

Mutual diffusion in ^3He - ^4He solutions near the critical vaporization line

R. I. Efremova and É. V. Matizen

Institute of Inorganic Chemistry, Siberian Branch, Academy of Sciences of the USSR

(Submitted 19 November 1984; resubmitted 18 March 1985)

Pis'ma Zh. Eksp. Teor. Fiz. **41**, No. 10, 416–418 (25 May 1985)

It is shown experimentally that the regular component of the mobility is larger than the singular component in the range of solutions studied. As a result, the thermodiffusion ratio and the thermal conductivity exhibit a special behavior with indices $\varphi = 1.2$ and $\psi = 0.63$, respectively.

The properties of solutions of helium isotopes near the critical point for vaporization have been the subject of active research in recent years. The equation of state of this system was studied in Refs. 1 and 2; the thermodiffusion ratio and the thermal conductivities were measured in Refs. 3 and 4; and optical scattering was measured in Ref. 5. Cohen *et al.*^{3,4} interpret their results as contradicting the theory of critical phenomena as it currently stands. According to the fluctuation theory,^{6,7} the thermodiffusion ratio should diverge as $\tau^{-0.63}$, while a divergence $\tau^{-1.2}$ was found in the experiments of Ref. 4. For the thermal conductivity the theory predicts a finite value at the critical point, while Cohen *et al.*⁴ found a divergence $\tau^{-0.63}$, $\tau = (T - T_c)/T_c$, where T_c is the critical temperature. Measurements of the width of the Rayleigh line, which is related to the mutual diffusion coefficient and the thermal diffusivity, by Miura *et al.*,⁵ did not resolve this contradiction. In an attempt to resolve it, we have now measured the mutual diffusion coefficients during the relaxation of macroscopic concentration gradients. The results explain the discrepancy between the experiments of Refs. 3 and 4 and the theory.

In the present experiments the diffusion coefficients D are measured in ^3He - ^4He solutions along near-critical isochores near the critical line as functions of the tempera-

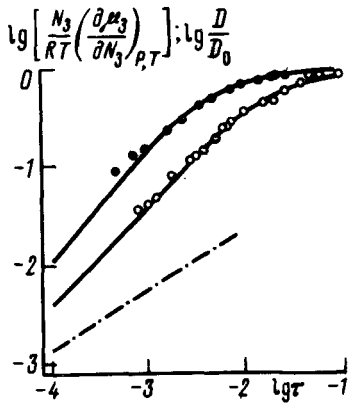


FIG. 1. 2— $N_3 = 0.046$; 4— $N_c = 0.205$.

ture and the concentration ($10^{-3} < \tau < 10^{-1}$; the concentrations are $N \equiv N_3 = 0.007, 0.046, 0.108,$ and 0.205 mole fraction of ^3He) by a method similar to that described in Ref. 8. This method involves measuring the time dependence of the dielectric constant in the lower part of an isothermal column of the solution of interest. A small concentration drop is initially arranged along the height of this column. The error in the determination of the diffusion coefficient, including the assignment error, is 5–10%.

The results of the measurements for the solutions with $N_3 = 0.046$ and 0.205 are shown in Fig. 1 (the results found for the two other solutions are similar). Here D_0 is the diffusion coefficient far from the critical point, given by $D_0 = \alpha_r RT [N_3(1 - N_3)n]^{-1}$, where α_r is the regular component of the kinetic coefficient $\alpha = Dn(1 - N_3)(\partial N_3/\partial \mu_3)_{P,T}$, which is directly related to the particle mobility $b = \alpha/N_3(1 - N_3)n$; μ_3 is the chemical potential per mole of the component with concentration N_3 ; n is the number density of particles; and R is the universal gas constant. The solid lines shown in the same figure are curves of $(N_3/RT)(\partial \mu_3/\partial N_3)_{P,T}$ as a function of τ calculated from the equation of state.¹ It follows from the agreement of the calculated curves and the experimental data that we have $\alpha = \alpha_r = \text{const}$; i.e., the singular part of this coefficient is still negligibly small in the temperature range studied. This conclusion agrees with the theory of Refs. 6 and 7, according to which the condition $\alpha_s \gg \alpha_r$ holds, according to our estimates, at temperatures below $\tau = 10^{-5}$; see Fig. 1, where the dot-dashed line is the temperature dependence of D_s/D_0 , where $D_s = k_B T/6\pi\eta r_c$, $r_c = r_0\tau^{-\nu}$ is the correlation radius, k_B is the Boltzmann constant, and η is the shear viscosity.

Let us examine some possible consequences of this conclusion. From Ref. 9 we have

$$K_T = T \left[\frac{\beta}{\alpha} \left(\frac{\partial N}{\partial \mu} \right)_{P,T} - \left(\frac{\partial N}{\partial T} \right)_{P,\mu} \right], \quad (1)$$

$$\lambda = \gamma - \frac{\beta^2}{\alpha} T, \quad (2)$$

where K_T is the thermodiffusion ratio, λ is the thermal conductivity, and β and γ , like the coefficient α introduced above, are Onsager coefficients determined by the relations between the flux densities and the thermodynamic forces. Near the critical point of binary solutions, according to the scaling theory,^{6,7} we would have

$$\alpha = \alpha_r + \alpha_s = \frac{k_B T n}{6\pi\eta r_c} \left(\frac{\partial N}{\partial \mu} \right)_{P,T} + \alpha_r, \quad (3)$$

$$\beta = \beta_r + \beta_s^- = - \left(\frac{\partial \mu}{\partial T} \right)_{N,P} \alpha_s + \beta_r, \quad (4)$$

$$\gamma = \gamma_r + \gamma_s = T \left(\frac{\partial \mu}{\partial N} \right)_{P,T} \left(\frac{\partial S^*}{\partial T} \right)_{\mu,P} \alpha_s + \gamma_r. \quad (5)$$

Here $\mu = \mu_3 - \mu_4$, and S^* is the entropy. Substituting (3)–(5) into (1) and (2), we find the following expressions for the increasing components of K_T and λ :

$$K'_T = \frac{(1 - N_3)N_3}{(\alpha_s + \alpha_r)R} \left[\frac{RT}{N_3} \left(\frac{\partial N_3}{\partial \mu_3} \right)_{P,T} \right]_s \left[\beta_r + \left(\frac{\partial \mu}{\partial T} \right)_{N,P} \alpha_r \right], \quad (6)$$

$$\lambda' = \frac{\alpha_s}{\alpha_s + \alpha_r} \left[T \left(\frac{\partial \mu}{\partial T} \right)_{N,P}^2 \alpha_r + 2T \left(\frac{\partial \mu}{\partial T} \right)_{N,P} \beta_r + \gamma_r \right]. \quad (7)$$

In the (square) brackets in (7) we have ignored terms which decrease toward the critical point. From (6) and (7) we see that the temperature dependences of these coefficients are determined by the singular terms $\{(\partial N_3/\partial \mu_3)_{P,T}\}_s \sim \tau^{-\varphi}$ ($\varphi \cong 1.2$) and $\alpha_s \sim \tau^{-\psi}$ ($\psi = 0.63$). We compared (6) and (7) with the experimental data of Ref. 4 for $N_3 = 0.80$ in the following manner: From the equation of state¹ we determined the values of $A(N_3) = [(RT/N_3)(\partial N_3/\partial \mu_3)_{P,T}]_s \tau^\varphi$ and $(\partial \mu/\partial T)_{N,P}$: 0.014 and -1.48×10^9 erg/(K · mole), respectively. Here $\alpha_r = 4.4 \times 10^{-16}$ mole²/(erg · cm · s), $\beta_r = -1.14 \times 10^{-7}$ mole/(K · s · cm), $\gamma_r = 2 \times 10^3$ erg/(cm · s · K), $\eta = 14 \times 10^{-6}$ g/(cm · s), and $r_c = 4.8 \times 10^{-8} \tau^{-0.59}$ cm. The first of these values was found from our calculations; the second and third are adjustable parameters; and the fourth and fifth were found from Ref. 10. Figures 2 and 3 show the results of this comparison. The solid lines correspond to (6) and (7) with $\alpha_s = 0$ in the denominator, while the dashed

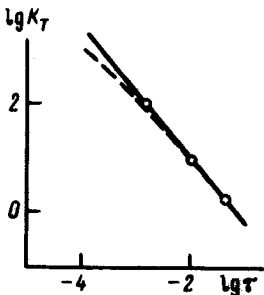


FIG. 2.

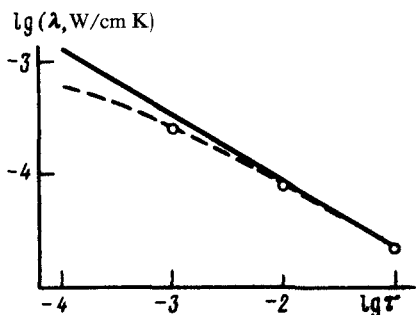


FIG. 3.

lines correspond to (1) and (2) after the regular terms have been subtracted; the points are experimental data from Ref. 4. Our data of Ref. 4 agree within the experimental errors and the errors of these calculations. It follows that our interpretation of the behavior of the kinetic coefficients is confirmed experimentally. The limiting behavior, on the other hand, of the kinetic coefficients, which follows from the fluctuation theory, should be observed at $\tau < 10^{-5}$, i.e., in the region with $\alpha_s \gg \alpha_r$. This behavior can, incidentally, be seen in Figs. 2 and 3, where the dashed lines show a tendency toward the limiting behavior at the critical point.

¹S. S. Leung and R. B. Griffiths, Phys. Rev. A **8**, 2670 (1973).

²B. Wallace, Jr., and H. Meyer, Phys. Rev. A **5**, 953 (1972).

³L. H. Cohen, M. L. Dingus, and H. Meyer, J. Low Temp. Phys. **49**, 545 (1982).

⁴L. H. Cohen, M. L. Dingus, and H. Meyer, Phys. Rev. Lett. **50**, 1058 (1983).

⁵J. Miura, H. Meyer, and A. Ikushima, J. Low Temp. Phys. **55**, 247 (1984).

⁶L. Mistura, Nuovo Cimento **B12**, 35 (1972).

⁷M. A. Anisimov, A. V. Voronel', and E. E. Gorodetskiĭ, Zh. Eksp. Teor. Fiz. **60**, 1117 (1971) [Sov. Phys. JETP **33**, 605 (1971)].

⁸G. Ahlers and F. Pobell, Phys. Rev. Lett. **32**, 144 (1974).

⁹L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred, §58, Nauka, Moscow (1953) (Fluid Mechanics, Addison-Wesley, Reading, Mass., 1959).

¹⁰K. Ohbayashi and A. Ikushima, J. Low Temp. Phys. **19**, 449 (1975).

Translated by Dave Parsons