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Finite system size effects in the interfacial dynamics of binary liquid films

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We study the relaxation dynamics of capillary waves in the interface between two confined liquid layers by means of molecular dynamics simulations. We measure the autocorrelations of the interfacial Fourier modes and find that the finite thickness of the liquid layers leads to a marked increase of the relaxation times as compared to the case of fluid layers of infinite depth. The simulation results are in good agreement with a theoretical first-order perturbation derivation, which starts from the overdamped Stokes’ equation. The theory also takes into account an interfacial friction, but the difference with no-slip interfacial conditions is small. When the walls are sheared, it is found that the relaxation times of modes perpendicular to the flow are unaffected. Modes along the flow direction are relatively unaffected as long as the equilibrium relaxation time is sufficiently short compared to the rate of deformation. We discuss the consequences for experiments on thin layers and on ultralow surface tension fluids, as well as computer simulations. © 2008 American Institute of Physics. [DOI: 10.1063/1.2953440]

I. INTRODUCTION

Phase separation is ubiquitous in nature. In liquids, or liquids dispersed with buoyant bodies such as colloids, polymers, or surfactants, small differences between the mutual attractions of the various molecules are capable of separating like molecules from unlike molecules. Given enough time, such systems fully separate into macroscopically large domains, only limited by walls confining the system. The geometry of the interface between such macroscopically separated domains is generally determined by a combination of various interfacial tensions $\gamma_{ij}$ and the geometry of the confining walls. Although the interface between two phases appears to be smooth on macroscopic scales, thermal excitations cause the interface to be rough on microscopic scales. The broadening of an interface by these so-called capillary waves\textsuperscript{1–3} should be distinguished from its intrinsic width caused by partial mixing of the molecules of both phases.\textsuperscript{4} For simple fluids interacting via van der Waals forces, the local density of one species changes monotonically across the interface from its bulk liquid value to zero.\textsuperscript{5,7} For ordinary molecular liquids with surface tensions in the mN/m range, the capillary roughness is relatively small, in the order of a few or tens of angstroms, and can be accessed experimentally by ellipsometry,\textsuperscript{8,9} x-ray scattering,\textsuperscript{10–12} and neutron\textsuperscript{13–15} reflectometry. Interestingly, in a recent series of papers, Aarts \textit{et al.}\textsuperscript{16–18} focused on colloid-polymer mixtures in which the interfacial tension between polymer-lean and polymer-rich phases is lowered to the nN/m range. Because of this ultralow surface tension, the characteristic length and time scales of the interfacial fluctuations are such (micrometers and seconds, respectively) that they can be studied in real space by means of confocal microscopy.

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An often-used approximation in capillary wave theory\textsuperscript{1,3} is that the wavelength of the fluctuation under investigation is much smaller than the thickness of the liquid layer below the interface and, in the case of two liquids, also much smaller than the thickness of the liquid layer above the interface. In many experimental situations, this approximation is valid and greatly simplifies the theoretical analysis.\textsuperscript{19} There are, however, situations in which the thickness of the liquid layer is of the same order of magnitude as the interfacial wavelength under consideration, or even smaller. For example, thin films with a thickness of (tens of) nanometers could be studied by means of x-ray scattering or neutron reflectometry,\textsuperscript{13,15} or thin films with a thickness of hundreds of nanometers by light scattering. Moreover, as noticed above, characteristic lengths in the micrometer range occur in ultralow surface tension fluids.\textsuperscript{16–18} Finite size effects may become noticeable in the dynamics of such systems even when the liquid layers are as thick as a hundred micrometers. Simultaneously, rapid advances in the field of microfluidics enable the production of ever smaller systems, possibly containing phase separating fluids.\textsuperscript{20,21} As the distances between walls in microfluidic devices decrease, the influence of finite size effects on liquid-liquid interfacial fluctuations will continue to increase.

We expect that in most computer simulations of phase separated systems,\textsuperscript{4,7,22–25} the dynamics of interfacial fluctuations are influenced by the finite thickness of the liquid layer(s) as well. Indeed, molecular dynamics simulations are usually limited to $10^5$ particles, which means that the simulation boxes are usually cubic with fluid layers of a few nanometers thick. Although in simulation work much attention has been given to equilibrium properties of the interface, such as molecular organization and structure and density profiles,\textsuperscript{4,7,23–25} to the best of our knowledge, no direct measurements have been reported on the dynamics of capillary interfacial fluctuations.
In this paper, we study, by means of particulate computer simulations, the dynamics of capillary interfacial fluctuations of a binary-liquid system with unlimited (periodic) area but with finite depth. We will consider both quiescent and slowly sheared systems. For the small wavelike perturbations considered here, we can neglect the nonlinear term in the general Navier–Stokes equation, but we will take into account the finite viscosity \( \eta \) of the fluid. This was already done by Jeng et al.,\textsuperscript{26} but these authors focused on the infinite depth systems. In fact, in this paper, we will focus on the overdamped limit, where viscosity dominates over inertia, and the system can be considered to be always in a quasisteady state. Also complementary to the work of Jeng et al.,\textsuperscript{26} we will take into account the effect of tangential friction \( \beta \) between the liquid layers. In order to clearly expose the finite size effects, we consider here two liquids of equal density \( \rho \), viscosity \( \eta \), and depth \( H \). In the equal density approximation, the influence of gravitational acceleration \( g \) can be ignored, or, equivalently, the capillary length \( \xi = \sqrt{\gamma / \Delta \rho g} \) is infinite. The above conditions have been chosen to match our simulations. We will compare the measured spectrum of relaxation times \( \tau_q \) of the capillary modes of wave vector \( q \) to a theoretical prediction and find quantitative agreement. A derivation of this expression is given in the appendices. The most prominent feature is a smooth crossover in the scaling of \( \tau_q \) from \( \tau_q \propto q^{-4} \) for small liquid layer depths (\( qH \ll 1 \)) to \( \tau_q \propto q^{-1} \) for large liquid layer depths (\( qH \to \infty \)). Each of the imposed conditions (overdamped motion, equal density, viscosity, and liquid depth) may, of course, be relaxed but will lead to more complicated theoretical expressions.

\[ \tau_q = \frac{4 \eta BH(\cosh qH \sinh qH + qH)}{\gamma qH(\sinh^2(qH) - (qH)^2) + \eta qH(\cosh qH \sinh qH - qH)} \]

\[ U_{LJ}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right], \quad (2) \]

where \( \epsilon \) and \( \sigma \) are the strength and range, respectively, and \( r_{ij} \) is the distance between particles \( i \) and \( j \). Both the potential and the derived force are smoothly truncated at the cutoff distance of \( 2.5\sigma \) to eliminate discontinuities at the latter distance. Unlike particles interact by the purely repulsive Weeks–Chandler–Andersen potential defined by \( U_{WCA}(r) = U_{LJ} + \epsilon \) for \( r \leq 2^{1/6}\sigma \) and \( U_{WCA}(r) = 0 \) for larger separations. In our simulations, Newton’s equations of motion are integrated numerically using the Verlet leap-frog algorithm with a time step of \( 0.002\tau \), where \( \tau = \sqrt{(m\sigma^2/\epsilon)} \) is the mass. The temperature used in the simulations is \( kT = 1.0\epsilon \), where \( k \) is Boltzmann’s constant. A thermostat is used to sample an isothermal system. Many thermostats interfere with the creation of hydrodynamics flow fields and therefore are not suited for the study of the interfacial fluctuations with boundaries, as hydrodynamics might play a significant role in such systems. We have used the friction and random forces of dissipative particle dynamics (DPD) to thermostat the system, as these forces are particularly designed to conserve local momentum, which is also the basis of the Navier–Stokes equation. In DPD, the friction force \( \mathbf{F}_{\text{fric}} \) and random force \( \mathbf{F}_{\text{ran}} \) between a pair of particles separated by a distance \( r \) within the cutoff distance \( r_c \) are given by

\[ \mathbf{F}_{\text{fric}} = -\frac{\kappa^2}{2kT}\left( \frac{r}{r_c} \right)^2 \left( \hat{\mathbf{r}} \cdot \Delta \mathbf{v} \right) \hat{\mathbf{r}}, \quad (3) \]

\[ \mathbf{F}_{\text{ran}} = \frac{\kappa}{\sqrt{\Delta t}} \left( \frac{1 - \frac{r}{r_c}}{r_c} \right) \zeta \hat{\mathbf{r}}, \quad (4) \]

where \( \kappa \) is the strength of the friction constant, which we set equal to \( 0.3\epsilon\tau^{1/2}\sigma^{-1} \) in this work, \( \hat{\mathbf{r}} \) is the unit vector in the direction of the line joining the two particles, \( \Delta \mathbf{v} \) is the velocity difference between the particle pairs, and \( \zeta \) is a random number with zero mean and unit variance. Compared with our previous work,\textsuperscript{27,28} the value of \( \kappa \) is chosen to be relatively small in order to avoid a too high viscosity of the fluid, as this would lead to extremely slow relaxation of the slowest interfacial modes. The geometry of our system is shown in Fig. 1. These rectangular boxes are periodic in the \( x \) and \( y \) directions, but a wall is used in the \( z \)-direction to simulate the finite size effect and also to impose shear. A bounce back rule is applied to keep the particles in the boxes where velocities were modified after collision as \( \mathbf{v}_i \rightarrow -\mathbf{v}_i \). To impose a shear rate \( \dot{\gamma} \), one of the walls is moved in the horizontal \( x \)-direction, and all particles colliding with this wall are bounced back with an additional velocity component corresponding to that of the wall. The height of the box is fixed to \( L_z = 2H = 17.1\sigma \), and the horizontal dimensions \( L_x = L_y = L \) are varied between \( L_x \), \( 2L_x \), and \( 4L_x \). Note that \( z \) is the direction normal to the fluid-fluid interface and that these choices enable us to study interfacial fluctuations at wavelengths larger than the depth of the fluid. The number of particles in the smallest box is \( N = 3500 \) with a density of \( \rho = 0.7 \). The number of particles in the other boxes are scaled accordingly. The boxes are equilibrated for \( 100\tau \) before the actual samples are analyzed for results.
III. ANALYSIS OF CAPILLARY WAVES

To disentangle capillary waves from the intrinsic width of the interface, at regular time instances we divide the simulation box into \( N_x \times N_y \times N_z \) cells. For every cell labeled by \((i, j, k)\) with \(i \in \{1, \ldots, N_x\}\), \(j \in \{1, \ldots, N_y\}\), and \(k \in \{1, \ldots, N_z\}\), we calculate the difference between the number of \(A\) particles and the number of \(B\) particles, \(\Delta N(i, j, k) = N_A(i, j, k) - N_B(i, j, k)\). The height \(h_{IF}(i, j)\) of the interface is then obtained in each column \((i, j)\) by least squares fitting to a tangent hyperbolic profile

\[
\Delta N_{\text{fit}}(i, j, k) = a(i, j) \tanh \left( \frac{z(k) - h_{IF}(i, j)}{w(i, j)} \right),
\]

where \(z(k)\) is the height of the center of the cell with \(z\)-index \(k\), \((a, w, h_{IF})\) are fit parameters: \(a(i, j)\) is related to the bulk density of \(A\) and \(B\) particles, \(w(i, j)\) is the intrinsic interfacial width, and \(h_{IF}(i, j)\) is the height of the interface in column \((i, j)\). When the intrinsic interfacial width is very small and the interface is centered around \(z=L_z/2\), as the case in our simulations, it is advantageous to choose an odd number of cells \(N_z\) in the \(z\)-direction because this will lead to a more accurate sampling of the steplike profile. From the interfacial height \(h_{IF}(i, j)\), we calculate its Fourier transform,

\[
h_q(t) = \frac{1}{N_x N_y} \sum_i \sum_j h_{IF}(i, j) \exp[i(q_x x(i) + q_y y(j))],
\]

where \([x(i), y(j)]\) is the location of the center of the column with indices \((i, j)\), and the wave vector \(q = q_x \hat{\mathbf{e}}_x + q_y \hat{\mathbf{e}}_y\) is chosen to be commensurate with the periodic box dimensions, i.e., \(q_x = (2\pi/\Lambda) n_x\) and \(q_y = (2\pi/\Lambda) n_y\) with \(n_x\) and \(n_y\) integer numbers. The amplitude of a capillary wave is then calculated as \(\langle h_q^* h_q \rangle = \langle h_q^2 \rangle\), where the pointy brackets indicate averaging over different time instances. To determine the relaxation times \(\tau_q\), we calculate the time correlation functions \(\langle h_q(t) h_q^* (0) \rangle\).

In our simulations, we choose the number of columns as \(N_z = N_y = 10\) and \(N_x = 7\) for the smallest box size. For larger boxes, \(N_x\) was kept the same, but \(N_y\) and \(N_z\) were scaled according to the box size. In the analysis, the wave numbers were varied between \(n_x = 0, \ldots, 4\) and \(n_y = 0, \ldots, 4\). Higher wave numbers were not selected to avoid discretization artifacts.

IV. RESULTS

A. Characterization of the fluids

In order to test our theoretical prediction in Eq. (1), we first need to determine independently the viscosity, surface tension, and interfacial friction of our fluids. We assume these quantities are independent of wave vector \(q\) in the range of wavelengths studied.

For the viscosity \(\eta\), we consider a box containing only \(A\) particles with periodic boundaries in all directions. The viscosity is obtained by slowly shearing using Lees–Edwards sliding-brick boundary conditions\(^\text{20}\) and dividing measured shear stress by applied shear rate. The result of this measurement is \(\eta = 1.23kT\sigma^3\).

The surface tension \(\gamma\) is determined in a box, periodic in all directions, containing a layer of \(A\) particles and a layer of \(B\) particles. The interface normals are along the \(z\)-axis. In such a configuration, the surface tension is related to the difference between the average normal pressure \(P_{zz}\) and average tangential \((P_{xx} + P_{yy})/2\) pressure:\(^\text{32}\)

\[
\gamma = \frac{L_z}{2} \left( P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}) \right),
\]

where the factor of 2 arises from the fact that there are two interfaces within each periodic box. The result of this measurement is \(\gamma = 1.23kT\sigma^2\).

Two fluid layers may have (partial) tangential slip, resulting in a tangential velocity difference \(\Delta v\) between the two surfaces. The tangential force per unit area exerted by the surface of one fluid on the surface of the other fluid is given, phenomenologically, by the product of slip velocity and interfacial friction coefficient \(\beta\)

\[
F^\beta = \beta \Delta v.
\]

Suppose we apply an overall shear rate \(\dot{\gamma}\) to a system containing layers of fluid \(A\) and \(B\). If there is a finite amount of slip, the effective shear rate \(b\) within the fluid layers will be lower than \(\dot{\gamma}\). From a simple consideration of force balances, knowing the viscosity \(\eta\) of the fluid layers, the following relation can be derived:

\[
\beta = \frac{\eta \cdot b}{L_z \cdot \dot{\gamma} - b}.\]

We have measured the effective shear rates \(b\) in the liquid layers for shear rates between 0.01 \(\tau^{-1}\) and 0.05 \(\tau^{-1}\) and found \(b/\dot{\gamma} = 0.76\), independent of applied shear rate \(\dot{\gamma}\). For our model, we therefore estimate an interfacial friction coefficient \(\beta = 0.228kT\sigma^4\).

B. Amplitudes of interfacial fluctuations

As long as the amplitudes of the interface fluctuations are small, the interfacial free energy can be approximated as
Simulations. Figure 2 also shows the theoretical prediction for the various capillary wave modes in equilibrium simulations.

The equipartition theorem predicts the following mean square energy contributions are of quadratic form and each complex and therefore effectively contributes to two modes, where the prime indicates summation over independent \( h_q \) in two adjacent quadrants of the \( q \) vector space. Since the free energy contributions are of quadratic form and each \( h_q \) is complex and therefore effectively contributes to two modes, the equipartition theorem predicts the following mean square amplitudes:

\[
\langle |h_q|^2 \rangle = \frac{k_B T}{\gamma L_x L_y q^2}.
\]

In Fig. 2, we show the mode amplitudes \( \langle |h_q|^2 \rangle \) for various box sizes \( L \) and wave vectors \( q \) as measured in equilibrium simulations. Figure 2 also shows the theoretical prediction Eq. (12) using the independently determined surface tension \( \gamma \). All data clearly coincide with the theoretical curve, indicating that our cell-based procedure to measure capillary interface fluctuations is valid.

C. Dynamics of interfacial fluctuations

We now proceed to measure the relaxation times \( \tau_q \) of the various capillary wave modes in equilibrium simulations. According to Onsager's regression hypothesis, the relaxation dynamics may be obtained from the autocorrelations \( \langle h_q(t) h_q^*(0) \rangle \). In Appendix B, we derive an equation of motion for \( h_q \) for overdamped capillary waves, which is valid up to the first order in \( h_q \) and at times beyond the ballistic regime. This equation of motion predicts an exponential decay of the autocorrelation

\[
\frac{\langle h_q(t) h_q^*(0) \rangle}{\langle |h_q|^2 \rangle} = \exp(-t/\tau_q).
\]

In the ballistic regime at early times, for reasons of time symmetry, the derivative of \( \langle h_q(t) h_q^*(0) \rangle \) must be zero near \( t=0 \). The relaxation times \( \tau_q \) are therefore extracted by fitting to an exponential decay in the region where the normalized autocorrelation decays from 0.75 to 0.05 (see Fig. 3). The lower limit serves to exclude the noisy data that occur at larger correlation times.

Figure 4 is the main result of this paper. We plot the measured relaxation times as a function of \( q \) for various box sizes and wave vectors. Clearly, our results are in the transitional region from a \( \tau_q \approx q^{-4} \) to a \( \tau_q \approx q^{-1} \) scaling. We also plot the theoretical prediction [Eq. (1) (solid line)] using the independently measured values of viscosity \( \eta \), surface tension \( \gamma \), and interfacial friction coefficient \( \beta \), and find good agreement between simulation and theory.

Comparing our relaxation times to the prediction for infinitely high liquid layers, \( \tau_q = 4 \eta / (\gamma \eta) \) (dashed line in Fig. 4), we observe that the inclusion of finite size effects is essential for the prediction of the dynamics of capillary modes when \( qH \) is of order 1 or smaller.

The often-used approximation of no-slip boundaries be-
between the liquid layers, corresponding to the case $\beta \to \infty$, is plotted as the dot-dashed line in Fig. 4. The differences between predictions with finite and infinite $\beta$ are small. Our measurements are not accurate enough to distinguish between these two cases. We remind the reader that our fluids have purely repulsive interactions between unlike particles. This may lead to much more interfacial slips than with real fluids, which usually have some attraction, whether strong or weak, even between unlike particles. The difference with the $\beta \to \infty$ limit may therefore even be smaller for real fluids.

So we find that the dominant parameter determining the amount by which confinement enhances the relaxation time of a capillary wave is the combination $qH$. To check this conclusion, we have investigated a box of reduced height $L_z=2H=10.26\sigma$ and width $L_x=L_y=17.1\sigma$. Note that Eq. (1) predicts that the precise enhancement will depend on the ratio $\eta q/\beta$. However, both in the limit $\beta \gg \eta q$ (no-slip boundaries between liquid layers) and $\beta \ll \eta q$ (slip boundaries), the resulting enhancement curve is a single function of $qH$. Figure 5 shows the enhancement of the relaxation times due to confinement versus $qH$ for both box heights (circles and squares) as well as for the cases $\beta \to \infty$ (dot-dashed line) and $\beta \parallel 0$ (solid line). We observe that the results of different box heights collapse onto a single curve close to the no-slip boundary prediction.

D. Influence of shear flow

We finally study the influence of shear flow on the relaxation dynamics of capillary waves. The first-order theory presented in the appendices predicts relaxation times $\tau_q$, which are independent of the applied shear rate $\dot\gamma$. We should be careful of this result, however, because inertial and other higher order effects may become dominant at higher shear rates. A correct theoretical treatment of this case would therefore involve including inertial terms in the hydrodynamic equations and deriving equations of motion for $h_q$ up to the second order. This is a topic of future research. Here we set ourselves the more modest task of studying the extent to which equilibrium predictions still apply under shear flow.

To a good approximation, the flow and relaxation in the vorticity ($y$) direction are decoupled from those in the flow ($x$)-direction. We therefore expect essentially unchanged relaxation times for modes perpendicular to the flow direction (i.e., wave vectors with component $q_x=0$). This is tested in Fig. 6 where we show the height autocorrelation of the mode given by $(n_z=0,n_y=1)$ at various shear rates. We confirm that in all cases the relaxation dynamics are similar even at relatively high shear rates.

The relaxation times of modes with a nonzero component in the flow direction can be severely affected, however. In Fig. 7, we present the height autocorrelation of the mode given by $(n_z=1,n_y=0)$ at various shear rates. Indeed, at small shear rates, the relaxation dynamics are similar to the equilibrium case; next, there is a small increase in relaxation time; and finally, the relaxation is accelerated by the flow at higher shear rates. We hypothesize that the relaxation time of a mode with $x$-component $q_x$ is not essentially altered by shear flow if this mode has relaxed sufficiently far before the shear flow has had a chance of deforming it. This means that we expect that $\tau q_x$ is not changed if $\gamma q_x^\infty \ll 1$, where $q_x^\infty$ is the relaxation time, in equilibrium, of a mode $(q_x,0)$. We test our

FIG. 5. Enhancement of relaxation times of capillary waves due to the confinement by solid walls vs the dimensionless parameter $qH$. Simulation results are from systems with $H=5.55\sigma$, $L=2H$, $L=4H$, and $L=8H$ (circles), and $H=5.13\sigma$ and $L=3.33H$ (squares). Three limits of the theoretical prediction [Eq. (1)] are also shown: the case of infinite interfacial friction $\beta$ (dot-dashed line), the case of zero interfacial friction $\beta$ (solid line), and the reference case of infinite liquid layer depth $H$ (dashed line).

FIG. 6. Normalized relaxation dynamics of capillary waves at different shear rates $\dot\gamma$ for the system with $L=4H$. In all cases, the wave vector is equal to $q=(2\pi/L)(0,1)$, which is perpendicular to the direction of flow.

FIG. 7. Normalized relaxation dynamics of capillary waves at different shear rates $\dot\gamma$ for the system with $L=4H$. In all cases, the wave vector is equal to $q=(2\pi/L)(1,0)$, which is in the direction of flow.
The crosses indicate modes that are relatively unaffected by shear flow (relaxation time changes by less than 20% change in relaxation time) and the circles indicate modes that are affected by the shear flow (more than 20% change).

**Figure 8.** Nonequilibrium phase diagram showing which modes are affected by shear flow in the $L=4H$ system. The spectrum of equilibrium relaxation times $\tau_{q_i}^\text{eq}$ of modes $(q_i,0)$ is given along the vertical axis, repeated for each inverse shear rate $1/\gamma$ studied. The crosses indicate modes that are relatively unaffected by the shear flow (relaxation time changes by less than 20% compared to equilibrium), whereas the circles indicate modes that are affected by the shear flow (more than 20% change).

**V. CONCLUSIONS**

We have studied the overdamped relaxation dynamics of capillary waves between two liquid layers enclosed by walls. The finite depths of the liquid layers lead to a large increase in the relaxation times of the larger wavelength modes. We have compared our simulation results to a theoretical calculation and found good agreement. It was also found that the inclusion of an interfacial friction $\beta$ in the theory only slightly changes the predictions of the relaxation times. Our measurements are not accurate enough to distinguish between the actual and infinite interfacial friction. Finally, we have shown that the relaxation dynamics are unaffected by shear flow for modes in the vorticity direction. Modes $q$ with a nonzero component in the flow direction are also relatively unaffected as long as $\gamma \tau_{q_i}^\text{eq} < 0.2$, where $\tau_{q_i}^\text{eq}$ is the relaxation time in equilibrium of a mode with wave vector $(q_i,0)$.

These results are of importance to experiments that probe the interfacial dynamics between thin (tens of nanometers) films or ordinary liquids, experiments on ultralow surface tension fluids at larger length scales (tens of micrometers), as well as applications of microfluidics. Moreover, the results are relevant for almost all simulation studies on the dynamics of liquid-liquid interfaces. Because in most simulation works the box dimensions are chosen rather similar along the different coordinate axes, the product $qH$ is of the order of 1 for the largest wavelength that fits in the simulated box. Specifically, for a cubic box ($qH=\pi$) the deviations from the $qH \to \infty$ limit may be small but distinguishable, while for larger $L/H$ ratios, the deviations increase strongly, as shown in this work.

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**APPENDIX A: FLOW FIELD BETWEEN SOLID WALLS AND A FLUCTUATING INTERFACE**

In this appendix, we will solve the flow field $\mathbf{u}$ and pressure field $P$ between solid walls and a fluctuating interface. Figure 1 shows the geometry of the problem: we consider a two-phase liquid system enclosed between walls at $z=0$ and $z=2H$. These walls are driven in the $x$-direction to produce an overall shear rate of $\gamma$, and the system is periodic in the $x$-direction with a period $L$. In the analysis, we will focus on the $x$ and $z$ coordinates, assuming without loss of generality of our results that the pressure and flowfields are translationally invariant in the $y$-direction.

The interface fluctuates around $z=H$. Let us describe its coordinates by a Fourier cosine series

$$h_{kq}(x,z) = H + \sum_{q=0}^{\infty} h_{q}(t) \cos qx, \quad (A1)$$

where $q = 2\pi n / L$, with $n$ a positive integer, in order to comply with our periodic setup. In the overdamped limit, viscosity dominates over inertia, the system is always in quasiequilibrium, and we can consider the relaxation of a standing wave described by the time dependence of the coefficients $h_{q}(t)$. Inclusion of sine terms in the above equation (to account for traveling waves) will then not be necessary. Our aim in this section is to solve the quasistationary Stokes’ equations,

$$\eta \nabla \cdot \mathbf{u} = \nabla P, \quad (A2)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (A3)$$

for the upper and lower fluids in the presence of the walls and the fluctuating interface described by the amplitudes $h_{q}(t)$. In the next section, we will consider force balances at the interface from which we will be able to derive an equation of motion for $h_{q}$ and determine the spectrum of relaxation times.

Let us first focus on the lower fluid between $z=0$ and $z=h_{kq}$. Periodic boundary conditions apply at $x=0$ and $x=L$, and the wall at $z=0$ forms a no-slip boundary. The boundary conditions at the interface require some more thought. Because the lower fluid is confined below the interface, the vertical ($z$-) velocity of the fluid at the interface is determined by the time evolution of the amplitudes $h_{q}(t)$,
where the dot above \( \dot{h}_q \) indicates differentiation with respect to time. If the amplitudes \( h_q \) are small, we may approximate this up to the first order in \( h_q \) as the vertical velocity at \( z = H \).

\[
u_z(x,H) = \sum_q \dot{h}_q(t) \cos qx - \frac{\partial u_z}{\partial z} \sum_q h_q \cos qx
\]

\[
= \sum_q \dot{h}_q(t) \cos qx. \tag{A5}
\]

In summary, we have the following boundary conditions:

\[
u_z(0,z) = u_z(L,z) \tag{A6}
\]

\[
u_z(x,0) = -\gamma \dot{H}, \tag{A8}
\]

\[
u_z(x,0) = 0 \tag{A9}
\]

\[
u_z(x,H) = \sum_q \dot{h}_q \cos qx. \tag{A10}
\]

Notice that we have not specified a boundary condition for the horizontal (\( x \)-) velocity at \( z = H \). We cannot specify it because we want to include the possibility of slip between the two fluids. We will be able to solve fully the set of equations in the next section when we balance tangential hydrodynamic forces.

Taking the divergence of Eq. (A2), the pressure field is found to obey Laplace’s equation \( \nabla^2 P(x,z) = 0 \). Already taking into account the periodic boundaries in the \( x \)-direction [Eqs. (A6) and (A7)], this suggests the following homogeneous solution to the flowfield in the \( x \)-direction:

\[
u_z(x,z) = \sum_{q \neq 0} \left[ (A_{q1} + B_{q2}z) \sin qx \sinh qz + (A_{q2} + B_{q3}z) \cos qx \sinh qz + (A_{q3} + B_{q4}z \cos qx \cosh qz) \right] + a + bz. \tag{A11}
\]

A similar expression may be written for \( u_z(x,z) \) with other coefficients \( \tilde{A}_{q1}, \ldots, \tilde{A}_{q4}, \tilde{B}_{q1}, \ldots, \tilde{B}_{q4}, \tilde{a}, \) and \( \tilde{b} \). Inserting the no-slip boundary condition, Eq. (A8) yields

\[
A_{q3} = 0, \quad A_{q4} = 0, \quad a = -\gamma \dot{H}. \tag{A12}
\]

Here and in the following, an expression such as \( A_{q3} = 0 \) means that the coefficients \( A_{q3} \) are zero for all allowed \( q \neq 0 \). The boundary condition Eq. (A9) yields

\[
\tilde{A}_{q3} = 0, \quad \tilde{A}_{q4} = 0, \quad \tilde{a} = 0. \tag{A13}
\]

The interface boundary condition, Eq. (A10), yields

\[
(A_{q2} + \tilde{B}_{q2}z \sinh qH + \tilde{B}_{q3}H \cosh qH = \dot{h}_y, \tag{A14}
\]

\[
\tilde{b} = 0. \tag{A16}
\]

Finally, using the incompressibility of the fluid [Eq. (A3)] we find the following relations for the coefficients of the flowfield:

\[
\tilde{B}_{q4} = -B_{q4}, \quad \tilde{qA}_{q4} = 0, \quad A_{q4} = 0 \tag{A17}
\]

So we come to the conclusion that we can express the flow field solely in terms of the unknown (for now) coefficients \( b, B_{q1}, \) and \( B_{q2} \). For ease of notation, we will also keep using the coefficients \( B_{q3} \) and \( B_{q4} \), but note that \( B_{q4} \) can be written in terms of \( B_{q3} \) by Eqs. (A14) and (A17) and that \( B_{q3} \) can be written in terms of \( B_{q1} \) by Eqs. (A15) and (A17).

In summary, the flowfield of the lower fluid is given by

\[
u_z(x,z) = -\gamma \dot{H} + bz + \sum_{q \neq 0} \left( \frac{B_{q3}}{q} + B_{q2}z \right) \sin qx \sinh qz + \left( \frac{B_{q4}}{q} + B_{q3}z \right) \cos qx \sinh qz + B_{q3}z \sin qx \cosh qx + B_{q2}z \cos qx \cosh qz \tag{A18}
\]

\[
u_z(x,z) = \sum_{q \neq 0} \left( \frac{B_{q4}}{q} + B_{q3}z \right) \sin qx \sinh qz + \left( \frac{B_{q3}}{q} + B_{q2}z \right) \cos qx \sinh qz + B_{q3}z \sin qx \cosh qx - B_{q2}z \cos qx \cosh qz. \tag{A19}
\]

Knowing the flow field, it is a simple task to calculate the pressure field from Eq. (A2),

\[
P(x,z) = P_0 + 2\gamma \sum_{q \neq 0} \left( B_{q4} \sin qx \sinh qz - B_{q3} \cos qx \sin qz + B_{q2} \sin qx \cosh qz - B_{q1} \cos qx \cosh qz \right), \tag{A20}
\]

where \( P_0 \) is a reference pressure (the average pressure in the absence of interfacial fluctuations).

Next, we focus on the upper fluid between \( z = h_{IF} \) and \( z = 2H \). If we transform to coordinates \( \xi = x \) and \( \xi = 2H - z \), the boundary conditions in these coordinates are given by

\[
u_\xi(0,\xi) = u_\xi(L,\xi) \tag{A21}
\]

\[
u_\xi(0,\xi) = u_\xi(L,\xi) \tag{A22}
\]

\[
u_\xi(\xi,0) = +\gamma \dot{H} \tag{A23}
\]

\[
(A_{q2} + \tilde{B}_{q2}z \sinh qH + \tilde{B}_{q3}H \cosh qH = \dot{h}_y, \tag{A15}
\]
\[ u_t(\xi,0) = 0 \quad (A24) \]
\[ u_t(\xi,H) = -\sum q \tilde{h}_q \cos q\xi. \quad (A25) \]

The solution to Stokes’ Eqs. (A2) and (A3) are then the same as for the lower fluid, only with \( \tilde{h}_q \) replaced by \(-\tilde{h}_q\) and \( \gamma \) replaced by \(-\gamma\). To distinguish the flow fields, we will label the coefficients which go with the flowfield of the upper fluid with primes, i.e., \( b'_q \) and \( B_{q'_1}, \ldots, B_{q'_4} \). At this point, we will make no assumptions about the relation between the coefficients \( B_{q'_i} \) and \( B_{q_j} \).

**APPENDIX B: FORCE BALANCES**

In this appendix, we will use the velocity and pressure fields derived in Appendix A to calculate the hydrodynamic stresses on the interface between the two fluids. Perpendicular to the interface, the hydrodynamic stresses must be balanced by the surface tension. Parallel to the interface, the difference between the hydrodynamic stresses is given by the interfacial slip force.

The hydrodynamic force per unit area on the interface due to the fluid below the interface is given by

\[ F^h = -\mathbf{\sigma} \cdot \hat{n}, \quad (B1) \]

where \( \mathbf{\sigma} \) is the stress tensor in the lower fluid close to the interface. Its components are given by

\[ \sigma_{\alpha\beta} = \eta \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) - \delta_{\alpha\beta} P, \quad (B2) \]

and \( \hat{n} \) is a unit vector normal to the interface. Up to the first order in \( h_q \), the latter is given by

\[ \hat{n}(x) = \left( \sum q h_q q \sin qx, 1 \right)^T. \quad (B3) \]

We will also need the unit vector tangential to the interface, which up to the first order in \( h_q \) is given by

\[ \hat{t}(x) = \left( 1, -\sum q h_q q \sin qx \right)^T. \quad (B4) \]

Using Eqs. (A18) and (A20), we find that the components of the hydrodynamic force perpendicular and parallel to the interface are given, up to the first order in \( h_q \), by

\[ F_{\perp}^h(x) = -\hat{n}^T \cdot \mathbf{\sigma} \cdot \hat{n} = P_0 + 2\eta \sum q \left\{ bh_q q \sin qx \right\} \]
\[ -B_{q3}qH \sin qx \sinh qH + B_{q1}qH \cos qx \sinh qH \]
\[ + (B_{q2} - B_{q4}qH) \sin qx \cosh qH \]
\[ -(B_{q3} - B_{q4}qH) \cos qx \cosh qH, \quad (B5) \]

\[ F_{\parallel}^h(x) = -\hat{t} \cdot \mathbf{\sigma} \cdot \hat{n} = -\eta b + 2\eta \sum q \left\{ -B_{q3}qH \sin qx \sinh qH \right\} \]
\[ -B_{q4}qH \cos qx \sinh qH \]
\[ -(B_{q3} + B_{q4}qH) \sin qx \cosh qH \]
\[ -(B_{q1} + B_{q2}qH) \cos qx \cosh qH \}. \quad (B6) \]

Let us now consider the elastic force on the interface due to surface tension. If the coordinates of the interface are given by \( h_{IF}(x,y,t) \), the interfacial free energy is given by Eq. (10). Up to the first order, a local change in the interfacial height at \((x,y)\) leads to a change in interfacial free energy given by

\[ \frac{\partial \mathbf{A}}{\partial h_{IF}(x,y,t)} = -\gamma \left( \frac{\partial^2 h_{IF}}{\partial x^2} + \frac{\partial^2 h_{IF}}{\partial y^2} \right). \quad (B7) \]

Using the Fourier cosine series [Eq. (A1)], we find a local free energy change of

\[ \frac{\partial \mathbf{A}}{\partial h_{IF}(x,y,t)} = \gamma \sum q \tilde{h}_q q^2 \cos qx. \quad (B8) \]

The elastic force (per unit area) due to the surface tension \( \gamma \) is therefore given up to the first order in \( h_q \) by

\[ F^e = \left( 0, -\gamma \sum q \tilde{h}_q q^2 \cos qx \right)^T. \quad (B9) \]

At any time and at any location along the interface, the total force in the normal direction must be zero

\[ F^h_{\parallel} - F^e_{\parallel} + F^\beta_{\parallel} = 0, \quad (B10) \]

where the prime in \( F^\beta_{\parallel} \) indicates that the hydrodynamic force originates from the upper fluid. As argued at the end of Appendix A, this can be found by replacing in Eq. (B5) all \( h_q \) by \(-\tilde{h}_q\) and all coefficients by primed versions (the minus sign arises in the equation above because the \( \xi \)-direction is opposite the \( z \)-direction). From Eq. (B10), we derive for each \( q \) up to the first order in \( h_q \)

\[ \gamma \tilde{h}_q q^2 = 2\eta(B_{q3} - B_{q4}qH)(qH \sinh qH - \cosh qH) \]
\[ + (B_{q1} - B_{q2}qH) \cosh qH \]

\[ + (B_{q3} - B_{q4}qH) \sinh qH \]. \quad (B11) \]

Let us next consider the forces in the tangential direction. If the upper and lower fluids slip past each other, they will experience a friction force given by

\[ F^\beta = \beta(\mathbf{u}(x,H^+) - \mathbf{u}(x,H^-)) \cdot \hat{t}. \quad (B12) \]

where \( \beta \) is the friction coefficient per unit area, \( \mathbf{u}(x,H^+) \) is the velocity of the upper fluid at the interface, and \( \mathbf{u}(x,H^-) \) is the velocity of the lower fluid at the interface. At the interface, the tangential hydrodynamic force due to the lower liquid is exactly canceled by the friction force, \( F^h_{\parallel} + F^\beta_{\parallel} = 0 \). Similarly the tangential hydrodynamic force due to the upper liquid is exactly canceled by the friction force \( F^e_{\parallel} + F^\beta_{\parallel} = 0 \). Adding and subtracting, respectively, these two expressions, we find that at any time and at any location along the interface the following balances must hold in the tangential direction:

\[ F^h_{\parallel} + F^e_{\parallel} = 0 \quad (B13) \]
\[ F^h_{\parallel} - F^e_{\parallel} + 2F^\beta_{\parallel} = 0. \quad (B14) \]

From the first equation, we find that \( B_{q2}^{\parallel} = -B_{q2}^e(i=1,\ldots,4) \), as could have been guessed from the symmetry. From the sec-
ond equation, we derive (for each \( q \)) up to the first order in \( h_q \)

\[
0 = (B_{q_3} - B'_{q_3})(\eta q(qH \sinh qH + \cosh qH) \\
+ \beta(\sinh qH + qH \cosh qH)) + (B_{q_1} - B'_{q_1}) \\
\times \{ \eta qqH \cosh qH + \beta qH \sinh qH \},
\]

as well as

\[
b = \frac{\gamma}{1 + \frac{q}{2\eta H}},
\]

in agreement with Eq. (9). In deriving the last equation, we have used the fact that the effective shear rates are equal in the upper and lower fluids, i.e., \( b' = -b \). Equation (B16) shows that the effective shear rate in the fluid goes asymptotically toward the applied shear rate \( \gamma \) as the interfacial friction \( \beta \) tends to infinity (no-slip shear flow). In the other limit, when the interfacial friction tends to zero, the effective shear rate in the fluid goes to zero (corresponding to two plug flows in opposite directions).

Although we now know that \( B'_{q_1} = -B_{q_1} \) and \( B'_{q_3} = -B_{q_3} \)

from Eqs. (B11) and (B15), it becomes apparent that only the differences \( B_{q_1} - B'_{q_1} \) and \( B_{q_3} - B'_{q_3} \) are required to find the relaxation times of the modes \( q \). Subtracting Eq. (A15) from the equivalent expression for the upper fluid and multiplying by \( q \), we find for each \( q \)

\[
2q\hat{h}_{q} = (B_{q_1} - B'_{q_1}) \{ \sinh qH - qH \cosh qH \} \\
- (B_{q_3} - B'_{q_3}) qH \sinh qH.
\]

From Eqs. (B11), (B15), and (B17), we derive, after some algebra, the following differential equation for \( h_q \):

\[
\frac{d\hat{h}_{q}}{dt} = \frac{\gamma q}{2H} \left[ \sinh(qH) - (qH)^2 \right] + \eta q \left[ \cosh(qH) \sin(qH/q) - qH \right] \\
- \frac{4 \eta \beta \cosh(qH) \sinh(qH + qH) + \eta qH \cosh^2(qH) + (qH)^2}{\eta q \beta H \sinh^2(qH) - (qH)^2} + \eta q \cosh(qH) \sinh(qH/q) - qH \right].
\]

Because the right hand side of the above equation is a negative constant for each \( q \), we have derived that each mode in a macroscopically applied perturbation of the interface will decay exponentially (at least within our overdamped and the first order approach) to zero. Onsager’s regression hypothesis states that the regression of microscopic thermal fluctuations at equilibrium follows the macroscopic law of relaxation. We therefore predict that the autocorrelations of the Fourier modes of the capillary (thermal) interface fluctuations are given up to the first order by

\[
\langle h_q(t)h_q(0) \rangle = \langle h_q^2 \rangle \exp(-t/\tau_q),
\]

where \( \langle h_q^2 \rangle \) is the mean-square amplitude of mode \( q \), and the relaxation time \( \tau_q \) is given by

\[
\tau_q = \frac{4 \eta \beta H \cosh(qH) \sinh(qH + qH) + \eta qH \cosh^2(qH) + (qH)^2}{\eta q \beta H \sinh^2(qH) - (qH)^2} + \eta q \cosh(qH) \sinh(qH/q) - qH \right].
\]

Several limits may be identified.

- When the fluid height \( H \) is much larger than the wavelength of the fluctuation of interest, the actual value of the friction coefficient \( \beta \) becomes irrelevant. In such a case, we have

\[
\lim_{qH \to \infty} \tau_q = \frac{4 \eta}{\gamma q}.
\]

This expression is in agreement with the result of Jeng et al.\textsuperscript{26} for overdamped liquid-liquid interface fluctuations.

- When the fluid height \( H \) is much smaller than the wavelength of the fluctuation of interest and the friction coefficient is sufficiently large, we have

\[
\lim_{qH \to 0} \lim_{\beta H/\eta \to \infty} \tau_q = \frac{24 \eta}{\gamma q^4 H^3}.
\]

- Finally, when the fluid height \( H \) is much smaller than the wavelength of the fluctuation of interest and the friction coefficient is negligible, we have

\[
\lim_{\beta H/\eta \to 0} \lim_{qH \to \infty} \tau_q = \frac{6 \eta}{\gamma q^3 H^3}.
\]

For two thin layers of fluid, according to the last two equations, we find that the relaxation times of fluctuations of the interface can change by a factor of 4, depending on the strength of the interfacial friction.


\textsuperscript{3}J. Rowlinson and B. Widom, \textit{Molecular Theory of Capillarity} (Clarendon, Oxford, 1982).