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How Thick Is a Liquid–Vapor Interface?

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The structure of the interface of an argonlike fluid in equilibrium with its vapor near the triple point is studied using Monte Carlo simulation. By referring particle coordinates to the capillary waves and calculating the transverse structure factor in that reference frame, one can determine the penetration depth of the capillary waves into the bulk as a function of the wave vector. The penetration depth of the lowest capillary mode is consistent with the interfacial thickness as determined from the intrinsic density profile, and the data for the higher modes suggest that the penetration depth might be independent of k.

KEY WORDS: Phase coexistence; fluid interface; capillary waves; intrinsic profile; wave penetration; computer simulation.

1. INTRODUCTION

The interface between coexisting liquid and gas phases has been a subject of some controversy in recent years. The crux of the problem is in the different results derived from two phenomenological models of the interface, both of which are physically reasonable. The first, the mean field approximation, which was originally formulated by van der Waals,(1) assumes that particle cores are uncorrelated by position and that local thermodynamics is valid, and decomposes the intermolecular interaction into a hard core plus a long-range attractive tail. Based on these considerations, one may derive the following expression for the density profile(2):

$$n(z) = 1/2[(n_l + n_g) - (n_l - n_g)\tanh(2\gamma z)] \qquad (1)$$

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where n_l and n_g are the respective liquid and gas densities. The quantity(3)

$$D = 1/\gamma = -(n_l - n_g)(dn/dz)^{-1}\,|_{z_0} \tag{2}$$

where z_0 is the location of the interface, may be taken as a measure of the thickness of the interface, and is a function of the range of the tail.

The second model is the capillary wave model of Buff *et al.*(4) They assumed that an interface of area $A = L^2$ could be defined by a height function $\xi(x, y)$, and expanded ξ in terms of its Fourier components:

$$\xi(\mathbf{x}) = \sum_k a(\mathbf{k}) \exp(i\mathbf{kx}) \tag{3}$$

Analysis of the energy required to distort the interface led to the following expression for the mean square amplitude, another measure of the interfacial thickness:

$$\begin{aligned}\langle \xi^2 \rangle = \sum_{k_2 > 0} \langle a(\mathbf{k})\, a(-\mathbf{k}) \rangle &= \frac{1}{\beta\sigma A} \sum_{k_2 > 0} (2a^{-2} + k^2)^{-1} \\ &\approx \frac{1}{4\pi\beta\sigma} \ln \frac{1 + 2(\pi a/l)^2}{1 + 2(\pi a/L)^2}\end{aligned} \tag{4}$$

where $a^2 = 2\sigma/mg(n_l - n_g)$, g is the gravitational constant, m is the mass per particle, σ is the surface tension, β is the inverse temperature, and l is the atomic diameter. The quantities l and L serve to define upper and lower limits on k, since the complete sum over k diverges. Further analysis of this results indicates that in the limit $A \to \infty$, $\langle \xi^2 \rangle$ diverges as $(-\ln g)^{1/2}$ as $g \to 0$, or conversely, in the limit $g \to 0$, $\langle \xi^2 \rangle$ diverges as $(\ln A)^{1/2}$ as $A \to \infty$. Thus, we see that the interfacial thickness is undefined in the thermodynamic limit.

Consideration of the fluctuations(5) of the potential tail that are ignored in the mean field theory shows that capillary waves must exist. The transverse structure factor takes the form(6)

$$\hat{S}(k, z_1, z_2) = \frac{1}{\beta} \frac{n'(z_1)\, n'(z_2)}{\sigma k^2 - \int n'(z)\, u'(z)\, dz} \tag{5}$$

where $u(r)$ is the potential of the force distorting the interface. The structure factor has the same k^{-2} behavior as $\langle \xi^2 \rangle$, which is indicative of long-range correlations in r space.

An interesting corollary of these results is that in the absence of gravity and on a hydrodynamic length scale the interface has the structure of a fat fractal,(7) since the change in area due to the distortion scales according to the high-k cutoff. It is a fat fractal because its surface has a nonzero measure in three dimensions in the presence of capillary waves. This cutoff defines the length scale, $\delta x = 1/k_{\max}$, and thus the change in area is

$$A_N \equiv \frac{A_0}{2} \sum_{k_2>0}^{N} k^2 \langle a_{(\mathbf{k})} a_{(-\mathbf{k})} \rangle = \frac{N^2}{2\beta\sigma} \tag{6}$$

But

$$N = k_{\max} L/2\pi = L/2\pi\, \delta x \tag{7}$$

and therefore $A_N \approx (\delta x)^{-2}$. The Hausdorff dimension of A_N, defined by $A(\delta x) = (\delta x)^{1-D}$,[8] is thus $D = 3$. This will be approximately true for a weak external field where $2a^{-2} \ll k^2$, since the correction to A_N is of order $-g \ln N$. It is easy to generalize this result to an arbitrary dimension, and one finds that the Hausdorff dimension D_{H} is $D_{\mathrm{H}} = 1 + D_{\mathrm{E}}$, where D_{E} is the Euclidean dimension of the interface.

Today, we regard the interface as an intrinsic interface broadened by the presence of thermally excited capillary waves. The question to be addressed is: How thick is the intrinsic interface, and how much is it broadened? In this paper, we present the results of the analyses of a Monte Carlo simulation of a liquid–vapor system. In particular, we have measured the width of the interface and compared it with an intrinsic interface to see how much broadening has occurred. We define a capillary frame of reference, and by comparing the transverse structure factor $\hat{S}(k, z)$ as calculated in this reference frame to that calculated in a bulk liquid, we determine the penetration depth of capillary waves into the bulk liquid as a function of k. We are interested in defining a capillary frame of reference since it also offers the possibility of decreasing the equilibration time of simulations of interfaces.

2. COMPUTER SIMULATIONS

The system used in our study consisted of 1728 particles of liquid argon at 84 K, just above the triple point, and with an average liquid density of 0.76 particles per unit volume. The interaction potential is a shifted, truncated Lennard-Jones 6–12 potential with $\varepsilon = 119.4$ K and $\sigma = 3.405$ Å, and the potential cutoff was at $r = 2.5\sigma$. We assume the radius of the particles to be 0.80σ. The liquid is in the center third of a cell of dimension $l \times l \times 3l$, where $l = 13.15\sigma$, and gas is in the upper and lower thirds. Periodic boundary conditions were imposed in all three directions. The interfaces are taken to be in the x–y plane and the origin of the coordinate system is taken to be in the center of the cell.

The system was well equilibrated to begin with, and was run over 8100 time steps of a Monte Carlo Metropolis(9) algorithm that was modified to move preferentially particles near the surface. The maximum step size in any direction is $\pm 0.1\sigma$, with an average absolute step size of $l = 0.093\sigma$, and the acceptance rate was 51.35%. Every tenth configuration was saved for performing our calculations. The average step size per particle (between every tenth configuration) was $0.223 \pm 0.05\sigma$, and the average total displacement per particle over all 8100 time steps was $4.273 \pm 2.153\sigma$.

Our method of preferentially moving particles near the surface during the simulation involved dividing the cell into 15 slabs in the x–y plane, numbering them 1–15 from bottom to top, and assigning a weight to each slab. In the center of the liquid, slab 7 will have a weight of 1, slabs 6 and 8, nearer to the surface, will have a weight of 2, and all of the others will have a weight of 4. These weights determine how many times we attempt to move a particle in the slab in the course of one pass. With this weighting scheme, the total number of attempted moves per pass is then

$$\sum_{\text{slabs}} (\text{weight for each slab})(\text{number of particles per slab}) \approx 4500$$

3. DENSITY PROFILE

We calculated the density $n(x, y, z)$ for each configuration, using a grid with eight subdivisions in the x and y directions and 400 subdivisions in the z direction, which provides a resolution of 0.1σ along the z axis. Specifically,

$$n(x, y, z) = (\pi r_1^2\, \delta z)^{-1} \left(\frac{4\pi}{3} r_2^3\right)^{-1} \sum_i \delta v_i(x, y, z) \tag{8}$$

where $r_1 = (13.15/8\sqrt{2})\,\sigma$ may be taken as the radius of a cylindrical probe, with $\delta z = 0.1\sigma$ as its thickness, $r_2 = 0.8\sigma$ is the atomic radius, and $\delta v_i(x, y, z)$ is the overlap volume of the ith atom with the probe centered at (x, y, z). The sum is over all particles overlapping the probe. Using smaller subdivisions in the x–y plane would cause the particles to look like delta functions. We averaged $n(x, y, z)$ over the x–y plane to obtain the density profile $n(z)$, and we calculated the standard deviation of this spatial average, $\delta n(z)$. Both quantities were averaged over both surfaces and over all configurations and these ensemble averages are presented in Fig. 1. Defining the interface as that region between $n(z) = 0.1n_l$ and $n(z) = 0.9n_l$, we find that the width of the interface is about 2.3σ. The function $\delta n(z)$ exhibits a peak in the interfacial region whose width is another measure of the width of the interface. This peak is about 2.7σ wide.

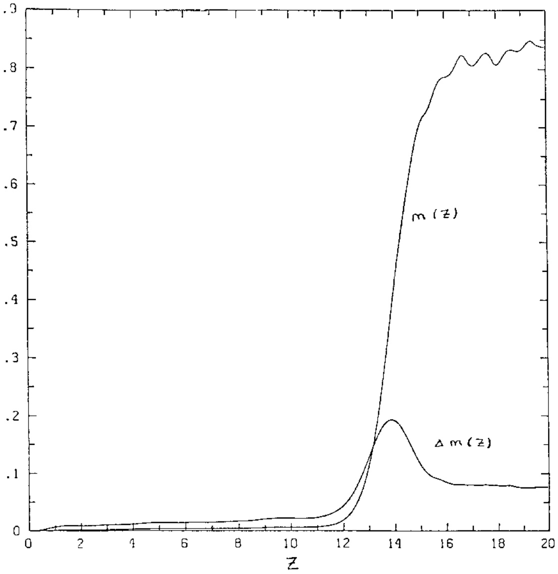

Fig. 1. The bulk density profile and its standard deviation.

Defining the location of the interface as that set of points in the x–y plane where the density is half the average bulk density, we may, for each configuration, locate the interface function $\xi_j(x, y)$ for each surface j on an 8×8 grid from the density $n(x, y, z)$. In Fig. 2, we present the ensemble average of the interface function. Included in this is an average over both surfaces, which could reduce the actual surface amplitude due to phase interference. We do this to reduce the noise on the surface, but this is not essential to any later results. Also, we note that since the surface is not flat, the capillary waves have not equilibrated. By averaging $\xi_j(x, y)$ over all pairs (x, y) for each surface, we find the average location of the two surfaces, z_1 and z_2. Averaging these over all configurations, we find that $\langle z_1 \rangle = -6.198\sigma$ and $\langle z_2 \rangle = 6.103\sigma$ with an average absolute amplitude of $\delta z = 0.416\sigma$. We use $\xi_j(x, y)$ along with z_1 and z_2 to define an intrinsic profile $n_i(z)$, the density profile in the absence of capillary waves. To do this, we first divide the configuration along the x–y plane at $z = 0$. Then, for each half of the configuration, we shift the z coordinate for each pair (x, y) of $n(x, y, z)$ by the amount $z_j - \xi_j(x, y)$. This has the effect of flattening out the interface. However, it should be noted that there will still be density variations within the interface due to variations in the local density profiles, and so the surface is not perfectly flat. Next, we averaged this "shifted" $n(x, y, z)$ over the x–y coordinates to obtain the intrinsic profile for the half of the system on which we have been working. Once we obtain an

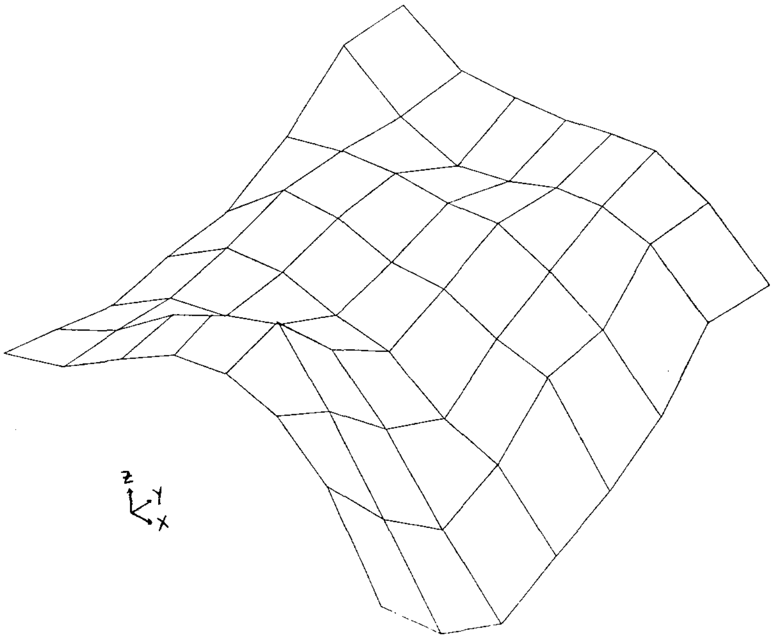

Fig. 2. The liquid–vapor interface.

intrinsic profile for each half of the configuration, we average over the halves to obtain $n_i(z)$, the intrinsic profile.

In Fig. 3, we present the ensemble averages of $n_i(z)$ and of the standard deviation of the spatial averaging performed in calculating $n_i(z)$. Note that the length scale is centered on the interface, which is at $z = 5.0$. We see that the standard deviation has a dip at the value of z where the interface is located. This is to be expected, since the intrinsic profile was defined in such a way so as to flatten out the interface. The peaks on either side of the dip are much reduced in magnitude over the corresponding peak for the bulk profile, and reflect the local variations in the density profile mentioned above. One can see that as we move away from the interface, a local linear translation is not the best way of transforming away the capillary waves. From these graphs, we obtain an interfacial thickness of 1.7σ, which suggests that it is of the order of the bulk correlation length, but we have made no attempt to measure this. The thickness of the interface is a function of the cross-sectional area, and should increase as $(\ln A)^{1/2}$ as the area is increased.

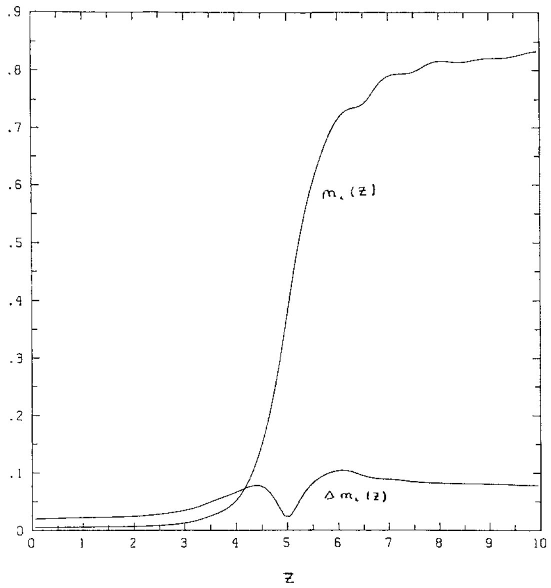

Fig. 3. The intrinsic density profile and its standard deviation.

4. THE CAPILLARY FRAME OF REFERENCE

A major obstacle in performing simulations of interfacial phenomena is that capillary waves move very slowly, thus requiring extremely long computer runs to obtain reasonable statistics. However, this obstacle would be removed if one could refer particle coordinates to the capillary waves. This has other advantages as well. The depth of the intrinsic interface is greater than zero, and there is considerable variance in the density within the interfacial region, which, along with the fact that the density is increasing rapidly from the gas to the liquid density, is a source of systematic errors in any interfacial quantity. A suitable choice of a capillary frame of reference can minimize these systematic errors. By comparison of the transverse structure factor calculated in this capillary frame of reference with the bulk structure factor, one may determine optimal definition of this reference frame.

For each configuration, we define

$$\delta z_i = (\xi(\mathbf{x}_i) - \langle z_j \rangle) \exp\{-1/2[(\xi(\mathbf{x}_i) - z_i)^2/b^2]\} \tag{9}$$

so that $z'_i = z_i + \delta z_i$ is the capillary coordinate of the *i*th particle, where $\xi(\mathbf{x}_i)$ is the z coordinate of the surface point corresponding to particle *i*,

$\langle z_j \rangle$ is the average z coordinate of surface j, and b, the depth parameter, is a measure of the thickness of the interface, and will be determined empirically. We are assuming that the amplitude of the capillary waves is symmetric with respect to the surface. The presence of the peaks in the standard deviation of the intrinsic profile indicates that capillary waves do not penetrate into the bulk of the liquid, and thus we want to confine our change of reference frame to particles near the surface.

For the purpose of locating the interface for points not on the grid, we treat the surface as a superposition of Gaussians centered on the grid points:

$$\xi(\mathbf{x}_i) = \sum_j a_j z(\mathbf{x}_j) \exp(-x_{ij}^2/2\sigma^2) \tag{10}$$

where the coefficients a_j are determined subject to the condition that $\xi(\mathbf{x}_i) = z(\mathbf{x}_j)$ for $\mathbf{x}_i = \mathbf{x}_j$, and where $\pi\sigma^2 = (L/8)^2$, the area of one block on the grid. Here, $\xi(\mathbf{x}_i)$ is an arbitrary point on the surface, $z(\mathbf{x}_j)$ is the interface at point $\mathbf{x}_j$ on the grid, and the sum is over all grid points.

We determine the best value of b by minimizing the difference between the structure factor calculated on the surface with a particular value of b and the bulk structure factor. In the absence of a detailed model of a nonuniform fluid without capillary waves, we have chosen the structure factor in the bulk liquid, far from the interfaces, as our reference point. We will determine the penetration depth of the capillary waves by looking at the deviation of the structure factor in the interfacial region from the reference. We will, however, have some irreducible noise from the gas side of the interface. We defined the structure factor as

$$\hat{S}(k, z) = \sum_i |J_0(kr_i)|^2 \tag{11}$$

where the sum is restricted to particles within $\delta z = \pm 1.3\sigma$ of z and J_0 is a zeroth-order Bessel function. We use $J_0(kr)$ in order to average out any x–y anisotropy arising from our choice of coordinate system and boundary conditions. Reducing the thickness of the slabs will increase the sensitivity of $\hat{S}(k, z)$ to the capillary transformation, but will increase noise due to the reduced number of particles per slab. Our values of b range from 0.5σ to 4.0σ by steps of 0.25σ, and we calculated $\hat{S}_b(k, z)$ for each value of b with z ranging from -8.0σ to 8.0σ by steps of 0.5σ; we averaged these over all configurations (see Fig. 4 for selected graphs with $b = 2.0\sigma$). For each configuration, we calculated the difference function

$$f_b(k) \equiv \sum_i |\hat{S}_b(k, z) - \hat{S}(k, 0)|^2 \tag{12}$$

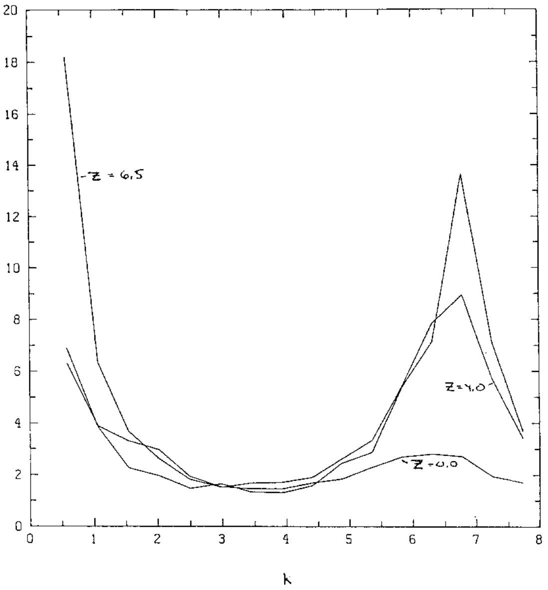

Fig. 4. The structure factor as a function of k for $b = 2.0\sigma$, for $z = 6.5\sigma$, 4.0σ, and 0.0σ.

where $\hat{S}(k, 0)$ is the bulk structure factor, and averaged this over all configurations. We looked for that value of b that minimized this function for a particular value of k. Because the system is isotropic in the x–y plane in pair space, the k values that we used denoted in order of increasing magnitude by $k_1, k_2, k_3, \ldots,$ were chosen so that $J_0'(kr)$ was zero for the maximum value of r, which for our case is 6.575σ. In Fig. 5, we present the ensemble average of $f_b(k)$ for the four lowest k values, and in Fig. 6, we present the standard deviation of the ensemble averages. The modes themselves are of course those of a circular drumhead with Neumann boundary conditions.

Examination of $f_b(k)$ shows that it has very weak minima for the k_1 and k_2 modes, and is essentially flat for higher modes. However, the weakness of the minima is such that we need to consider the effects of noise. To do this, we calculated the standard deviation of $\langle f_b(k) \rangle$, $\delta\langle f_b(k) \rangle$ (see Fig. 6). We find that, for the k_1 mode, $\delta\langle f_b(k) \rangle$ has a clear minimum at $b = 2.0\sigma$, and for the k_2 mode, there is an inflection point at $b = 2.0\sigma$, with $\delta\langle f_b(k) \rangle$, being flat for $b < 2.0\sigma$ and monotonically increasing for $b > 2.0\sigma$. For the higher k modes, $\delta\langle f_b(k) \rangle$ is essentially flat.

The depth parameter b is a measure of how much we have transformed away from the lab frame. Small values of b correspond to small particle shifts and small deviations from the lab frame, while large values of b

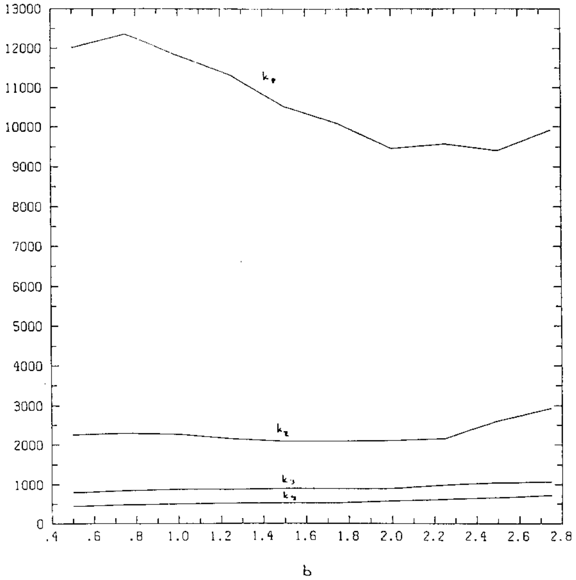

Fig. 5. The difference function for $b = 0.50\sigma$ to 2.75σ and the four lowest k modes.

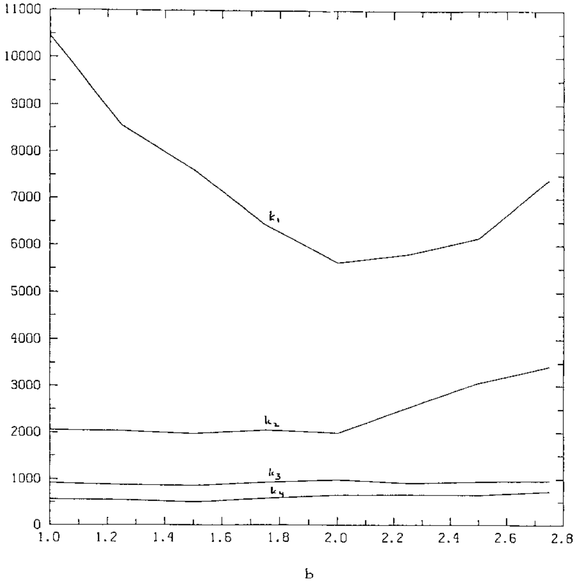

Fig. 6. Standard deviation of the difference function.

correspond to large particle shifts. A value of zero for b would leave the system in the lab frame. The minimum for the k_1 mode indicates that as $b \rightarrow 2.0\sigma$, systematic errors due to the presence of capillary waves in the interface are reduced, reaching a minimum at 2.0σ; increasing b beyond 2.0σ moves the particles farther than necessary, introducing spurious correlations, thus increasing systematic error. The flatness of $\delta\langle f_b\rangle$ for the k_2 mode for $b < 2.0\sigma$ indicates that the k_2 mode contributes little to capillary motion, and the fact that it increases monotonically for $b > 2.0\sigma$ again indicates the introduction of spurious correlations from having moved particles too far. The higher k modes also appear to contribute little to capillary motion, but the data are too noisy to be conclusive.

Thus, we take as our criterion for determining the best of b as that value that minimizes the noise, and we see that the minimizing value for the k_1 mode is clearly $b = 2.0\sigma$. The fact that the minimum for the k_1 mode and the inflection point for the k_2 mode both occur for $b = 2.0\sigma$ suggests that the penetration depth might be independent of k, but this needs further investigation.

CONCLUSIONS

We have found that the width of an intrinsic interface in our model system is about 1.7σ, which is broadened by thermally excited capillary waves to about 2.7σ at 84 K. By referring particle coordinates to the capillary coordinates and comparing the transverse structure factor $\hat{S}(k, z)$ calculated in that reference frame to that calculated in a bulk liquid, we can determine the penetration depth of capillary waves into the bulk liquid. We find that the penetration depth of the lowest k mode is 2.0σ, which is of the order of the width of the intrinsic profile. Examination of the next lowest mode suggests that the penetration depth is independent of k, although this needs further investigation.

Since the k_1 mode is the dominant contribution to the capillary waves, and since the data suggest, although they do not conclusively prove, that the penetration depth is independent of k, we take the value of $b = 2.0\sigma$ as being the thickness of the interface at 84 K and as generating the best definition of the capillary frame of reference. Further work is needed to show that the system does indeed equilibrate more quickly in the capillary frame, and this would involve calculating the pressure and chemical potential. An interesting method of calculating the capillary contribution to these quantities is to regard the capillary transformation, which is a local coordinate transformation, as analogous to the local gauge transformations used in defining quantum gauge fields. One then needs to determine the invariants of this transformation, and from these invariants determine the chemical potential and pressure contributions needed to maintain the invariance. This requires further study.

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