do not increase sufficiently rapidly with density; again, the choice of analytic form for $f(r)$ is probably responsible.[15] One other discrepancy between theory and experiment is quite puzzling. We find anisotropies of the order of 100 m/sec for the longitudinal modes and 150 m/sec for the transverse modes, whereas anisotropies of this size have been observed[14] only in the transverse velocity of hcp ^{4}He. Since crystalline helium is thought[19] to solidify into one or several large crystallites, it is not clear why these anisotropies have not been observed, although we note that no measurements have yet been made on an oriented sample.

*Work supported in part by the Air Force Office of Scientific Research.

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[9]We neglect a 1% correction to $W(r)$ involving averages of f^2 in the denominator.

[10]See Eqs. (38) and (39) of FW.

[11]In the notation of FW reference 5, Eq. (6) follows directly from the single approximation $\mathrm{Tr}\{AM^{-1}A\} \simeq \mathrm{Tr}\{(AMA)^{-1}\}$.

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INTERFACIAL DENSITY PROFILE FOR FLUIDS IN THE CRITICAL REGION

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(Received 16 September 1965)

Webb and collaborators[1] recently measured the reflectivity of the interface in a cyclohexane-methanol mixture just below the consolute temperature T_c, with a view toward establishing the temperature dependence of interfacial width. The data were analyzed in terms of a concentration profile of the form imposed by the Maxwell–van der Waals theory,[2]

$$\rho(z) = \tfrac{1}{2}[\rho_1 + \rho_2 - (\rho_1 - \rho_2)\tanh(2z/L)], \qquad (1)$$

where z is vertical height, and $\rho(z)$ is the concentration of that species whose lower and upper bulk phase values are ρ_1 and ρ_2, respectively. On this basis the experiments indicated that the characteristic interfacial width parameter L varied as $(T_c - T)^{-\mu}$, with $\mu = 0.76 \pm 0.1$. It is our purpose in this note to sketch results of a general theory of interfacial structure, based in part upon use of capillary waves as

suitable relevant collective coordinates,[3] which we believe provides a more suitable theoretical interpretation.

In order to free the analysis from the specific profile form (1), it is convenient to have available the general first Born approximation to interfacial reflectivity, which is adequate in the experimental region investigated; for normal incidence its ratio to the Fresnel (infinitely sharp interface) result R_F is

$$R/R_F = |\int_{-\infty}^{\infty} P(z)\exp[i(k_1+k_2)z]dz|^2,$$

$$P(z) = -(\rho_1-\rho_2)^{-1}d\rho/dz, \quad k = 2\pi n/\lambda. \qquad (2)$$

Here, the dielectric constant is presumed linearly related to $\rho(z)$, the index of refraction varies between bulk phase values n_1 and n_2, and λ is the wavelength of visible light. For profile (1), Eq. (2) reproduces the Eckart[4] reflectivity formula employed in reference 1. Over half the reported temperature range, the reflectivity measurements provide a direct measure of the second moment of the distribution $P(z)$, $\langle z^2\rangle$.[5] Closer to the critical point these measurements are more sensitive to the details of the density profile.

The general theory of interface dividing surface distortion may be established with complete rigor and detail in the grand ensemble. For present purposes, though, one may provide an intuitive appraisal. If, by virtue of thermal agitation, the instantaneous dividing surface between phases 1 and 2 is $z(x,y)$, the probability for such a displacement may be taken proportional to $\exp[-\beta W(z)]$, where W is a functional of z equal to the isothermal reversible work necessary at equilibrium to impose the disturbance and $\beta = 1/kT$. W consists both of work against gravity, and against a surface tension γ_0:

$$W = \tfrac{1}{2}(\rho_1-\rho_2)mg\int\int z^2(x,y)dxdy + \gamma_0\int\int(1+z_x{}^2+z_y{}^2)^{1/2}dxdy. \qquad (3)$$

If the distorted surface is represented as a Fourier series,

$$z(x,y) = \sum A(\vec{k})\exp(i\vec{k}\cdot\vec{s}), \qquad (4)$$
$$\vec{s} = x\vec{i}+y\vec{j},$$

linearization of the second integrand in Eq. (3) yields a distorted surface description in terms of decoupled harmonic surface waves.

On account of the decoupling, and consequent factoring of the distortion probability, computation of various surface averages is straightforward. By virtue of the inhibition of surface diffuseness implied by fixed surface, it is reasonable to suppose a sharp discontinuity in density, between bulk phase values, across surface $z(x,y)$. With this additional assumption, and in the macroscopic limit (so k sums pass to integrals), one calculates the relevant second moment to be

$$\langle z^2\rangle = (4\pi\gamma_0\beta)^{-1}\ln[1+\tfrac{1}{2}\alpha^2 k_{max}{}^2], \qquad (5)$$
$$\alpha^2 = 2\gamma_0/(\rho_1-\rho_2)mg,$$

where k_{max} is an upper cutoff on Fourier components permitted to $z(x,y)$. Evaluation of the free energy born by the collective surface modes leads additionally to the following relation between γ_0 and the experimentally measurable surface tension γ:

$$\gamma_0 = \gamma + 3k_{max}{}^2/16\pi\beta. \qquad (6)$$

The density discontinuity across $z(x,y)$ furthermore identifies γ_0, not γ, with the approximate surface-tension formula proposed by Fowler,[6] and suggests that it should bound the experimental quantity from above.

In order to maintain the integrity of capillary waves as independent collective coordinates, it is mandatory to select k_{max} inversely proportional to the interface width, $k_{max}\approx\pi/L$. With this choice, Eq. (5) becomes a transcendental equation for $\langle z^2\rangle$. Figure 1 displays the numerical solution for the comparable cyclohexane-aniline mixture[7] for which γ is available, along with a transcription of the corresponding data from reference 1. The calculations may be fitted well over their temperature

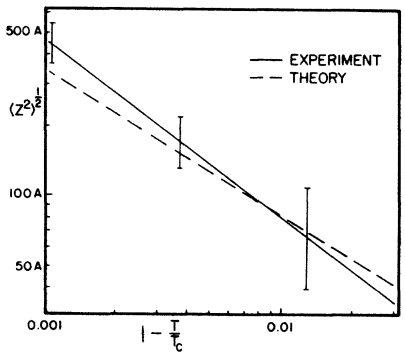

FIG. 1. $\langle z^2\rangle$ for planar interface in the critical region.

range by a curve with characteristic width exponent $\mu = 0.63 \pm 0.03$.

Of equal importance, with explanation of the reflectance experiments, are the purely theoretical questions concerning the fundamental role of the external gravitational field. Although detailed analysis must await our fuller exposition of the general interfacial theory, we remark that Eqs. (5) and (6) predict that the diffuse planar interface diverges in width logarithmically as $g \to 0$ (T fixed), and that γ suffers simultaneously a bounded anomaly, also of logarithmic character.

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*A portion of the underlying theory was presented by one of us (F.P.B) in the Proceedings of the Thirty-Eighth National Colloid Symposium, 11-13 June 1964, Austin, Texas (to be published).

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OBSERVATION OF RESONANT LATTICE MODES BY INELASTIC NEUTRON SCATTERING*

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This Letter reports the observation by inelastic neutron scattering of resonant lattice modes due to a small concentration of W atoms in a Cr host crystal.

The modification of the modes of vibration of a lattice due to the substitution of heavy or light impurities for some of the host atoms has been the subject of much recent discussion. The scattering of neutrons by such a defect structure has been considered by Krivoglaz,[1] Kagan and Iosilevskii,[2] and Brout and Visscher.[3] More recently, Elliott and Maradudin[4] have given a detailed discussion of neutron scattering by the defect modes and have shown, with explicit calculations, how information about such modes can be obtained from the experiments. It was this work which provided the stimulus for our experiments.

The type of lattice mode which occurs near a defect depends on whether the mass of the impurity M' is less or greater than M, that of the host atoms. In the former case, a localized mode appears with a frequency above the frequency distribution of the host lattice, while in the latter there is a resonant mode within the allowed frequency range of the host. This mode is characterized by a large amplitude of vibration at the defect, decaying into a normal lattice mode of the host at large distances. The frequencies and lifetimes of phonons with frequencies near that of the resonant mode are considerably affected by the presence of the defects. Elliott and Maradudin[3] show that, for a cubic lattice, a small concentration c of impurities which do not affect the interatomic force constants causes a frequency shift Δ and