{\xi}_q = -\xi_q(t = 0) + s \, \xi_q(s)$ 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 $\dot{\phi}_q = s \, \dot{\phi}_q$ take into account that the nonzero initial conditions will be in only the surface-displacement variables, $\dot{\xi}_q$ and $\ddot{\xi}_q$. 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)]

$$\Psi_u = B \exp(-m \, z) \quad \text{and} \quad \Psi_v = B \exp(m \, z),$$

(II.71)

$$m_u = \sqrt{q^2 + s \, \frac{\rho}{\eta}} \quad \text{and} \quad m_v = \sqrt{q^2 + s \, \frac{\rho}{\eta}}$$

(II.72)

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

Note that the real part of $m_u$ and $m_v$ must be positive. Also, because $q$ may be negative, the potential function is always taken as $\dot{\phi}_u = A \exp(-|q| \, z)$ and $\dot{\phi}_v = A \exp(|q| \, z)$. 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

$$-q^2 K_e \ddot{\xi}_q - q^2 K_v \ddot{\xi}_q + \left[ \eta \left( \frac{\partial \hat{\psi}_q}{\partial z} \bigg|_q + \frac{\partial \hat{\psi}_q}{\partial x} \bigg|_q \right) \right] = 0,$$

(II.73)

where care is required to transform $\frac{\partial \hat{\psi}_q}{\partial x}$. 

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

\[
\hat{\xi}_q = \lim_{z \to 0} \hat{v}_{zq}, \quad (II.74)
\]

\[
\hat{\xi}_q = \lim_{z \to 0} \hat{v}_{zq}, \quad (II.75)
\]

\[
\hat{\xi}_q = \lim_{z \to 0} \hat{v}_{zq}, \quad (II.76)
\]

\[
\hat{\xi}_q = \lim_{z \to 0} \hat{v}_{zq}, \quad (II.77)
\]

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 \( [\rho \hat{\phi}_q] = \rho \hat{\phi}_q - \rho \hat{\phi}_q \) so that

\[
\begin{bmatrix}
\rho \hat{\phi}_q \\
\end{bmatrix} = \left( \frac{m}{q|m-q|^2} \rho + \frac{m}{q|m-q|^2} \rho \right) s \hat{\xi}_q + \left( \frac{i q}{q|m-q|^2} \rho - \frac{i q}{q|m-q|^2} \rho \right) s \hat{\xi}_q \quad (II.78)
\]

where the limit

\[
\lim_{\eta \to 0} [\rho \hat{\phi}_q] = \rho \left( \frac{\rho}{q} \right), \quad \text{and} \quad \lim_{\eta \to 0} [\rho \hat{\phi}_q] = \rho \left( \frac{\rho}{q} \right)
\]

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

**Computation of** \( \eta \frac{\partial \hat{v}_{zq}}{\partial z} \). 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
\[
\left[ \eta \frac{\partial \hat{v}_z}{\partial z} \right] = \left\{ i q |q| \left( \frac{m_u}{|q|m - |q|} \eta - \frac{m_h}{|q|m - |q|} \eta \right) \hat{s}_q - q^2 \left( \frac{i q}{|q|m - |q|} \eta - \frac{i q}{|q|m - |q|} \eta \right) \right\} \hat{s}_q \text{ (II.79)}
\]
and the limit, as the viscosity of the phases vanishes, is
\[
\lim_{\eta \to 0} \left[ \eta \frac{\partial \hat{v}_z}{\partial z} \right] = i q \left[ \eta - \eta \right] \hat{s}_q \text{ and } \lim_{\eta \to 0} \left[ \eta \frac{\partial \hat{v}_z}{\partial z} \right] = i q \left[ \eta - \eta \right] \hat{s}_q
\]
and this does not depend on \( \hat{s}_q \), as is required by the harmonic-oscillator model.

**Computation of** \( \left[ \eta \left( \frac{\partial \hat{v}_z}{\partial z} + \frac{\partial \hat{v}_z}{\partial x} \frac{\partial x}{\partial \eta} \right) \right] \). The tangential balance couples both the normal and the
tangent plane displacements to give
\[
\left[ \eta \left( \frac{\partial \hat{v}_z}{\partial z} + \frac{\partial \hat{v}_z}{\partial x} \frac{\partial x}{\partial \eta} \right) \right] = i q \left( \frac{m - |q|}{|q|} \eta - \frac{m - |q|}{|q|} \eta \right) \hat{\xi}_q - \left( \frac{m + |q|}{|q|} \eta + \frac{m + |q|}{|q|} \eta \right) \hat{\xi}_q \text{ (II.80)}
\]
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 \( \omega_q \) and
the damping frequency \( \Gamma_q \) as
\[
\omega_q^2 = \frac{\omega}{m_u - |q| + \frac{m_h}{m - |q|}} \frac{q^2}{\omega}, \text{ (II.81)}
\]
which reduces to Eq. (II.63) in the limit of small viscosity. However,
\[
\Gamma_v = \frac{\bar{\varphi}_v q^2 \cdot |q|}{m_n \cdot \rho + m_h \cdot \rho} \quad (11.82)
\]

which does not reduce to \( \bar{\varphi}_v \). [Eq. (11.62)], but rather accounts for the effect of the renormalized transverse viscosity \( \bar{\varphi}_v \).

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

\[
a_i = \frac{\rho}{m_n \cdot |q| + m_h \cdot |q|} \quad (11.83)
\]

\[
a_2 = \frac{2i \cdot q \cdot |q|}{m_n \cdot \rho + m_h \cdot |q| \cdot \rho} \quad (11.84)
\]

for the normal balance so that

\[
\omega^2 \hat{\xi}_v + \Gamma_v \hat{\xi}_v + \hat{\eta}_v + a_1 \hat{\xi}_v - a_2 \hat{\xi}_v = 0, \quad (11.85)
\]

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

\[
\omega^2 \hat{\xi}_v + \Gamma_v \hat{\xi}_v + \hat{\eta}_v = 0
\]

holds, but the spectral width is determined by \( \bar{\varphi}_v, |q| \) and not by \( (\eta + \eta) \).

Define the functions

\[
b_1 = -\frac{i \cdot q}{|q|} \left( m_n - |q| \right) \eta - \left( m_h - |q| \right) \eta, \quad (11.87)
\]

\[
b_2 = \left( m_n + |q| \right) \eta + \left( m_h + |q| \right) \eta \quad (11.88)
\]

For the tangent plane, we find
Define \( \tilde{K} = K_r + sK_u \) and expand the derivative terms in Eqs. (II.85) and (II.89) to find the linear equations

\[
K_r q^2 \ddot{\xi}_q + (K_u q^2 + b_2) \ddot{\xi}_q + b_1 \dot{\xi}_q = 0.
\]  
(II.89)

It follows that

\[
\tilde{M} = \begin{bmatrix}
\omega_q^2 + \Gamma_q s + s^2 & a_1 s^2 - a_2 s \\
\Gamma_q s + s^2 & \tilde{K} q^2 + s b_2
\end{bmatrix},
\]  
(II.93)

\[
\tilde{L} = \begin{bmatrix}
\Gamma_q + s & a_1 s - a_2 \\
b_1 & K_u q^2 + b_2
\end{bmatrix}.
\]  
(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. [6]] and \( \tilde{\gamma} = \gamma + (g \Delta \rho/q^2) + B \), the mean-squared elevation computed for Eq. 29 in Ref. [6], which is

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

generalizes to

\[
\langle \xi_q \xi_q^* \rangle = \frac{K_B T}{(\gamma q^2 + \Delta \rho g + B \rho^4)A_0}.
\]  
(II.95)

Note that the dispersion equation is
\[ \text{det}(M) = 0, \]  

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 \( \gamma, K_e, K_{\nu}, \) 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 \( \xi \) and \( \xi \). These spectra are not observable with the surface light scattering instrument described in this text. Because \( \left\langle \xi(s) \xi(0) \right\rangle \) 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. \( \left\langle \xi(s) \xi(0) \right\rangle \) is calculated from the free energy

\[ F_e = G \left[ u_{\alpha}, u_{\alpha} - 1/2(u_{\alpha})^2 \right] + K (u_{\alpha})^2, \]

which goes to the functional

\[ R_e = \frac{\bar{G}}{2} \int \left( \frac{\partial \tilde{\xi}}{\partial x} \right)^2 \sqrt{a} \, dx \, dy. \]  

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

\[ \left\langle \xi(0) \xi(0) \right\rangle = \frac{K_{\nu} T}{K_e q^2} \]  

\[ \left\langle \xi(0) \xi(0) \right\rangle = 0. \]

This completes the construction of the linear response theory for a single interface. Additional details are given in Ref. [6] 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 [4].
Examples showing results obtained with this SRF, whose theoretical underpinnings are outlined in Mann et al. [6], 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:

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

Multiplying both sides by \( \begin{pmatrix} \xi_{q}^{*}[0] & \xi_{q}^{*}[0] & \xi_{q}^{*}[0] & \xi_{q}^{*}[0] \end{pmatrix} \), we obtain:
\[
\begin{pmatrix}
\xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] \\
\xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] \\
\xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] \\
\xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s] & \xi_q^*[0] \xi_q [s]
\end{pmatrix}
= \text{Inverse}
\begin{pmatrix}
m11 & m12 & m13 & m14 \\
m21 & m22 & m23 & m24 \\
m31 & m32 & m33 & m34 \\
m41 & m42 & m43 & m44
\end{pmatrix}
\begin{pmatrix}
n11 & n12 & n13 & n14 \\
n21 & n22 & n23 & n24 \\
n31 & n32 & n33 & n34 \\
n41 & n42 & n43 & n44
\end{pmatrix}
\]

Here
\[
denom001 = 2 q^2 \begin{pmatrix}
-2 \\
+ \exp \left( 2 \left( \frac{|q|}{m} \right) h_v \right) \\
\left[ -1 + \exp \left( 2 \left( \frac{|q|}{m} \right) h_v \right) \right] \left[ -1 + \exp \left( 2 \left( \frac{m}{m} \right) h_v \right) \right]
\end{pmatrix}
\]

\[m11 (\ast \ zetaQHatUMUpperNormalCoef \ 2 \ast) = - q^2 \frac{\tilde{f}}{\mu} + s n11\]

\[m12 (\ast \ xiQHatUMUpperNormalCoef \ 2 \ast) = s n12\]
\( m13 (\ast \text{zetaQHatMBUpperNormalCoef} 2 \ast) = \text{vanDerWaalsTerm} + s \ n13 \)

\( m14 (\ast \text{xiQHatMBUpperNormalCoef} 2 \ast) = s \ n14 \)

\[ n11 (\ast \text{zetaQUMUpperNormalCoef} 2 \ast) \]

\[
= - \left( \frac{\left[ -1 + \exp\left( 2 m h_0 \right) \right]}{2 s m} \left[ 1 + \exp\left( 2 m h_0 \right) \right] q^2 \right) \frac{\rho}{\text{denom001}} + \frac{s \ \rho \ m}{q^2 - |q| m} + q^2 \bar{y}_v
\]

\[ n12 (\ast \text{xiQUMUpperNormalCoef} 2 \ast) \]

\[
= i q \left( \frac{-2 \eta + 2 \eta}{m} \right) + \frac{1}{\text{denom001}} \left[ -1 + \exp\left( 2 |q| h_0 \right) \right] q^2 \left[ \left[ 1 + \exp\left( 2 m h_0 \right) \right] - 4 \exp\left( |q| m + m h_0 \right) \right] \frac{\rho}{\text{denom001}} + \frac{s \ \rho}{q^2 - |q| m}
\]

\[ n13 (\ast \text{zetaQMBUpperNormalCoef} 2 \ast) = \]

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

\[ n14 (\ast \text{xiQMBUpperNormalCoef} 2 \ast) = \]

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

\[ m21 (\ast \text{zetaQHatUMLowerNormalCoef} 2 \ast) = \text{vanDerWaalsTerm} + s \ n21 = \text{vanDerWaalsTerm} + s \ n13 \]

\[ m22 (\ast \text{xiQHatUMLowerNormalCoef} 2 \ast) = s \ n22 = -s \ n14 \]

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\[ m_{23} \left( \text{zetaQHatMBLowerNormalCoef}_2 \right) = -q^2 \frac{\bar{\nu}}{m_b} + s n_{23} \]

\[ m_{24} \left( \text{xiQHatMBLowerNormalCoef}_2 \right) = s n_{24} \]

\[ n_{21} \left( \text{zetaQUMLowerNormalCoef}_2 \right) = n_{13} \]

\[ n_{22} \left( \text{xiQUMLowerNormalCoef}_2 \right) = -n_{14} \]

\[ n_{23} \left( \text{zetaQMBLowerNormalCoef}_2 \right) = \]

\[ \left( \begin{array}{c}
2 s \frac{m}{\rho} \left[ \frac{1}{1 + \exp \left( \frac{2 |q| h_0}{m_b} \right)} \right] \left[ 1 + \exp \left( \frac{2 m h_0}{m_b} \right) \right] q^2 \\
- \frac{1}{\text{denom001}} \left( \left[ 1 + \exp \left( \frac{2 |q| h_0}{m_b} \right) \right] \left[ 1 + \exp \left( \frac{2 m h_0}{m_b} \right) \right] q^2 \right) \frac{s \rho m}{q^2 - |q| m_b} + q^2 \frac{\bar{\nu}}{m_b} 
\end{array} \right) \]

\[ n_{24} \left( \text{xiQMBLowerNormalCoef}_2 \right) = \]

\[ i q \left( \begin{array}{c}
\left[ -1 + \exp \left( \frac{2 |q| h_0}{m_b} \right) \right] q^2 \\
+ \frac{1}{\text{denom001}} 
\end{array} \right) \]

\[ \left( \begin{array}{c}
-1 + \exp \left( \frac{2 |q| h_0}{m_b} \right) - \exp \left( \frac{2 m h_0}{m_b} \right) q^2 \\
+ \exp \left( \frac{2 m h_0}{m_b} \right) q^2 - 4 \exp \left( \left| q + m h_0 \right| h_0 \right) \frac{s \rho m}{q^2 - |q| m_b} 
\end{array} \right) \]

\[ m_{31} \left( \text{zetaQHatUMUpperTangentCoef}_2 \right) = s n_{31} \]

\[ m_{32} \left( \text{xiQHatUMUpperTangentCoef}_2 \right) = -q^2 K_c + s n_{32} \]

\[ m_{33} \left( \text{zetaQHatMBUpperTangentCoef}_2 \right) = s n_{33} \]

\[ m_{34} \left( \text{xiQHatMBUpperTangentCoef}_2 \right) = s n_{34} \]
\[
\begin{align*}
n31 & (\ast \text{zetaQUMUpperTangentCoef2} \ast) \\
& = -\frac{1}{|q|} \left[ 2q^2 \left( \frac{1}{m} \right) \eta_m^2 \right] \\
& \quad \times \left( -2|m(\eta_m + q)| \eta_m - 2|m(\eta_m + q)| \right) \\
& \quad \times \left( -4 \exp\left( \frac{|q| + m \eta_m}{m} \right) + 2 \left( |q| + m \eta_m \right) \right) \\
& \quad \times \left( q^2 - m^2 \right) \eta_m
\end{align*}
\]
\[ n43 \ast \text{zetaQMBLowerTangentCoef}2 \ast \]

\[
\left\{ \eta + \frac{\frac{m_h}{|q|}}{q} + \frac{1}{\text{denom001}} \right\}
\]

\[ = -\left\{ \eta + \left( -1 + \exp\left(2 \frac{m h_0}{|q|}\right) \right) \left( -1 + \exp\left(2 |q| h_0\right) \right) \right\}
\]

\[
\times \left\{ \frac{2}{\text{denom001}} \left[ 1 + \exp\left(2 \frac{m h_0}{|q|}\right) + \exp\left(2 |q| h_0\right) \right] \right\}
\]

\[
\left\{ -4 \exp\left[\left(\frac{|q|}{m} + m\right) h_0\right] + \exp\left[2\left(\frac{|q|}{m} + m\right) h_0\right] \right\}
\]

\[ \left( m^2 + q^2 \right) |q| \right\}
\]

\[ n44 \ast \text{xiQMBLowerTangentCoef}2 \ast \]

\[
\left\{ \frac{q^2 K_r}{\text{denom001}} \left[ 8 \exp\left[\left(\frac{|q|}{m} + m\right) h_0\right] q^3 \left( q^2 - m^2 \right) \right] \right\}
\]

\[
\times \left\{ -\cosh\left(\frac{m h_0}{m}\right) m \sinh\left( q h_0 \right) + \eta \right\}
\]

\[
\left( \frac{m^2 + q^2}{|q|} \right) \right\}
\]

We simplify this by keeping its \[\left\langle \xi_q^* [0] \xi_q [0] \right\rangle\] and \[\left\langle \xi_q^* [0] \zeta_q [0] \right\rangle\] components and dropping its \[\left\langle \xi_q^* [0] \zeta_q [0] \right\rangle\] and \[\left\langle \xi_q^* [0] \xi_q [0] \right\rangle\] 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 \[\left\langle \xi_q^* [0] \xi_q [s] \right\rangle\] upper interface term when plotting the theoretical results shown in Fig. II-26 for comparison with our experimental data:
\[
\left( \langle \zeta_q^* [0] \zeta_q [s] \rangle \right)_{u,m} = \text{Re} \left( \langle \zeta_q^* [0] \zeta_q [0] \rangle \right)
\]

Noting that

\[
\left( \langle \zeta_q^* [0] \zeta_q [0] \rangle \right)
\]

\[k_b \text{ temperature} \left( \gamma \rho + \frac{\rho - \rho_m}{\rho_m} g + B_q q^4 + \text{vanDerWaalsTerm} \right)\]

\[= \left[ \gamma \rho + \frac{\rho - \rho_m}{\rho_m} g + B_q q^4 + \text{vanDerWaalsTerm} \right] \times \left[ \gamma \rho + \frac{\rho - \rho_m}{\rho_m} g + B_q q^4 + \text{vanDerWaalsTerm} \right] - \text{vanDerWaalsTerm}^2 \]

this can be succinctly written as
\begin{align*}
\left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{u.m, u.m} &= k_B \text{ temperature } \left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) \\
&= \frac{1}{\left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{u.m} \right) + \left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) - \text{vanDerWaalsTerm}}.
\end{align*}

\begin{align*}
\left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{u.m, u.m} &= k_B \text{ temperature } \left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) \\
&= \frac{1}{\left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) + \left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) - \text{vanDerWaalsTerm}}.
\end{align*}

Noting that
\begin{align*}
\left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{u.m, u.h} &= \left\langle \zeta_q[0] \zeta_q^*[0] \right\rangle_{u.m, m.h} \\
&= k_B \text{ temperature } \times \text{vanDerWaalsTerm} \\
&= \frac{1}{\left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) + \left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) - \text{vanDerWaalsTerm}}.
\end{align*}

where
\begin{align*}
\bar{\gamma}_{u.m} &\rightarrow \gamma + \frac{|\rho - \rho|}{q^2 + B_{u.m} q^2} \quad \text{and} \quad \bar{\gamma}_{m.h} \rightarrow \gamma + \frac{|\rho - \rho|}{q^2 + B_{m.h} q^2}
\end{align*}

and
\begin{align*}
\left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{m.h, m.h} &= k_B \text{ temperature } \left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) \\
&= \frac{1}{\left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) + \left( \frac{\bar{\gamma} q^2 + \text{vanDerWaalsTerm}}{m.h} \right) - \text{vanDerWaalsTerm}}.
\end{align*}

Additionally,
\begin{align*}
\left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{u.m, u.m} &= 0 \text{ when no monolayer is present} \\
\left\langle \zeta_q^*[0] \zeta_q[0] \right\rangle_{u.m, u.m} &\neq 0 \text{ when a monolayer is present.}
\end{align*}
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 $\left\langle \begin{pmatrix} \xi_q^*[0] \\ \xi_q \end{pmatrix}_{m,b} \right| \left\langle \begin{pmatrix} \xi_q^*[0] \\ \xi_q \end{pmatrix}_{m,b} \right\rangle$, shown in Fig. II-28, may be added by using the approach and information provided above to obtain:

$$\left\langle \begin{pmatrix} \xi_q^*[0] \\ \xi_q \end{pmatrix}_{m,b} \right| \left\langle \begin{pmatrix} \xi_q^*[0] \\ \xi_q \end{pmatrix}_{m,b} \right\rangle = \text{Re}$$
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:

\[
\begin{align*}
\text{vanDerWaalsTerm} &= -\frac{\varepsilon^2}{\varepsilon_0^2} \left( \frac{\text{HamakerConstant}}{12 \pi \varepsilon_0^2} \right) \quad (\text{* The vanDerWaalsTerm function has more sophisticated forms, which are easily accommodated. *}) \\

(\text{Note that an Under-script "u, m" denotes the upper-middle interface and that an Under-script "m, b" denotes the middle-bottom interface throughout this manuscript. *})
\end{align*}
\]

\[
\begin{align*}
\bar{\gamma}_{u,m} &\rightarrow \gamma + \frac{|\rho - \rho|}{q^2} g + B_v q^2, \\
\bar{\gamma}_{m,b} &\rightarrow \gamma + \frac{|\rho - \rho|}{q^2} g + B_v q^2, \\
\bar{\gamma}_{u,m} &\rightarrow \gamma + B_v q^2, \\
\bar{\gamma}_{m,b} &\rightarrow \gamma + B_v q^2, \\
m \rightarrow \text{positiveRealRoot} \left[ q^2 + \frac{i \omega \rho}{\eta} \right], \\
m \rightarrow \text{positiveRealRoot} \left[ q^2 + \frac{i \omega \rho}{\eta} \right], \\
m \rightarrow \text{positiveRealRoot} \left[ q^2 + \frac{i \omega \rho}{\eta} \right].
\end{align*}
\]
The viscoelastic coefficients we take to be zero.

\[ s \to i \omega, B_s (\text{bending modulus}) \to 0, B_s (\text{bending modulus}) \to 0, \]
\[ B_s (\text{bending viscosity}) \to 0, B_s (\text{bending viscosity}) \to 0, \]
\[ \gamma_v (\text{transverse surface viscosity}) \to 0, \gamma_v (\text{transverse surface viscosity}) \to 0, \]
\[ K_v (\text{surface shear plus dilational elastic modulus}) \to 0, \]
\[ K_v (\text{surface shear plus dilational viscosity modulus}) \to 0, \]
\[ q \to \text{surface Wave Number}, h_0 \to \text{interfacial Thickness}, \]
\[ \rho \to \text{density Upper Phase}, \rho \to \text{density Middle Phase}, \rho \to \text{density Bottom Phase}, \]
\[ \eta \to \text{viscosity Upper Phase}, \eta \to \text{viscosity Middle Phase}, \eta \to \text{viscosity Bottom Phase}, \]
\[ \gamma \to \text{interfacial Tension Upper Middle Interface}, \]
\[ \gamma \to \text{interfacial Tension Middle Bottom Interface}, \]
\[ g \to \text{gravitational Acceleration}, k_b \to 1 (\text{Drop Boltzmann constant scalefactor}) \]
\[ \omega \to 2\pi \text{ selected Frequency Values For Power Spectrum Axis} \]

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 $1.1 \times 10^{-21}$ 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. [4] and Mann et al. [6]).
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 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 $1.1 \times 10^{-21} \text{J}$, 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 critical 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 critical Casimir-Polder force term for the lower interface that manifests itself as the film thins.
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. [6] and the derivations of Meyer et al. [4]. 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. [4], [48] and [6]). 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 for allowing 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-25 and II-27. 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-25 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-25 and Fig. II-27) indicates that a change occurs (in both the position and height) in the power spectra 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):

\[
\text{Gradient} \rightarrow \{\text{Re}[\delta_{\text{interfacialTensionSought}} \text{powerSpectrumFitUsingMannSRF} /. \{\text{Re}'[\text{eqn_}] \rightarrow 1, \\
\text{Im}'[\text{eqn_}] \rightarrow -i, \text{Abs}'[\text{eqn_}] \rightarrow 1\}], \\
\text{Re}[\delta_{\text{viscosityLowerPhaseSought}} \text{powerSpectrumFitUsingMannSRF} /. \{\text{Re}'[\text{eqn_}] \rightarrow 1, \\
\text{Im}'[\text{eqn_}] \rightarrow -i, \text{Abs}'[\text{eqn_}] \rightarrow 1\}], etc.\}
\]

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_] \rightarrow 1 is needed if you decide to computationally back-calculate K_s and \(\sigma_s\) 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-F: *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:


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):


SLSS-6.8.4 Patent Disclosures (held by OAI):


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

$\varepsilon_x$  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).

$\eta$  Viscosity.

$\eta_b$  Viscosity of the bottom phase.

$\eta_m$  Viscosity of the middle phase.

$\eta_u$  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.

$F_c = G \left[ u_{\alpha}, u_{\alpha}, -1/2(u_{\alpha})^2 \right] + K (u_{\alpha})^2$, 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.

$\gamma$  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.

$$\overline{\gamma}_{m,b} = \gamma_{m,b} + \left( \frac{\rho - \rho_b}{\rho} \right) \frac{g}{m_b} + B_q q^2, \text{ dressed interfacial tension for middle-bottom interface.}$$

$$\overline{\gamma}_{u,m} = \gamma_{u,m} + \left( \frac{\rho - \rho_u}{\rho} \right) \frac{g}{m_u} + B_q q^2, \text{ dressed interfacial tension for upper-middle interface.}$$

$$\overline{\gamma}_{v,m,b} = \gamma_{v,m,b} + B_q q^2, \text{ dressed transverse surface viscosity at the middle-bottom interface.}$$

$$\overline{\gamma}_{v,u,m} = \gamma_{v,u,m} + B_q q^2, \text{ dressed transverse surface viscosity at the upper-middle interface.}$$

$$\Gamma_0 = 2q^2 \left( \frac{\eta_{m,b}}{\rho - \rho_b} \right)$$

$\Gamma_1$ Chemical species.

$$\Gamma_{\kappa} = 2K_\kappa^2 \left( \frac{\eta_{u,m}}{\rho + \rho_b} \right)$$

$$\Gamma_{q} \approx \Gamma_{\kappa} \left( \frac{q}{K_\kappa} \right)^2, \text{ decay coefficient.}$$

$h_0$ Interfacial thickness.

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

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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.

$I_{ih}$ Intensity of horizontally (H) polarized scattered light that was vertically (V) polarized before scattering.

$I_{iv}$ 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.

$l_{\text{photon}}$ 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.

$\lambda$ Vacuum wavelength of the laser light used in experiment.
\( \lambda_0 \)  
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).

\[
m_h = \text{the positive real root of } \sqrt{q^2 + \frac{\rho}{\eta}}
\]

\[
m_m = \text{the positive real root of } \sqrt{q^2 + s \frac{\mu}{\eta}}
\]

\[
m_u = \text{the positive real root of } \sqrt{q^2 + s \frac{\mu}{\eta}}
\]

M  
A magnification factor for the grating that determines the ripplon wave numbers \( K \), 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.

\( N = K, \sigma_n \), a dimensionless group that essentially represents the number of grating lines seen by the ripplons capillary waves) on the fluid interface.
\[ N_{ca} = \frac{\omega_m}{|q|} \left( \frac{\gamma}{\eta + \eta} \right)^{1/3}, \text{ capillary number.} \]

\[ N_M \quad \text{Mach number or amplitude-to-wavelength ratio.} \]

\[ P \quad \text{Pressure tensor.} \]

\[ P(\omega) \quad \text{Power spectrum.} \]

\[ P_i(K_s, \omega) \quad \text{Model of power spectrum with instrument function } F^2. \]

\[ P_s[q, \omega] \quad \text{Model of power spectrum without instrument function } F^2. \]

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

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

\[ \text{PDF } \quad \text{Probability Distribution Function.} \]

\[ \Psi \quad \text{Velocity stream function, which along with the velocity potential function } \phi \text{ represents the velocity field.} \]

\[ \phi \quad \text{Velocity potential function, which along with the velocity stream function } \Psi \text{ represents the velocity field.} \]

\[ \phi_k \quad \text{Orientation of grating lines with respect to scattering plane.} \]

\[ q = k_s - k, \text{ where } k_s \text{ is the wave vector of the incident light, } k \text{ is that of the scattered light, and } q \text{ is the scattered wave vector.} \]

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

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

\[ Q \quad \text{An instrument scaling factor that includes factors such as the quantum efficiency of the detector. } Q \text{ can be set equal to 1 for our purposes.} \]
Distance detector is from detected scattering volume.

Pathlength of light used to calculate the Rayleigh ratio.

Model of correlation function with instrument function $F^2$.

Average value for $R_i$.

Model of correlation function without instrument function $F^2$.

The Real part of a number or expression.

Rayleigh ratio.

Density of the bottom phase.

Density of the middle phase.

Density of the upper phase.

$i \omega$, where $i = \sqrt{-1}$.

Asymptotic Standard Error = \[ \frac{\sigma}{\sqrt{2 \times (\text{number of samples})}} \], where $\sigma$ is the standard deviation.

Surface Light Scattering Spectroscopy.

Surface Response Function.

Standard deviation (Std. dev.).

The magnified beam width just before the surface, normal to the magnified beam propagation direction.

is the variance, where $\sigma$ is the standard deviation.

Spot size measured perpendicular to the laser beam, i.e., $\sigma_s = 0.066535 \text{ cm (intensity measured at the } 1/e^2 \text{ points} = 4 \sigma.)$. 

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\( \sigma_{xy} = \frac{\sigma_{E_{\text{meq}}}}{e_x} \).

t  Time.

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

\( \tau^* \)  Turbidity.

\( T \)  Temperature.

\( \theta \)  Scattering angle.

\( U_n \)  The projector to the tangent plane and the grating orientation of the spectrometer.

\( \nu \)  The velocity field in the z-direction.

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

\[
\tau^* = \int \Re \ d\Omega(\theta, \phi) .
\]

\( \text{VLS} \)  Volume Light Scattering.

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

\[
\omega_0 = \left( \frac{\gamma q^2 |q|}{\rho + \rho_b} \right)^{\frac{1}{2}}
\]

\[
\omega_k = \left( \frac{\gamma K_c^2 |K|}{\rho + \rho_b} \right)^{\frac{1}{2}}
\]

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

\[
\omega_q = \left( \frac{\gamma K_c^2 |K|}{\rho + \rho_b} \right)^{1/2} \left( \frac{q}{K_c} \right)^{3/2} = \omega_k \left( \frac{q}{K_c} \right)^{3/2} .
\]

center frequency.

\( \omega_i^{(n)} \)  Weights used in Gauss-Hermite quadrature.
\( \xi \) The fluctuation amplitude tangential to the fluid-fluid interface.

\[ \xi_{\text{multiple}} \approx \frac{\lambda r}{l_{\text{photon}}} \ll 1 \text{ mm} \, , \text{ multiple scattering speckle.} \]

\[ \xi_{\text{single}} \approx \frac{\lambda r}{d_{\text{beam}}} \approx 1 \text{ mm} \, , \text{ single scattering speckle.} \]

\( Y = 1 / (2N_c)^2 = \left( \frac{\omega_c}{\Gamma_c} \right)^2 \).

\( \zeta \) The fluctuation amplitude normal to the fluid-fluid interface.

\[ \zeta_{\text{vort}} = \nabla \times \mathbf{v} = \nabla \times \mathbf{v}_1 \, , \text{ vorticity.} \]

\( \zeta_{(m,b)} \) 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.