

Surface Tension and Viscosity of Xenon Near Its Critical Point*

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We have measured the spectrum of light scattered inelastically from thermal excitations on the surface of liquid xenon near its critical point, deduced the temperature dependence of the surface tension σ and the effective kinematic viscosity $\bar{\nu}$, examined the Fisk-Widom relation between the surface tension and the long-range correlation length ξ , and obtained numerically the Kawasaki critical contribution to the thermal diffusivity. The surface tension and the effective kinematic viscosity along the coexistence curve may be represented by $\sigma = (62.9 \pm 1.8)(1 - T/T_c)^{1.302 \pm 0.006}$ dyn/cm and $\bar{\nu} = [448 + 12(T_c - T)] \pm 15$ microstokes.

We have measured the surface tension σ and the effective kinematic viscosity $\bar{\nu}$ of xenon along its coexistence curve in the temperature range $0.070^\circ\text{K} < T_c - T < 5^\circ\text{K}$ by using the techniques of optical mixing spectroscopy¹ to observe the spectrum of light scattered inelastically from thermal excitations on the liquid-vapor interface.²⁻⁴ We have found that over this entire temperature range the surface tension obeys the power law

$$\sigma = (62.9 \pm 1.8)(1 - T/T_c)^{1.302 \pm 0.006} \text{ dyn/cm} \quad (1)$$

and that the effective kinematic viscosity is slowly varying along the coexistence curve:

$$\bar{\nu} = [448 + 12(T_c - T)] \pm 15 \text{ microstokes.} \quad (2)$$

Using these results, we have examined the Fisk-Widom relation⁵ which predicts that the scaled interfacial thickness L' , defined by the equation

$$L' = \frac{1}{c} \frac{1}{\beta^2} \frac{\sigma(\rho^2 \kappa_T)}{(\rho_l - \rho_v)^2}, \quad (3)$$

may be identified with the Ornstein-Zernike correlation range ξ for temperatures close to T_c . Here, ρ_l and ρ_v are the densities of the liquid and vapor phases, respectively; κ_T is the isothermal compressibility; and β is the critical exponent which describes the shape of the coexistence curve. The constant c is a parameter of order unity whose value is determined by the form of the chemical potential as a function of density $\mu(\rho)$ in the two-phase region $\rho_v < \rho < \rho_l$. Finally, we have calculated numerically the critical component of the thermal diffusivity along the coexistence curve predicted by the Kadanoff-Swift⁶ and Kawasaki⁷ mode-mode coupling theories.

In our experiment, an incident beam of parallel light enters a high-pressure optical cell whose

temperature is stabilized to within 0.001°K . Temperatures are measured with a platinum resistance thermometer in accordance with the 1948 International Practical Temperature Scale. The incident beam passes upward through the liquid xenon toward the liquid-vapor interface at an angle of 56° to the surface normal. Light which scatters downward from the interface at a scattering angle θ measured from the specular reflection passes out of the cell and is collected by a converging lens. The scattering angle is selected by moving an observation pinhole in the focal plane of this lens a measured distance from the position of the specular reflection. This distance is kept constant throughout the experiment. Its value and the value of the index of refraction of the fluid uniquely determine θ and hence the wave vector \vec{K} of the surface fluctuation observed. At each temperature, the index of refraction is obtained using the formula of Garside, Molgaard, and Smith.⁸ In our experiment \vec{K} is always near 2000 cm^{-1} , and thus the fluctuation studied is always a propagating wave. To avoid variations in \vec{K} caused by coupling of laboratory vibrations to the fluid surface, the table is acoustically isolated and its level is servostabilized to 10^{-5} rad.

A photomultiplier tube is located directly behind the observation pinhole. Light falling on this phototube contains three distinct spectral components: One component, the local oscillator, consists of light scattered elastically from the exit window; the other two components correspond to light Doppler shifted by frequencies $\pm \omega_0$ from reflection off surface waves with wave vectors $\pm \vec{K}$. Optical mixing occurs on the photocathode, producing three separate features in the photocurrent spectrum $P(\omega)$. The first feature, a pair of peaks occurring at $\pm \omega_0$, results from the heterodyne beat between the local oscillator

and each Doppler-shifted light wave. The second characteristic, a pair of "self-beat" peaks located at frequencies $\pm 2\omega_0$, is produced by mixing between the two Doppler-shifted components. The final feature, a spectral line centered around $\omega = 0$, results from the "self-beating" of spectral components within each Doppler-shifted wave. Our instruments measure $P(\omega) + P(-\omega)$ for positive ω . The peaks are broadened because of viscous damping of the surface waves. As T approaches T_c for constant \vec{K} , the effects of damping increase, ω_0 decreases, and the three peaks coalesce.

Cruchon, Meunier, and Bouchiat⁹ derived an approximate theoretical expression for the photocurrent spectrum described above. This derivation predicts the heterodyne component of $P(\omega)$ to be given by

$$S(\omega) \propto \frac{1}{1 + [(\omega - \omega_0)/\Gamma]^2} + \frac{1}{1 + [(\omega + \omega_0)/\Gamma]^2} + \frac{\Gamma}{\omega_0} \left\{ \frac{(\omega_0 - \omega)/\Gamma}{1 + [(\omega_0 - \omega)/\Gamma]^2} + \frac{(\omega_0 + \omega)/\Gamma}{1 + [(\omega_0 + \omega)/\Gamma]^2} \right\}, \quad (4)$$

where Γ is the half-width of the Lorentzian describing the scattered light and ω_0 is the frequency of the surface wave of wave vector \vec{K} . The self-beat contribution to $P(\omega)$ is given by the convolution of $S(\omega)$ with itself.

In analyzing our data, Γ and ω_0 are treated as adjustable parameters chosen to give the best least-squares fit to the experimental photocurrent spectra. The amplitudes of the heterodyne and the self-beat components of $P(\omega)$ as well as the shot-noise level are also treated as adjustable parameters. By studying the error surface of the resulting five-parameter fit in the vicinity of our optimum values and by observing the effects of weighting various portions of the spectra more heavily than others, we conclude that systematic fitting errors in Γ and ω_0 are less than the experimental scatter listed in our results.

At each temperature, values of the surface tension and viscosity are deduced from the values of Γ and ω_0 by using the dispersion relation governing the propagation of surface waves on the liquid-vapor interface. In applying the dispersion relation, we assume that the kinematic viscosities in both phases are equal, i.e., $\eta_l/\rho_l = \bar{\nu} = \eta_v/\rho_v$, where η_l and η_v are the shear viscosities in the liquid and vapor phases, respectively. This assumption has been made by previous workers and is supported by experimental data for CO_2 .⁴ Moreover, the use of the single viscosity parameter $\bar{\nu}$ in the dispersion relation enables us to fit our photocurrent spectra quite accurately. If the assumption $\eta_l/\rho_l = \eta_v/\rho_v$ is not satisfied in xenon, then $\bar{\nu}$ must be considered as an average or effective kinematic viscosity used in fitting our data. The form of the dispersion relation suggests that in this case our deduced values of $\bar{\nu}$ should nearly equal the weighted average $(\eta_l + \eta_v)/(\rho_l + \rho_v)$. In fact if we calculate $(\eta_l + \eta_v)/(\rho_l + \rho_v)$ from the semiempirical formula of Lennert and Thodos¹⁰ we find that this quantity agrees

within 2% with our values of $\bar{\nu}$, even though the predicted¹⁰ values of the kinematic viscosities differ by as much as 20% in the two phases.

In fitting the early theoretical formula of Cruchon, Bouchiat, and Meunier [Eq. (4)] to our experimental photocurrent spectra, we noticed a slight but reproducible discrepancy in the tails of the peaks. Kramer¹¹ then derived an alternative formula for the photocurrent spectrum which can be fitted to our data with significantly greater accuracy. Independently, Bouchiat and Meunier¹² have recently given a rigorous theoretical derivation of the photocurrent spectrum, the results of which agree with Kramer's calculation. Figure 1 shows a typical experimental spectrum along with the best fits obtained from the approximate formula [Eq. (4)] and from the rigorous formula of Refs. 11 and 12. The rms error of the fit with the latter form is 30% smaller. The values of ω_0 deduced from the two different theoretical line shapes are nearly equal, while the half-width Γ is 4% larger in the fit with the corrected formula.

By fitting the corrected theoretical line shape of Ref. 12 to our experimental photocurrent spectra we have deduced the temperature dependence of σ shown in Fig. 2 and summarized in Eq. (1). The scatter in the data points is due primarily to fluctuations in the intensity of the local oscillator during the course of a run. Our deduced value of the effective kinematic viscosity $\bar{\nu}$ is given by Eq. (2). These results depend upon the critical temperature T_c of the sample, which was determined in two independent ways: by adjusting T_c to give the best power-law fit to our surface tension data, and by observing the disappearance of the meniscus. Both determinations separately give $T_c = 289.726 \pm 0.002^\circ\text{K}$, in good agreement with values generally reported in the literature.

Earlier measurements of the surface tension in xenon by Smith, Gardner, and Parker¹³ from

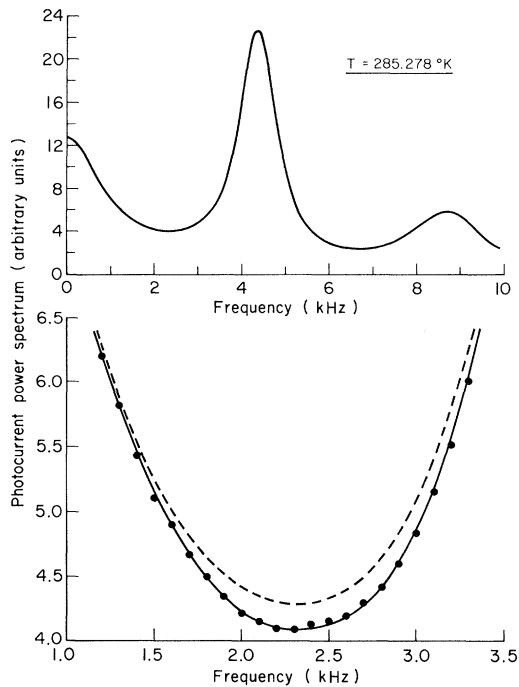


FIG. 1. Top, a typical photocurrent spectrum produced by light scattered inelastically from thermal excitations on the surface of liquid xenon. The three principal features shown are discussed in the text. Bottom, an enlargement of the spectrum near 2 kHz showing the region of discrepancy between the experimental data (closed circles) and the early formula of Cruchon, Bouchiat, and Meunier (dashed line). The solid line corresponds to the formula derived by Kramer.

189 to 286°K using the method of capillary rise appear to give surface-tension values 10–15% smaller than the present measurements. However, if we reanalyze their capillary-rise data using the more accurate density calculations of Garside, Molgaard, and Smith we find $\sigma = 61.6(1 - T/T_c)^{1.295}$ dyn/cm. This agrees very well with our measurements of σ in the region where the measurements overlap, as shown in Fig. 2. This agreement is especially satisfying because our measurements depend only weakly on the difference in density of the two phases, while the capillary-rise results are proportional to that difference.

We now examine the validity of the Fish-Widom relation which predicts that the scaled interface thickness L' defined by Eq. (3) may be identified with the Ornstein-Zernike correlation range ξ , which has been measured in xenon by observing the angular anisotropy of scattered light.^{14,15} (Since experimental values of the actual interface

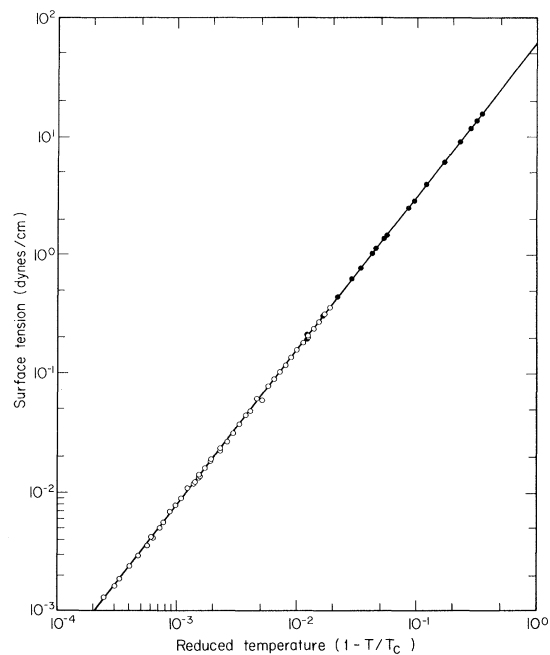


FIG. 2. Surface tension σ of xenon as a function of the reduced temperature $1 - T/T_c$. The open circles correspond to our measurements, the closed circles to the corrected data of Smith, Gardner, and Parker.

thickness L have been obtained in only one instance,¹⁶ and in that case for a binary mixture, we cannot compare our calculated values of L' with measured values of L .)

An immediate consequence of the assumption $L' = \xi$ is the Widom equality¹⁷ $\mu + \nu = \gamma' + 2\beta$, where μ , ν , and γ' are the critical exponents characterizing the temperature variation of the surface tension σ , the correlation range ξ , and the quantity $(\partial\rho/\partial\mu)_T = \rho^2\kappa_T$. This equality, which may be derived by more general arguments than those leading to Eq. (3), serves to test the temperature dependence of the theory. Using our value of $\mu = 1.302 \pm 0.006$ and the following values of the other exponents^{14,15,18}: $\nu = 0.57 \pm 0.05$, $\gamma' = 1.21 \pm 0.03$, $\beta = 0.345 \pm 0.01$, we find that $\gamma' + 2\beta - \nu - \mu = 0.03 \pm 0.06$. Therefore, the temperature dependence of L' is consistent with that of ξ within experimental error.

On the other hand, agreement between the magnitudes of L' and ξ depends upon the value of the parameter c in Eq. (3). Fisk and Widom estimate c to lie in the range 1.0 to 1.5 for several forms of the chemical potential in the interface. Using our measurements of the surface tension and the measured values $\rho^2\kappa_T = (\partial\rho/\partial\mu)_T = (3.46 \pm 0.11) \times 10^{-10}(1 - T/T_c)^{-1.21 \pm 0.03}$ g²/erg cm³,¹⁵ $\beta = 0.345$

± 0.01 ,¹⁸ and $\rho_l - \rho_v = 3.98(1 - T/T_c)^{0.345}$ g/cm³,¹⁸ we find that within experimental error L' is in numerical agreement with the measurements of ξ made by Giglio and Benedek¹⁴ and Smith¹⁵ provided that $c = 0.83 \pm 0.15$. This value of c is somewhat lower than the estimates of Fisk and Widom. However, the seriousness of the discrepancy is difficult to estimate until more is known about the form of the chemical potential in the two-phase region.

Finally, we may calculate from our data the contribution to the thermal diffusivity predicted by the Kawasaki mode-mode coupling theory in the hydrodynamic limit. This contribution is given approximately by $k_B T / 6\pi\eta\xi = 2.4 \times 10^{-4} (1 - T/T_c)^{0.57 \pm 0.05} (T/T_c) (\rho_c/\rho)$ erg sec/g, where k_B is Boltzmann's constant. In this computation, we have chosen an average value of the shear viscosity η equal to the quantity $\rho\bar{v}$ with \bar{v} evaluated at $T = T_c$. This numerical prediction of the mode-mode coupling theory makes it particularly important to measure the linewidth Γ of light scattered quasielastically from the bulk phases of xenon along the coexistence curve, since Γ measures the thermal diffusivity.¹⁹ The difference between the measured total thermal diffusivity and the Kawasaki critical contribution would then establish the relative importance of the critical and noncritical components of the thermal diffusivity along the coexistence curve.

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