Experiments on mutual diffusion and the behavior of the width of the Rayleigh line near the critical vaporization line in ³He–⁴He solutions

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Results are given of the first direct experimental investigations of the coefficient D of mutual diffusion for four solutions of the helium isotopes near the critical vaporization line. The results obtained agree well with experimental results obtained by measuring the Rayleigh line width, which have been given in the literature. However, there are considerable differences in the interpretation of the various results. It is shown that the features of the behavior of the coefficient of mutual diffusion and of the Rayleigh line width are related to features in the derivative of the chemical potential with respect to concentration, for a regular behavior of the macroscopic mobility, and this must be taken into account in interpreting experiments on the Rayleigh line width.

Mixtures of the helium isotopes have recently come to act as a model system for studying the behavior of the kinetic properties of binary solutions near the critical vaporization line. This is connected with the fact that a rich array of experimental material has been collected up to now on many equilibrium and kinetic properties of the helium isotopes and their mixtures, which makes comparison with existing theories appreciably simpler. One can become acquainted with the detailed literature devoted to this problem from, for example, Miura et al.[1] We will discuss work which has appeared recently. Cohen et al.[2,3] studied the behavior of the thermal diffusion ratio K_T and conductivity λ, and the scattering of light by critical fluctuations in ³He–⁴He solutions was studied by Miura et al.[1] These authors, who interpreted their results in the light of the theory of interacting modes,[4,5] noted that the behavior of K_T and λ did not agree with the theory,[4,5] while the behavior of the autocorrelation function in the light scattering spectrum is understandably consistent with the conclusions from this theory. It seems to us that our direct measurement of the mutual diffusion coefficient in ³He–⁴He solutions can bring some understanding into this problem. We calculated the coefficient of mutual diffusion D from the relaxation time of a macroscopic concentration gradient. Such measurements of the diffusion coefficient are preferable to those according to the width of the Rayleigh line, which is determined not only by the mutual diffusion coefficient but also by some equilibrium properties and by the thermal diffusivity. In addition, the mutual diffusion coefficient is associated with only one Onsager coefficient, while the thermal diffusion coefficient and the thermal conductivity in a solution are determined by a greater number of Onsager coefficients. Reliable results on the coefficient of mutual diffusion should thus simplify the interpretation of existing experimental results on the kinetic properties of solutions of the helium isotopes and render them more unambiguous. It can be added to this that earlier work, in which one of the present authors took part, in studying diffusion near the vaporization point of weak CO_2–Ne and CO_2–Ar solutions[6,7] showed that the Onsager coefficient characterizing the macroscopic mobility in the temperature region $10^{-4} < \tau < 10^{-1}$, where $\tau = (T - T_K)/T_K$ (T_K is the critical temperature), does not reveal any singularity and coincides with the mobility of the particles. A similar result was obtained in the present work on studying the temperature dependence of the coefficient of mutual diffusion in weak ³He–⁴He solutions.

In our previous work,[1] using the results on the coefficients of mutual diffusion, given here in complete detail, we calculated the temperature dependences of the thermal diffusion ratio K_T and of the thermal conductivity λ and obtained $K_T \propto \tau^{-\varphi}$ ($\varphi = 1,2$) while $\lambda \propto \tau^{-\psi}$ ($\psi = 0.6$). These values of the critical indices φ and ψ agree with those found in the experimental work.[3] We thus showed that the experimentally observed departure of the kinetic coefficients K_T and λ from the asymptotic dynamic scaling laws is connected with the fact that the regular part of the mobility is appreciably greater than its singular part in the temperature range studied.

Measurements of the diffusion coefficient were carried out by a method similar to that described by Ahlers and Pobell.[9] The method consists of measurement of the change in the concentration of a solution in the process of diffusion at constant temperature, with the concentration determined from the dielectric susceptibility using a plane capacitor, placed in the lower part of a vertical column of the solution studied, contained in a copper cell. The initial drop in concentration was produced by converting the system from a two-phase to a single-phase state on rapid heating up to the temperature of the experiment. The upper capacitor plate consisted of a copper block 2 mm high, perforated with 0.5 mm diameter holes, so that the effective dimension l_T, over which the temperature equilibrates is appreciably less than the dimensional l_N, over which the concentration equilibrates, and the time $t_T \ll t_N$. Near the critical vaporization point, because of the strong concentration dependence of the density and of the dielectric susceptibility associated with it, it is essential to carry out the experiments with a small concentration drop, so that the linear Fick diffusion equation can be applied to describe the diffusion process, from which it is easy to determine the coefficient of mutual diffusion
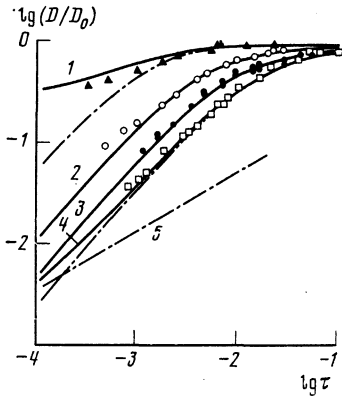
FIG. 1. The coefficient of mutual diffusion in helium isotope solutions as a function of the reduced temperature and the concentration. The points are the experimental values and the solid curves are the results calculated from Eq. (2): 1) for $N_3 = 0.007$, $(n - n_k)/n_k = 0.05$; 2) $N_3 = 0.046$, $n = n_k$; 3) $N_3 = 0.108$, $(n - n_k)/n_k = 0.02$; 4) $N_3 = 0.205$, $n = n_k$ (n is the molar density). The continuation of curves 1 and 4 by the dashed-dot curves represents the calculated behavior of the mutual diffusion coefficients when $n = n_k$; 5) are the results of a calculation according to Eq. (3).

$$\partial N_3/\partial t = D(\partial^2 N_3/\partial x^2), \tag{1}$$

where t is the time, x is the coordinate and N_3 is the concentration expressed in mole fractions of ^{3}He. In our experiments the concentration drops at the end of the diffusion process decreased and the time dependence of the concentration acquired an exponential form with a single relaxation time. The mutual diffusion coefficient D was determined from this time with an uncertainty of 5–10%.

The experimental results on the coefficient of mutual diffusion as a function of reduced temperature are shown in Fig. 1 by the points. The ordinate axis shows on a logarithmic scale the value of D/D_0, where $D_0 = bRT$ is the coefficient of mutual diffusion, measured far from the critical points, where the solution can be considered ideal, b is the mobility associated with the corresponding Onsager coefficient, and R is the gas constant. Four solutions were studied with concentrations $N_3 = 0.007; 0.046; 0.108; 0.205$. The solutions with $N_3 = 0.046$ and 0.108 had the critical density, while the solution with $N_3 = 0.007$ and 0.205 had a density differing from the critical value by 5% and 2% respectively. The smooth curves in Fig. 1 are calculated values of D/D_0. The calculation was carried out according to the equation of nonequilibrium thermodynamics[10]

$$\frac{D}{D_0} = \frac{N_3}{RT}\left(\frac{\partial\mu_3}{\partial N_3}\right)_{P,T}, \tag{2}$$

where μ_3 is the chemical potential of ^{3}He in the solution, per mole. The dot-dash curves here are calculated from Eq. (2) for solutions with $N_3 = 0.007$ and 0.205 for the critical density. The dot-dash straight line 5 represents a calculation of the asymptotic temperature dependence of the value of D/D_0 according to the equation

$$D/D_0 = k_B T/6\pi\eta^*r_c D_0, \tag{3}$$

which follows from the scaling theory of critical phenomena.[4,5] Here k_B is Boltzmann's constant, η^* is the high-frequency viscosity, $r_c = r_0\tau^{-\nu}$ is the correlation radius and ν

is its critical index. The calculation was carried out for the following values of the parameters: $T = 4$ K; $\eta^* = 14\times10^{-6}$ g·cm^{-1}·sec^{-1}[11]; $r_c = 4.8\times10^{-8}\tau^{-0.59}$ cm[11]; $D_0 = 5.6\times10^{-5}$ cm^2·sec^{-1} (the result obtained in our experiments). Although the data taken from Ohbayashi and Ikushima[11] refer to pure ^{3}He, the correctness of such a calculation follows from the fact that since the singular parts of the thermal diffusivity coefficients D_T practically coincide for pure ^{3}He and ^{4}He, then the singular part of the coefficient of mutual diffusion D for solutions should, according to Mistura,[5] be close to the singular part of D_T for the pure components.

It follows from the agreement, within the experimental and calculated uncertainties, between our results and the curves calculated according to Eq. (2) that, for the regular mobility, the features of the behavior of the coefficient of mutual diffusion in the temperature range studied ($10^{-4} < \tau < 10^{-1}$) are determined by the derivative of the chemical potential with respect to the concentration. We note that the analytical form of the temperature dependence of D/D_0, obtained from the equation of state,[12] is of a rather complicated form. However, this relation can be represented in a simpler form. We separate the derivative of the chemical potential with respect to the concentration into two terms, corresponding to the regular and singular parts. Then we obtain for solutions with the critical density

$$\frac{D}{D_0} = 1\Big/\left[\frac{RT}{N_3}\left(\frac{\partial N_3}{\partial\mu_3}\right)'_{P,T} + \frac{RT}{N_3}\left(\frac{\partial N_3}{\partial\mu_3}\right)''_{P,T}\right], \tag{4}$$

where the regular and singular parts of the derivative are denoted by single and double dashes respectively. We can establish from the equation of state[12] that

$$(RT/N_3)(\partial N_3/\partial\mu_3)'_{P,T} \cong 1,$$

$$(RT/N_3)(\partial N_3/\partial\mu_3)''_{P,T} = a(N_3N_4)^\varepsilon\tau^{-\tau},$$

where a is a coefficient independent of concentration and temperature. We then have $\gamma = 1.2$, $\varepsilon = 1.1$ and $a = 5.37\times10^{-2}$. It follows from Eq. (4) that as the critical isochore approaches the critical point of the solution, when the regular term is small compared with the singular term and can be neglected

$$D/D_0 \cong \tau^\tau/a(N_3N_4)^\varepsilon. \tag{5}$$

Far from the critical point the singular term can be neglected and

$$D/D_0 \to 1. \tag{6}$$

It should be noted here that Eqs. (5) and (6) are better satisfied, the smaller the concentration of one of the components. Such a limiting behavior is seen in Fig. 1. It also follows from Fig. 1 that the dependence in Eq. (3), obtained from scaling theory, should evidently be observed for the concentration range studied at temperatures closer to T_K (for $\tau < 10^{-4}$). Finally, the dependence of the coefficient of mutual diffusion on the composition is quite evident from Fig. 1. The results obtained here for ^{3}He–^{4}He solutions, as has already been mentioned, agree with the results of work on measuring the mutual diffusion coefficients in CO_2–Ne

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and CO_2–Ar solutions.[6,7] On the other hand, however, they contradict the conclusions about the behavior of the coefficient in ^{3}He–^{4}He solutions, drawn by analyzing results obtained by determining the intensity autocorrelation function (the Rayleigh line width) in the light scattering spectrum.[1] Miura et al.[1] maintain that the temperature dependence of the coefficient of mutual diffusion for all the solutions they studied ($N_3 = 0.95, 0.79$ and 0.63) is almost independent of the composition, and practically coincides with the temperature dependence of the thermal diffusivity D_T for pure ^{3}He. We note that, as will be seen from the further analysis, our experimental results of determining the coefficient of mutual diffusion confirm the experimental results on the Rayleigh line width taken from Table I of Miura et al.[1] The problem lies in disagreements in the interpretation of the results obtained.

The normalized autocorrelation function of the light scattering intensity near the vaporization critical point of the binary solutions measured by Miura et al.[1] can be written in the form[13]

$$g^{(2)}(t) = 1 + [g^{(1)}(t)]^2. \tag{7}$$

According to Cohen et al.,[14] the first order correlation function for binary solutions is

$$g^{(1)}(t) = \frac{1}{S_1\pi/\Gamma_+ + S_2\pi/\Gamma_-}$$

$$\times \left[\frac{S_1\pi}{\Gamma_+} \exp(-\Gamma_+ t) + \frac{S_2\pi}{\Gamma_-} \exp(-\Gamma_- t) \right], \tag{8}$$

where S_1 and S_2 are functions of the equilibrium thermodynamic functions and the kinetic transport coefficient, $\Gamma_\pm$ has the meaning of an inverse relaxation time of critical fluctuations and is related to the Rayleigh line width:

$$\Gamma_\pm = \tfrac{1}{2}k^2(D_T + D(1+A) \pm \{[D_T + D(1+A)]^2 - 4D_T D\}^{1/2}), \tag{9}$$

where k is the change in wave vector on scattering.

$$A = (K_T^2/TC_{P,c})(\partial\mu/\partial c)_{P,T},$$

K_T is the thermal diffusion ratio, $C_{P,c}$ is the heat capacity at constant pressure and mole fraction c, $\mu = \mu_3/m_3 - \mu_4/m_4$, $m_{3,4}$ are the molecular weights of the helium isotopes, $D_T = \lambda/\rho C_{P,c}$ is the thermal diffusivity, λ is the thermal conductivity, ρ is the mass density, and D is the mutual diffusion coefficient. Now, if the values of D_T, D and A are known, the values of Γ_+ and Γ_- can be evaluated and compared with the experimental results given in Table I of Miura et al.[1] for a solution with $N_3 = 0.79$. We have carried out such a calculation. The values of K_T and λ were taken from experimental work.[3] The values of the specific heat $[C_{P,c} - C_{v,c}]$ were obtained from the equation of state,[12] the experimental values of $C_{v,c}$ were taken from Brown and Meyer.[15] The value of $(\partial\mu/\partial c)_{P,T}$ was estimated from the equation of state.[12]

Our calculated temperature dependences of Γ_- and Γ_+ are shown in Fig. 2 (solid curves). It can be seen that $\Gamma_+ \gg \Gamma_-$ for $\tau < 10^{-2}$. A calculation of the values of S_1 and S_2 showed that in the same temperature interval they differ
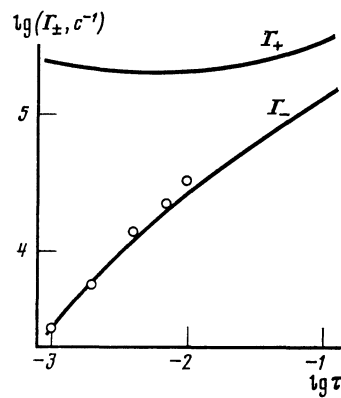

FIG. 2. The width of the Lorentz component of the Rayleigh lines as a function of the reduced temperature for a solution with $N_3 = 0.79$. For $\tau < 10^{-2}$, the width $\Gamma_+ \gg \Gamma_-$. This leads to only one component (Γ_-) being observed in the light scattering intensity autocorrelation function. The solid curve are the results of a calculation according to Eq. (9), the points are experimental values.[1]

little from one another. The second term in square brackets in Eq. (8) is thus much more important than the first, and this should be reflected experimentally in the existence of a single relaxation time for critical fluctuations. This conclusion agrees with the results of Miura et al.[1] We also show here their experimental values for the magnitudes of Γ_- taken from Table I there (the points). It can be seen from the figure that the calculated Γ_- curve, obtained by taking account of our measurements of the coefficients of mutual diffusion, and the experimental results[1] agree well with one another. Nevertheless, the conclusion that the coefficients of mutual diffusion of helium isotope[1] solutions are composition-independent is contradicted by our measurements, shown in Fig. 1. What is the cause of this disagreement?

Miura et al.[1] found that the Rayleigh line width is independent of composition, within the limits of experimental uncertainty, over the whole temperature range studied, $10^{-3} < \tau < 10^{-2}$. This fact evidently provided the basis for maintaining that the diffusion coefficient is also independent of composition. In fact, when we carried out a calculation of the Rayleigh line width for all the solutions studied by Miura et al.[1] (taking account of the composition dependence of the diffusion constant which we obtained) we did indeed find it hard to distinguish these solutions according to the Rayleigh line width. The point is that, as can be seen from Eq. (9), the Rayleigh line width depends not only on D, but also on D_T and A. It is the competition between these quantities in Eq. (9) which leads to the fact that the Rayleigh line width for the solutions studied[1] are the same within the limits of experimental uncertainty.

The temperature dependences of the coefficients of mutual diffusion obtained taking our measurements into account and those calculated by Miura et al.[1] are shown in Fig. 3. The points on the graph are the data of Table I of Miura et al.[1] They calculated the values of D according to an equation analogous to Eq. (9), with a value of Γ corrected by 15%. They made this correction because experimentally measured Rayleigh line width for pure ^{3}He departs systematically by 15% from the value of Γ calculated from thermodynamic
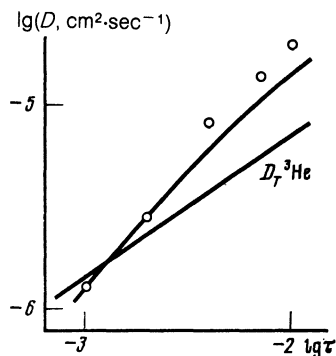
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FIG. 3. The coefficient of mutual diffusion for a solution with $N_3 = 0.79$ as a function of the reduced temperature: the points are values from Miura et al.[1]; the full curve is calculated from Eq. (2), taking account of D_0 obtained in our measurements; the straight line is the thermal diffusivity of ^{3}He.

data for ^{3}He. The full curve is the result of our calculation according to Eq. (2) for $N_3 = 0.79$ and taking account of D_0 obtained from our measurements. For comparison, the behavior of the thermal diffusivity D_T for ^{3}He (Ref. 11) is shown in the figure (a straight line plot). It can be seen from Fig. 3 that the full curve and the points agree with one another within the limits of experimental uncertainty. This again implies that our determination of the mutual diffusion coefficients does not disagree with the experimental results of Miura et al.[1] Consequently, such agreement confirms our views on the behavior of the coefficients of mutual diffusion near the critical vaporization line for ^{3}He–^{4}He solutions. The values of D for solutions with $N_3 = 0.79$ and D_T for ^{3}He in the region of comparison are close in magnitude, but have different temperature dependences.

We shall now estimate the temperature region where the asymptotic behavior of the coefficient of mutual diffusion should appear on the critical isochore for a given solution with concentration N_3. We start from the condition

$$D^{(1)} \lesssim D^{(2)}, \tag{10}$$

where $D^{(1)} = D_0 (N_3/RT)(\partial \mu_3/\partial N_3)_{P,T}$ while the value of $D^{(2)}$ is calculated according to Eq. (3). For the calculation, we take $D_0 = k_B T/6\pi \eta r_0$, $\gamma = 2\nu$, $\eta = \eta^*$ is the shear viscocity, and r_0 is a quantity of the order of atomic dimensions. We obtain, as a result the following criterion:

$$\tau_1 \lesssim [a(N_3 N_4)^\varepsilon]^{1/\nu}. \tag{11}$$

For solutions with $N_3 = 0.01, 0.10, 0.50$, and 0.80, for example, the limiting temperature is found to be equal to $\tau_1 = 3.0 \times 10^{-6}, 1.4 \times 10^{-4}, 8.5 \times 10^{-4}$ and 3.9×10^{-4}.

It is evident that apart from the crossover temperature τ_1, there exists yet another temperature where the coefficient of mutual diffusion change its temperature dependence. According to Eq. (5) this occurs for $D = D_0$, i.e.,

$$\tau_2 = [a(N_3 N_4)^\varepsilon]^{1/\tau}. \tag{12}$$

For solutions with $N_3 = 0.01, 0.10, 0.50$, and 0.80 these crossover temperatures are, respectively, $\tau_2 = 1.3 \times 10^{-3}$, $8.8 \times 10^{-3}, 2.5 \times 10^{-2}$ and 1.6×10^{-2}.

Near the binary solution critical vaporization line, the features of the behavior of the coefficient of mutual diffusion are thus determined in the temperature interval $\tau_1 < \tau < \tau_2$ by the derivative of the chemical potential with respect to the concentration, when the behavior of the mobility (the Onsager coefficient) is regular. It is clear from Eq. (11) that for the helium isotopes solutions, of any concentration, it is not possible to expect that in the temperature range $\tau > 10^{-3}$ an essentially asymptotic behavior cannot be expected in the behavior of the coefficient of mutual diffusion, as implied by the theory of interacting modes.

While we were preparing the revised version of this article, two more papers have appeared,[16,17] devoted to the problems discussed here. In particular theoretical results have been obtained[16] which agree with earlier work carried out in our laboratory.[6–8] The article by Cohen et al.,[17] which is a continuation of their earlier investigations,[1–3] discusses experiments on the Rayleigh line width without taking account of the composition dependence of the diffusion coefficient, which renders their conclusions insufficiently accurate, as before.

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