VISCOUS DAMPING OF THERMAL EXCITATIONS ON THE INTERFACE OF CRITICAL FLUID MIXTURES

J. S. Huang
Department of Physics, and Laboratory for Atomic and Solid State Physics,
Cornell University, Ithaca, New York 14850

and

W. W. Webb
Department of Applied Physics, and Laboratory for Atomic and Solid State Physics,
Cornell University, Itaca, New York 14850
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Measurements of the time-dependent correlation function for small-angle scattering of visible light by the interface in a fluid mixture to within 3×10^{-3}°K of its critical temperature T_c have revealed thermal excitations with exponential relaxation times τ up to about 20 sec. Analysis has shown that τ varies inversely as the wave number Q and diverges on approaching the critical temperature as $(1-T/T_c)^{-1.27}$. Identification of τ with viscous damping of hydrodynamic waves on the interface permits determination of the critical behavior of the shear viscosity which is found to be at most only weakly divergent.

By measuring the real-time correlation function of the light scattered from the interface between the two fluids in equilibrium in binary mixtures just below the critical temperature T_c we have directly observed thermal-equilibrium interface fluctuations having relaxation times τ extending to many seconds near T_c. By combining these new observations with recent interfacial energy measurements, we have determined the behavior of the shear viscosity very close to the critical point for comparison with the disparate predictions of dynamic scaling[1] and modified mean-field theories.[2,3] Our measurements extended to temperatures within 0.003°K of T_c ($T_c = 45.14$°C). Our correlation times included the range $0.005 \leq \tau/2 \leq 10$ sec which is equivalent to a spectral resolution of better than $1/10^{16}$ for scattering of visible light.

Excitations of a free fluid surface having the properties of capillary gravitational surface waves (ripplons)[4] are well known: The dispersion relations are available[5,6]; the spectrum of thermal excitations has been calculated,[7] and inelastic scattering of light from the waves has been accomplished[8] and confirmed.[9] Free-surface results are generally consistent with known fluid properties, and experiments have been recently extended to noncritical fluid interfaces.[10-12] What we have found are similar excitations on the critical interface in a binary mixture, where the interfacial free energy (surface tension) and the density difference $\Delta\rho$ vanish as $T \to T_c$, leaving viscous forces to dominate the observable interfacial excitations and producing dramatic "critical slowing down" of their time variations.

These interfacial excitations can be represented by local variations of the height of the interface expandable in the form $\xi = Ae^{iQx}e^{St/\tau_0}$. The appropriate dispersion relation of these excitations (neglecting the gravitational effects and assuming equal shear viscosities $\eta_1 = \eta_2 = \eta$ for the two coexisting phases) can be written in the dimensionless form[10,13,14]

$$S^2 + \tfrac{1}{2}S[1 + (1+2S)^{1/2}] + y = 0, \quad (1)$$

where $y = \omega_0^2\tau_0^2$, $\tau_0 = \rho/2\eta Q^2$, and $\omega_0^2 = \sigma Q^3/2\rho$, with $\rho = \frac{1}{2}(\rho_1+\rho_2)$ the average of the densities ρ_1 and ρ_2 of the two phases, σ the interfacial surface tension, and Q the wave number.

For $y > 0.155$, the two roots $S' \pm iS''$ of Eq. (1) are complex, describing propagating wave motion with frequency $\omega = -S''/\tau_0$ and decay time $\tau' = -\tau_0/S'$. For $y \leq 0.155$, the two roots S_1 and S_2 are real and negative, corresponding to nonpropagating, exponentially relaxing excitations described by the autocorrelation function

$$G(Q,t) = \frac{k_B T}{\sigma Q^2 A}(S_1 - S_2)^{-1}(S_2 e^{S_1 t/\tau_0} - S_1 e^{S_2 t/\tau_0}), \quad (2)$$

where k_B is Boltzmann's constant, T the absolute temperature, and A the area.[9] In the limit $y \ll 0.155$, the time constants τ_1 and τ_2 of the two relaxation modes are

$$\tau_1 = -\frac{\tau_0}{S_1} = \frac{4\eta}{\sigma Q}, \quad (3)$$

$$\tau_2 = -\frac{\tau_0}{S_2} = \frac{\rho}{\eta Q^2}. \quad (4)$$

Equations (3) and (4) show that measurements

of the exponential relaxation times of the overdamped excitations combined with measurements of the interfacial energy σ yield the shear viscosity η in the critical region. Thus, we studied the system cyclohexane-methanol in which Warren and Webb[15] had recently measured σ in the critical region. We had previously measured the temperature dependence of the intensity of the specular reflection in this system in order to study the diffuse transition zone at the interface.[16,17] In the present experiments we observed the light scattered by interface excitations[18] in nonspecular directions such that $10^2 \lesssim Q < 10^3$ cm^{-1} and measured its time dependence $C(Q,t)$, which is proportional to $[G(Q,t)]^2$.

The measurement of $C(Q,t)$ was performed as follows: The light beam from a 1-mW He-Ne laser is totally reflected from the interface of a suitably thermostated, previously prepared, high-purity sample of the critical mixture.[17] The diffuse scattered intensity is measured with a photomultiplier located by a cathetometer and screened by a pinhole to define the angular resolution of the detecting system to better than 5 $\times 10^{-4}$ rad. The output of the phototube is amplified by a wide-band dc amplifier and recorded in the frequency-modulated mode on magnetic tape with a recorder providing uniform, linear response from 0 to 2.5 kHz at a signal-to-noise ratio >40 dB. The data recorded over times of ~15 min were then digitized by a fast analog-to-digital converter and analyzed with the help of an IBM-1800 computer to determine

$$C(Q,t)=\frac{1}{T}\int_0^T [I(Q,t')-\bar{I}(Q)] \times [I(Q,t'+t)-\bar{I}(Q)]dt', \quad (5)$$

where

$$\bar{I}(Q)=\frac{1}{T}\int_0^T I(Q,t')dt' \quad (6)$$

and I is the photomultiplier current proportional to light intensity. This procedure is capable of high effective spectral resolution, tolerates large dc signals, and is easily set up. Thus it offers advantages over pulse correlation and heterodyne spectroscopy. We have tested for and excluded spurious experimental effects on $C(Q,t)$ due to optical geometry, bulk scattering, and laser heating.

Several illustrative results are shown in Fig. 1, where $C(Q,t)$, as traced from the graphical print out of the computer, is plotted against the time delay t. At $\Delta T \lesssim 0.5$°C, $C(Q,t)$ displays a near-perfect single exponential decay as shown by curve A (the theoretical fit is expressed by the closed circles). At slightly lower temperatures (0.7°C $< \Delta T < 1.0$°C), the second relaxation mode corresponding to S_2 in Eqs. (1) and (2) also becomes significant as shown in curve B. Here the amplitude of the second relaxation mode is about 9% of the first relaxation mode. At $T_c - T > 1.3$°C we begin to see underdamped waves, and $C(Q,t)$ displays characteristic oscillatory behavior as shown in curve C. We have measured the values of τ_1 as a function of the incident and scattering angles which determine the magnitude of the wave vector Q of the ripplons that scatter light in the direction (θ, Φ). The angular dependence of τ_1 yields the Q dependence of $\tau_1(Q,\Delta T)$.[8] The results are shown in Fig. 2. It is quite clear that $\tau_1(Q,\Delta T)$ varies inversely as Q, precisely in accord with the theoretical prediction for the overdamped interfacial waves.[10,13]

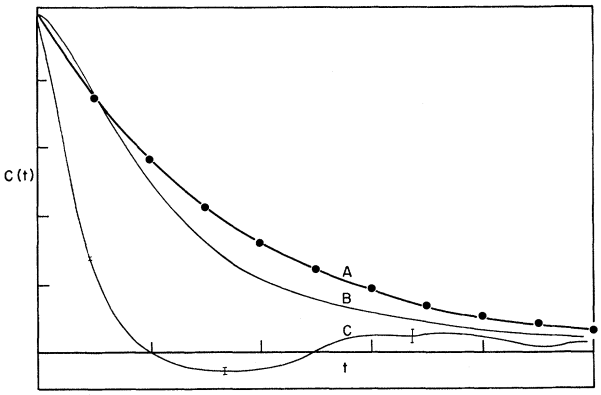

FIG. 1. Real-time correlation functions $C(t)$ are plotted against time delay t. Curve A illustrates single exponential relaxation modes at $\Delta T \sim 0.23$°C. The closed circles represent the theoretical exponential fit with a relaxation time $\frac{1}{2}\tau_1$. Curve B shows two exponential relaxation modes at $\Delta T \sim 0.75$°C; the rounded top near $t \sim 0$ is an effect of the second relaxation mode. The scale of t for curve B is $\frac{1}{10}$ of curve A. Curve C exhibits the characteristic oscillatory behavior of $C(t)$ at $\Delta T \sim 1.3$°C. The scale of t for curve C is $\frac{1}{2}$ of curve B. Bars indicate uncertainties.

The various sets of data in Fig. 2 correspond to various temperatures. Thus the temperature dependence of τ_1 can be presented by taking the values of $\tau_1(Q,\Delta T)$ at an arbitrary value of Q (220 cm^{-1}) and plotting them against ΔT, as shown on a log-log scale in Fig. 3. We find a straight-line fit such that $\tau_1 \propto (T_c - T)^{-\Omega^*}$, where $\Omega^* = 1.27 \pm 0.03$. Since Eq. (3) shows that $\eta \propto \tau\sigma$, and Warren and Webb[15] have found that $\sigma \propto \Delta T^{\mu}$, where $\mu = 1.23$

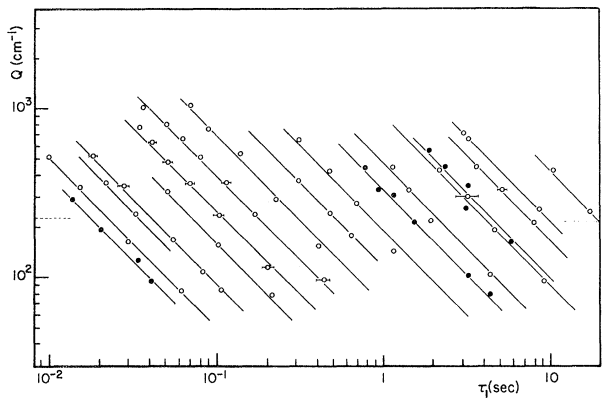

FIG. 2. The time constant τ_1 corresponding to the principal relaxation mode is plotted against wave vector Q at the various temperatures. The solid lines are drawn with slopes of -1. The dotted line indicates the value of Q selected for Fig. 3. Closed points are used to distinguish several closely spaced temperatures.

± 0.02 for the same system, we conclude that

$$\eta = \eta_0\left(1-\frac{T}{T_c}\right)^{(-\Omega^*+\mu)} = \eta_0\left(1-\frac{T}{T_c}\right)^{0.04\pm 0.05}, \qquad (7)$$

assuming an uncertainty of ± 0.0015°C in T_c. Thus the average shear viscosity of the critical binary mixture seems to exhibit an extremely weak divergence, if any. η_0 works out to be 0.034 ± 0.02 P, which is in agreement with expected values outside the critical region.

We have also measured the angular distribution of the diffuse scattered intensity and have found that $dI/d\Omega$, the diffuse intensity per unit solid angle, has the correct magnitude and is inversely proportional to Q^2 as predicted by Mandelstam's theory[7] of the thermal excitations on liquid surfaces. The theory[7,11] also predicts the temperature dependence $dI/d\Omega \propto \sigma^{-1} \propto (\Delta T)^{-\mu}$, depending on the surface tension alone in the case of total reflection. We found that $dI/d\Omega \propto \Delta T^{-1.2\pm 0.2}$, in agreement with the critical exponent $-\mu = -1.23 \pm 0.02$ measured by Warren and Webb.[15] Determination of the relative intensities at small ΔT were complicated by the turbidity of the system. At $\Delta T \sim 0.01$°C, only 3% of the incident light passes through a 5-cm-thick cell because of the strong critical scattering. However, we were able to correct for the losses due to turbidity, which we have measured and found in agreement with other published measurements.[19]

These experiments have established the existence of persistent excitations of the critical interface that are increasingly damped as $T \to T_c$ with the dominant relaxation time diverging as τ_1

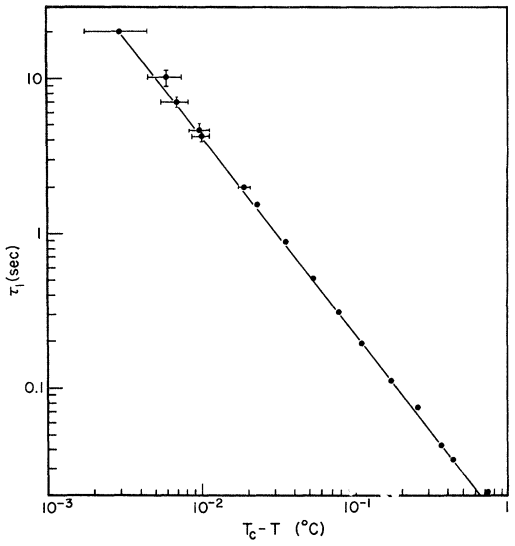

FIG. 3. The time constants τ_1 corresponding to the selected value $Q = 220$ cm^{-1} are plotted against ΔT on a log-log scale. The solid line represents the best least-squares-fit straight line with slope $-\Omega^* = 1.27 \pm 0.03$.

$= \tau_{01}(1-T/T_c)^{-\Omega^*}$, where $Q\tau_{01} = (18 \pm 0.2) \times 10^{-4}$ sec cm^{-1} and $\Omega^* = 1.27 \pm 0.03$. For $Q = 220$ cm^{-1}, $\tau_{01} = 8.20 \times 10^{-6}$ sec.

Assuming that these excitations are correctly described by macroscopic hydrodynamic theory as interfacial "waves" subject to viscous damping, the critical slowing down is due to relative weakening of the interfacial tension forces as $T \to T_c$ and not due to a critical divergence of the shear viscosity which appears to be no more than very weakly divergent. Earlier experiments much farther from T_c in a similar system had shown up to 15% increases of η.[20] The absence of a strong divergence of the shear viscosity is entirely consistent with Swift's dynamic-scaling prediction[1] but not with earlier predictions[2,3] of mean-field theories which suggest readily detectable divergences.

Our identification of the interface excitations as overdamped hydrodynamic interfacial waves seems to be established by the complete consistency of the magnitude and the Q dependence of τ_1, the appearance of the second relaxation time with the correct magnitude, and the transition to the propagating wave mode precisely as expected. That these excitations have nearly thermal equilibrium distribution is demonstrated by the absolute magnitude, the Q dependence, and the temperature dependence of $dI/d\Omega$.

Finally, we should note that the diffuse nature of the critical interface that we have previously

discovered[17] seems to play no role in these excitations, probably because the dominant interfacial inhomogeneities contributing diffuseness have characteristic lengths like the coherence length ξ which is much smaller than the wavelengths and the depth of the moving layers in the excitations involved in these experiments. It seems unlikely that the diffuse interface structure has concealed a divergence of the shear viscosity since it could only introduce an alternative, diffusive relaxation mechanism in the interface that would be expected to vanish as $T \to T_c$, revealing any divergence of η.

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Subsequent to submission of this Letter, measurements of the shear viscosity η above T_c have been reported by Arcovito, Falaci, Roberti, and Mistura, who find a weak divergence of $\Delta\eta$ above T_c in a system (cyclohexane-analine) very similar to ours. It was analyzed as a logarithmically diverging term $\Delta\eta(T)$ superimposed on a monotonic term η'. We find that these data are also consistent with a weak-power-law divergence $\eta \sim \Delta T^{-0.07 \pm 0.015}$. Furthermore, we note that the form we chose, $\eta \sim \Delta T^{-0.04}$, to present our results below T_c can be represented accurately by a logarithmic divergence of $\Delta\eta = \eta - \eta' = -A \ln(1 - T/T_c) + B$, with $A \cong 0.13$ and $B \cong -0.61$. We believe that neither set of data has distinguished between a logarithmically divergent term in η and a weak-power-law divergence.

[1]L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968); J. Swift, Phys. Rev. 173, 257 (1969).
[2]M. Fixman, J. Chem. Phys. 36, 310 (1962); K. Kawasaki, Phys. Rev. 150, 291 (1966).
[3]J. M. Deutch and R. W. Zwanzig, J. Chem. Phys. 46, 1612 (1967).
[4]W. Brouwer and R. K. Parthria, Phys. Rev. 163, 200 (1967).
[5]H. Lamb, Hydrodynamics (Dover Publications, New York, 1932), p. 363.
[6]V. G. Levich, in Physicochemical Hydrodynamics, translated by Scripta Technica, Inc. (Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1962), p. 603.
[7]L. I. Mandelstam, Ann. Physik 41, 609 (1913).
[8]R. H. Katyl and Uno Ingard, Phys. Rev. Letters 19, 64 (1967), and 20, 248 (1968).
[9]J. Meunier, D. Cruchon, and M.-A. Bouchiat, Compt. Rend. 268, 92 (1969), and 267, 32 (1968), and 266, 301, 255 (1968).
[10]M. Papoular, J. Phys. Radium 29, 81 (1968).
[11]J. Meunier, D. Cruchon, and M.-A. Bouchiat, to be published.
[12]U. Ingard, private communication.
[13]D. R. Watts (unpublished).
[14]This expression differs somewhat from the dispersion relation for capillary waves on a free surface and can be derived from Papoular's results [Ref. 10, Eq. (9)] for the appropriate case.
[15]C. Warren and W. W. Webb, to be published.
[16]G. H. Gilmer, W. Gilmore, J. Huang, and W. W. Webb, Phys. Rev. Letters 14, 491 (1965).
[17]J. S. Huang and W. W. Webb, to be published.
[18]Lord Rayleigh, Scientific Papers (Cambridge University Press, London, England, 1912), Vol. V, p. 388.
[19]B. Chu, J. Chem. Phys. 67, 1969 (1963).
[20]T. M. Reed and T. E. Taylor, J. Phys. Chem. 63, 58 (1959).
[21]G. Arcovito, C. Falaci, M. Roberti, and L. Mistura, Phys. Rev. Letters 22, 1040 (1969).

DIRECT MEASUREMENTS OF LINEAR GROWTH RATES AND NONLINEAR SATURATION COEFFICIENTS OF INSTABILITIES*

Alfred Y. Wong and Francis Hai
Department of Physics, University of California, Los Angeles, California 90024
(Received 26 May 1969)

An experimental method of perturbation about a nonlinear equilibrium state is employed to examine linear growth rates and nonlinear saturation coefficients. This procedure is illustrated by the experimental investigation of finite-amplitude unstable-collisional drift waves in a highly ionized plasma. Preliminary experimental results are compared with existing linear and nonlinear theories.

We wish to report an experimental method of measuring both the linear growth rate and the nonlinear saturation rates of an unstable mode. Recently, various authors have begun to investigate the nonlinear saturation mechanisms—such as mode-mode coupling,[1] wave-particle scatter-