Kawasaki-Einstein-Stokes Formula and Dynamical Scaling in the Critical Region of a Binary Liquid Mixture: Isobutyric Acid in Water*

S. P. Lee, W. Tscharnuter, and B. Chu
Chemistry Department, State University of New York at Stony Brook, Stony Brook, New York 11790

(Received 3 April 1972)

The Rayleigh linewidth Γ of isobutyric acid in water has been measured by means of signal correlation at the critical solution concentration between 0.003 and 30°C above the critical mixing temperature T_c over a range of scattering angles θ varying from 20° to 140°. The results are analyzed according to the mode-mode coupling theory of Kawasaki in the $K \to 0$ limit, and at $K\xi \gg 1$.

Halperin and Hohenberg[1] have proposed that for all values of $K\xi$ the decay rate Γ should be a homogeneous function of K and ξ^{-1}, where the same correlation length ξ governs the critical behaviors of both static and dynamic properties of the system,

$$\Gamma = K^Z H(K\xi), \tag{1}$$

with Z being the degree of homogeneity and $K = (4\pi/\lambda)\sin(\frac{1}{2}\theta)$. According to the mode-mode coupling theory of Kadanoff and Swift,[2] Eq. (1) becomes $\Gamma = BK^Z$ in the critical limit ($\xi K \gg 1$), where B is a temperature-independent constant and $Z = 3$; and reduces to $\Gamma = DK^2$ in the hydrodynamic limit ($\xi K \ll 1$), where D is the binary diffusion coefficient. A specific form of $H(K\xi)$ has been derived first by Kawasaki[3] and subsequently by Ferrell,[4] using the approximate Ornstein-Zernike form of the correlation function to include all values of X $[=(K\xi)^{-1}]$:

$$\Gamma = AK^3(2/\pi)[X + X^3 + (1 - X^4)\arctan(X^{-1})], \tag{2}$$

where $A = k_B T/16\eta_{hf}^*$ with η_{hf}^* being the high-frequency shear viscosity which is assumed to be independent of $K\xi$ in the theory. According to Kawasaki, the value of η_{hf}^* should lie in the interval $\eta_r^* < \eta_{hf}^* < \eta_r^* + \eta_s^* = \eta^*$. η_r^* is the value of the shear viscosity if there is no critical anomaly, while η_s^* is the singular part of the shear viscosity exhibiting the asymptotic critical behavior. Furthermore, Kawasaki has obtained a formula for the mutual diffusion coefficient of a binary mixture,

$$D = k_B T/6\pi\eta_{hf}^*\xi, \tag{3}$$

which is analogous in form to the Einstein-Stokes equation for the mass diffusion coefficient of spheres of radius r. The correlation length ξ diverges as $\xi = \xi_0\epsilon^{-\nu}$ with $\epsilon = (T - T_c)/T_c$ and ν being another critical exponent.

During the past two years there have been many comparisons between experiment and theory. Unfortunately, the first verifications by Bergé *et al.*[5] and by Henry, Swinney, and Cummins[6] were invalid. Firstly, a best fit of Eq. (2) using three adjustable parameters of A, ξ_0, and ν invariably gives a good fit but incorrect magnitudes for the three parameters, especially for ξ_0 and ν. In fact, the Kawasaki equation (2) is quite insensitive to multiparameter fits. Even fairly poor data produce impressive log-log plots of Γ/K^3 versus $K\xi$. Secondly, Eq. (2) represents the theoretical Kawasaki linewidth due to critical contribution. Scaling of the thermal conductivity of carbon dioxide near the critical point by Sengers and Keyes[7] shows the presence of an appreciable background for one-component fluid systems. Since then, deviations from Eq. (2) have been observed for binary fluid systems of perfluoromethyl cyclohexane in carbon tetrachloride[8] and 3-methylpentane in nitroethane[9] without using A, ξ_0, and ν as adjustable parameters. Thus, η_{hf}^* should not be assumed to be independent of temperature even if we neglect background contributions. The emphasis has been in comparing experimental Rayleigh linewidth data of one-component fluid systems, such as xenon[10,11] and sulfur hexachloride,[12] with the Kawasaki theory. In the $K \to 0$ limit, the thermal diffusivity χ has been separated into two parts: $\chi = \Lambda_r/\rho C_p + k_B T/6\pi\eta_{hf}^*\xi$, where Λ_r, ρ, and C_p are the regular nondivergent or background thermal conductivity, the density, and the specific heat at constant pressure, respectively. The second term is the Kawasaki critical contribution. η_{hf}^* is assumed to be constant in Eq. (3). On the other hand, the hydrodynamic shear viscosity may be expressed as[13]

$$\eta^* = (E/\alpha)(\epsilon^{-\alpha} - 1) + F\epsilon + G, \tag{4}$$

where E, F, and G are constants and α is another exponent. Thus, the separation of χ (or D) into regular and singular parts may not be straightforward since η_{hf}^* appears in the denominator.

A slightly different approach for comparing experiment with the Kawasaki theory is to utilize Eq. (3). Berge and Dubois[14] have shown the validity of Eq. (3) over large temperature ranges by taking $\eta_{hf}^* = \eta^*$. Their results were preliminary and agreements to within 10% could be considered as good. We want to determine whether (a) $Z = 3$, (b) η_{hf}^* is dependent upon temperature, (c) $\eta_{hf}^* < \eta^*$, (d) Eq. (3) is valid, (e) a background contribution, if any, exists in critical binary mixtures, and finally whether deviations between experiment and theory can be attributed to the approximate Ornstein-Zernike form of the correlation function in the Kawasaki equation (2) and to the vertex correction.[15] For these purposes we have measured the Rayleigh linewidth of concentration fluctuations of isobutyric acid in water as a function of the correlation length ξ and the momentum transfer vector $\vec{K}$ in the range $11 \geq \xi K \geq 0.0067$. Details of our experiments will be published elsewhere.

A total of 505 linewidths were measured at the critical solution concentration in the temperature interval $0.003°\text{C} \leq T - T_c \leq 30°\text{C}$ for scattering angles varying from 20° to 140°. Each linewidth was obtained from a 95- to 100-point least-squares fit of the exponential current correlation function to $\pm(0.5-1)\%$. Thus, our data represent over 50 000 measurements. In this Letter, we shall limit our discussions to results in the $K \to 0$ limit and in the critical region ($\xi K \gg 1$). Our conclusions concerning (a)–(e) are as follows:

(a) According to dynamical scaling, Γ varies as K^3 in the critical region. Figure 1 shows a typical log-log plot of Γ versus K at $\Delta T = T - T_c = 0.003°\text{C}$. For the exponent Z we find $2.976 \pm 1.5\%$ at $\Delta T = 0.003°\text{C}$ and $3.046 \pm 1.5\%$ at $\Delta T = 0.006°\text{C}$. Thus the mean value of Z from two separate independent determinations is 3.01 ± 0.03, which is in excellent agreement with $Z = 3$ as predicted by the mode-mode coupling theory. The fact that $Z = 3$ also shows that background contributions must be negligible in the critical region.

(b) If we take $Z = 3$, we find $A = (1.054 \pm 0.3\%) \times 10^{-13}$ cm³/sec at $\Delta T = 0.003°\text{C}$ and $(1.065 \pm 0.3\%) \times 10^{-13}$ cm³/sec at $\Delta T = 0.006°\text{C}$. The errors quoted are standard deviations. We further obtained $A = 1.115 \times 10^{-13}$ cm³/sec at $\Delta T = 0.025°\text{C}$. The slight variations in A are outside of our experimental error limits and show that η_{hf}^*, like the hydrodynamic shear viscosity η^*, depends upon temperature in the critical region.

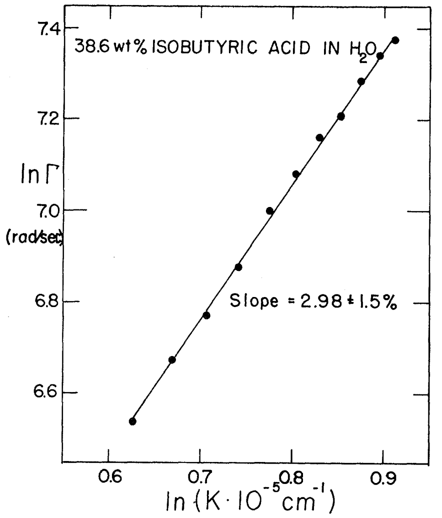

FIG. 1. Log-log plot of the decay rate Γ as a function of K at $T - T_c = 0.003°\text{C}$.

(c) A comparison of η_{hf}^* $(= k_B T/16A)$ with the hydrodynamic shear viscosity[16] shows that $\eta_{hf}^* < \eta^*$. However, this conclusion is less certain since the η^* measured by the capillary method is susceptible to error in the critical region because of gravitational effects. Furthermore, the simplest vertex correction to the decay rate of concentration fluctuations contributes to 0.4%,[15] while with the modified Ornstein-Zernike correlation function η_{hf}^* (e.g., for xenon) is increased by about 6%.[11] Thus, the experimental data showing $\eta^* \approx 1.25 \eta_{hf}^*$ are approximate in the critical region. Furthermore, with $\eta^* \approx 1.06 \eta_{hf}^*$ in the hydrodynamic region, it appears necessary to account for this change by introducing a correction term f which depends upon $K\xi$. Thus, $\eta_{hf}^* = \eta^* f(K\xi)$.

(d), (e) To test the validity of Eq. (3), we need to know η_{hf}^*, D, and ξ from independent measurements. The mutual diffusion coefficient was obtained from $D = (\lim K \to 0)\Gamma/K^2$ in the nonlocal hydrodynamic ($\xi K \leq 1$) and the hydrodynamic ($\xi K \ll 1$) regions by means of optical-mixing spectroscopy. The correlation length ξ was obtained from independent measurements of the angular distribution of scattered intensity. In the analysis of our intensity data, we have corrected for volume, attenuation, density fluctuations, stray light, and residual dust scattering. A least-squares fit of 84 selected intensity data points[17] gives $\xi_0 = (3.57 \pm 0.07) \times 10^{-8}$ cm and $\nu = 0.613 \pm 0.001$. The errors quoted again represent standard deviations. Finally, we take the viscosity data of Woermann and Sarholz[18] and those of Allegra, Stein, and Allen,[16] and assume that η_{hf}^*

TABLE I. A typical comparison of D (in 10^{-8} cm^2/sec) with $k_BT/6\pi\eta^*\xi$.

$T-T_c$	D	D_{WS} [a]	D_{ASA} [b]	D/D_{ASA}
0.250	3.21_2	3.007	3.017	1.06
0.500	5.06_4	4.767	4.810	1.05
5.010	26.3_4	24.64	24.74	1.06
10.95	52.6_8	48.24	48.58	1.08
30.00	186_4	···	(185.1) [c]	1.01

[a] WS denotes viscosity data from Woermann and Sarholz (Ref. 18).

[b] ASA denotes viscosity data from Allegra, Stein, and Allen (Ref. 16).

[c] Extrapolated value.

$=\eta^*$. Table I shows a typical comparison of the measured diffusion coefficients and those computed by means of Eq. (3) with $\eta_{hf}^*=\eta^*$. The computed D differs from the measured D by about 6% over the entire temperature range (0.75 to 30°C). This signifies that η^* and η_{hf}^* must have the same temperature dependence.

If we take $\eta_{hf}^*=k_BT/6\pi D\xi$, a least-squares fit of our data according to Eq. (4) gives $E=1.40\pm1.31$, $G=-0.894\pm2.11$, $F=-3.33\pm4.53$, and $\alpha=-0.388\pm0.152$. The corresponding values from a least-squares fit using the viscosity data of Woermann and Sarholz[18] are $E=1.33\pm0.40$, $G=-0.68\pm0.04$, $F=-3.3\pm1.4$, and $\alpha=-0.37\pm0.04$. The parameters in Eq. (4) are very sensitive to minor variations in experimental data and we should not take their magnitudes seriously. Nevertheless, we show evidence that $-1<\alpha<0$, signifying the presence of a cusp in the critical viscosity anomaly. This viscosity anomaly must be a weak one, and the exact mathematical character is not known since present-day data are not sufficiently precise to make the very fine but definitive distinctions among a logarithmic divergence, a very weak power-law divergence, and a cusp. We do feel that the possibility of a cusp is very high in view of such good agreement with the modified mode-mode coupling theory of Kawasaki.

Recently, Kawasaki and Lo[19] obtained a relation $f(K\xi)$ between the so-called high-frequency viscosity η_{hf}^* and the hydrodynamic shear viscosity η^*. Their results show that for $K\xi\ll1$, $f(K\xi)\simeq0.948$, which agrees to within 1% with our measured $\eta_{hf}^*/\eta^*\simeq0.944$. In the critical region for $7.74<K\xi<10.3$, as shown in Fig. 1, $f(K\xi)$ varies from 0.833 to 0.813, which agrees to within a few percent with our measured $\bar{\eta}_{hf}^*$(averaged over $7.74<K\xi<10.3)/\eta^*\simeq0.80$. There η^* was computed from Eq. (4) using the viscosity data of Allegra, Stein, and Allen.[16] If we take their measured viscosity, then $\bar{\eta}_{hf}^*/\eta^*\simeq0.84$. The agreement between theory and experiment in the hydrodynamic as well as the critical region is indeed amazing. By neglecting the weak vertex corrections, it appears that we need not even invoke a breakdown of the approximate Ornstein-Zernike correlation function. It should be noted that, with $D=k_BT/6\pi\eta^*\xi f(K\xi)$, where $f(K\xi)$ corrects for the nonlocal shear viscosity, we have obtained agreement to within the error limits of our experiments for $K\xi\ll1$ and $\gg1$ from independent measurements of D, ξ, and η^*.

We thank Professor G. F. Allen for making his viscosity data available prior to publication.

---

*Work supported by the National Science Foundation.

[1] B. I. Halperin and P. C. Hohenberg, Phys. Rev. 177, 952 (1969).

[2] L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968); J. Swift, Phys. Rev. 173, 257 (1968).

[3] K. Kawasaki, Phys. Lett. 30A, 325 (1969), and Ann. Phys. (New York) 61, 1 (1970), and Phys. Rev. A 1, 1750 (1970), and in Dynamical Theory of Fluctuations near Critical Points, Proceedings of the International School of Physics "Enrico Fermi," Course LI, Varenna, Italy, 1970 (Academic, New York, to be published).

[4] R. A. Ferrell, Phys. Rev. Lett. 24, 1169 (1970).

[5] P. Berge, P. Calmettes, C. Laj, M. Tournarie, and B. Volochine, Phys. Rev. Lett. 24, 1223 (1970).

[6] D. L. Henry, H. L. Swinney, and H. Z. Cummins, Phys. Rev. Lett. 25, 1170 (1970).

[7] J. V. Sengers and P. H. Keyes, Phys. Rev. Lett. 26, 70 (1971).

[8] B. Chu, D. Thiel, W. Tscharnuter, and D. V. Fenby, in Proceedings of the International Conference on Light Scattering in Liquids, Paris, France, July 1971 (unpublished), and to be published.

[9] R. F. Chang, P. H. Keyes, J. V. Sengers, and C. O. Alley, Phys. Rev. Lett. 27, 1706 (1971).

[10] I. W. Smith, M. Giglio, and G. B. Benedek, Phys. Rev. Lett. 27, 1556 (1971).

[11] H. L. Swinney, D. L. Henry, and H. Z. Cummins, to be published.

[12] T. K. Lim, H. L. Swinney, K. H. Langley, and T. A. Kachnowski, Phys. Rev. Lett. 27, 1776 (1971); G. T. Feke, G. A. Hawkins, J. B. Lastovka, and G. B. Benedek, Phys. Rev. Lett. 27, 1780 (1971).

[13] M. E. Fisher, Rep. Progr. Phys. 30, 615 (1967).

[14] P. Berge and M. Dubois, Phys. Rev. Lett. 27, 1125 (1971).

[15] S. M. Lo and K. Kawasaki, Phys. Rev. A 5, 421 (1972).

[16] J. C. Allegra, A. Stein, and G. F. Allen, to be pub-

lished.

[17] B. Chu, F. J. Schoenes, and W. P. Kao, J. Amer. Chem. Soc. 90, 3042 (1968).

[18] D. Woermann and W. Sarholz, Ber. Bunsenges. Phys. Chem. 69, 319 (1965).

[19] K. Kawasaki and S. M. Lo, "Nonlocal Shear Viscosity and Order Parameter Dynamics near the Critical Point of Fluid" (to be published).

Superfluid Helium in Restricted Geometries*

Timothy C. Padmore
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 29 February 1972)

Superfluid flow in restricted geometries is discussed in the framework of the Landau quasiparticle theory. A recently observed linear temperature dependence of ρ_n for helium flowing in powders is explained in terms of a model geometry which can be fairly described as "zero-dimensional." Further experiments are suggested for exploring other features of restricted geometries and testing the zero-dimensional model.

Measurements of superfluid helium flow in compressed powders and Vycor glass were reported recently by Pobell *et al.*[1] They found that the normal fluid density ρ_n was much enhanced over its bulk value. In addition, a striking linear dependence of ρ_n on temperature was observed for $T \lesssim 0.5$ K. The fact that the experiments were performed in the temperature range $0.1\text{ K} \lesssim T \lesssim 1$ K allows one to take advantage of the Landau quasiparticle picture[2] to discuss the experiments theoretically. In this paper are advanced some very simple arguments, based on the quasiparticle picture, which allow us to understand this result. In addition, specific predictions are given for ρ_n and the specific heat in various (experimentally realizable) geometries.

Consider first two simple examples of restricted dimensionality: flow between parallel plates, and flow in a straight tube of rectangular cross section. These geometries and the coordinate system for the problem are illustrated in Figs. 1(a) and 1(b). (Ignore, for the time being, the dashed lines and the dimension d_0.)

The pore sizes in the experiments are generally ~20–100 Å. We will therefore assume that the dimensions (d_2, d_1) in the examples are much greater than either the superfluid healing length (~1 Å), the range of the wall potential (~2–3 Å), or the roton wavelength (~4 Å). Consequently, we do not expect any important contributions to the thermodynamics from the surfaces *per se* (for example, via localized surface states), and we can apply the Landau treatment[2] to calculate ρ_n. We also expect that for $T \lesssim 0.5$ K the roton contributions can, as usual, be ignored and will therefore consider only phonon states assuming the usual dispersion relation $\epsilon_0(k) = \hbar c k$, where c is the sound velocity and k the phonon wave number.

Suppose that the background fluid has a velocity $\vec{v}_s = v_s \hat{z}$. Then the momentum density is

$$\vec{J} = \rho \vec{v}_s + V^{-1} \sum_{\vec{k}} \hbar \vec{k} n_{\vec{k}}, \tag{1}$$

where in the second term (which gives the momentum of the excitations) $n_{\vec{k}}$ denotes the number of states with wave number $\vec{k}$ and V is the volume. It is elementary to show that $n_{\vec{k}} = n(\epsilon(\vec{k}))$, where $n(\epsilon) = [\exp(\epsilon/k_B T) - 1]^{-1}$ and $\epsilon(\vec{k})$, the spectrum in the frame of the walls, equals $\epsilon_0(\vec{k}) + \hbar\vec{k}\cdot\vec{v}_s$. Provided $v_s \ll c$, Eq. (1) can be linearized to give

$$\begin{aligned}\vec{J} &\approx \rho\vec{v}_s + \hbar^2 V^{-1} \sum_{\vec{k}} (\vec{v}_s \cdot \vec{k})\vec{k}\, dn(\epsilon_0)/d\epsilon \\ &\equiv (\rho - \rho_n)\vec{v}_s,\end{aligned} \tag{2}$$

which defines

$$\rho_n = -\hbar^2 V^{-1} \sum_{\vec{k}} k_z^2\, dn(\epsilon_0)/d\epsilon. \tag{3}$$

In the bulk system the $\vec{k}$ sum is $V(2\pi)^{-3}\int d^3k$. For the flow between the plates it becomes $A(2\pi)^{-2} \times \sum_{k_x} \int dk_y dk_z$, where A is the area of the plates.

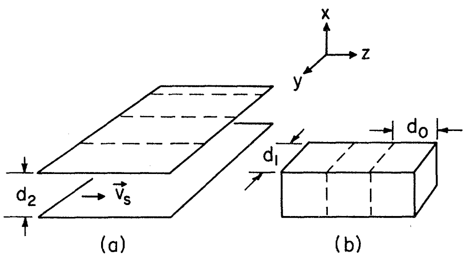

FIG. 1. Geometries for 2D and 1D superfluid flow. Dashed lines, positions of the repulsive potentials in the Kronig-Penney construction.