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Abstract

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ON THE RELAXATION MECHANISM IN THE CRITICAL REGION OF DEMIXING

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At the critical point of demixing of a binary liquid system, the diffusion rate falls to zero, which is associated with the vanishing of the derivative of the chemical potential with respect to the mole fraction (^{1,2}).

In accordance with Onsager' s hypothesis in the thermodynamics of irreversible processes, the mean rate of decay of concentration fluctuations must be linearly related to the diffusion flux. If this assumption remains valid also in the critical region, then investigation of the properties of diffusion in the vicinity of the critical point may serve as a means of studying the mechanism of fluctuations in a multicomponent system.

The change in the mole fraction of the concentration of a component, as calculations show (^{3}), in comparatively small volumes–for example, over the length of a light wave–occurs extremely slowly (for some systems a noticeable change in mole fraction occurs only after 10^3 sec.). By virtue of Onsager' s hypothesis it follows that, in the critical region, concentration equilibrium must be established slowly.

Considering the free energy of the system as a function of the volume V and of the mole fraction of component N_2 at constant temperature, we find the pressure of the system P in a nonequilibrium state:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\partial}{\partial V} F(V, N_{20} + \varepsilon) = -\frac{\partial F(V, N_{20})}{\partial V} - \varepsilon \frac{\partial^2 F(V, N_{20})}{\partial N_{20} \partial V}, \quad (1)$$

$$P - P_0 = -\varepsilon \frac{\partial}{\partial V} \left(\frac{\partial F}{\partial N_2}\right)_{N_2 = N_{20}},$$

where $N_2 = N_{20} + \varepsilon$; N_{20} is the value of the mole fraction of the second component in the state of thermodynamic equilibrium.

Using the relation

$$\frac{\partial}{\partial N_2} = \left(\frac{\partial}{\partial n_2}\right)_{n_1} - \left(\frac{\partial}{\partial n_1}\right)_{n_2} \tag{2}$$

(n_1 and n_2 are, respectively, the numbers of moles of the first and second components in the solution, $n_1 + n_2 = 1$), we obtain

$$P - P_0 = -\varepsilon \frac{\partial}{\partial V}(\mu_{20} - \mu_{10}). \tag{3}$$

Since at the critical point of a binary system the conditions

$$\left(\frac{\partial \mu_2}{\partial N_2}\right)_{P,T} = 0, \qquad \left(\frac{\partial^2 \mu_2}{\partial N_2^2}\right)_{P,T} = 0, \tag{4}$$

must be satisfied, then, restricting ourselves to the first two terms of the expansion, we may write

$$\mu_{20} = \mu_{2,\mathrm{k}} + \beta_2 (N_{20} - N_{2,\mathrm{k}})^3. \tag{5}$$

On the other hand, the difference $P - P_0$ between the true and the equilibrium pressure in the state of the system with density $\rho + \delta\rho$ is equal to (^{4})

$$P - P_0 = \frac{\tau\rho}{1 - i\omega\tau}\,(c_0^2 - c_\infty^2)\,\mathrm{div}\,\mathbf{v} \tag{6}$$

(c is the speed of sound, $c_0 = c$ for $\omega\tau \ll 1$; $c_\infty = c$ for $\omega\tau \gg 1$; ω is the frequency; τ is the relaxation time).

The change in density is associated with the motion of the liquid; thereby the change in the mole fraction δN_2 is also determined. It is then related to the liquid velocity $\mathbf{v}$ by the continuity equation

$$\frac{d\delta N_2}{dt} + N_2\,\mathrm{div}\,\mathbf{v} = 0. \tag{7}$$

The basic assumption of work (^{3}), that the rate of change of the concentration of one of the components is determined by the gradient of its chemical potential, leads to the equation of isothermal diffusion in the critical region of stratification

$$\frac{\partial N_2}{\partial t} = -\frac{D_0}{RT}\,\mathrm{div}\,(N_2\,\mathrm{grad}\,\mu_2)\,. \tag{8}$$

On the basis of expansion (5),

$$\operatorname{grad}\mu_2 = 3\beta_2\left(N_2 - N_{2,\mathrm{k}}\right)^2 \operatorname{grad} N_2. \tag{9}$$

Using equations (7) and (8), one may write

$$-N_2 \operatorname{div}\mathbf{v} - \mathbf{v}\operatorname{grad} N_2 = -\frac{3\beta_2 D_0}{RT}\left(N_2 - N_{2,\mathrm{k}}\right)\left[\left(N_2 - N_{2,\mathrm{k}}\right)(\operatorname{grad} N_2)^2 + \right.$$

$$\left. + 2N_2(\operatorname{grad} N_2)^2 + N_2\left(N_2 - N_{2,\mathrm{k}}\right)\Delta N_2\right]. \tag{10}$$

If $N_{20} \to N_{2,\mathrm{k}}$, then approximately

$$N_2 \operatorname{div}\mathbf{v} + \mathbf{v}\operatorname{grad} N_2 = \frac{6\beta_2 D_0}{RT} N_2\left(N_2 - N_{20}\right)(\operatorname{grad} N_2)^2. \tag{11}$$

Equating the right-hand sides of equations (3) and (6) and using $\operatorname{div}\mathbf{v}$ from (11), we obtain an expression for determining the relaxation time τ:

$$\left(N_2 - N_{20}\right)\frac{\partial}{\partial V}\left(\mu_{20} - \mu_{10}\right) =$$

$$= \frac{\tau\rho\left(c_0^2 - c_\infty^2\right)}{1 + \omega^2\tau^2}\left[\frac{\mathbf{v}}{N_2}\operatorname{grad} N_2 + \frac{6\beta_2 D_0}{RT}\left(N_2 - N_{20}\right)(\operatorname{grad} N_2)^2\right]. \tag{12}$$

Hence

$$\tau = \frac{A}{2B\omega^2} + \sqrt{\frac{A^2}{4B^2\omega^4} - \frac{1}{\omega^2}}, \tag{13}$$

where

$$A = \rho\left(c_0^2 - c_\infty^2\right)\frac{\mathbf{v}}{N_2}\operatorname{grad} N_2, \qquad B = \left(N_2 - N_{20}\right)\frac{\partial}{\partial V}\left(\mu_{20} - \mu_{10}\right).$$

A direct estimate shows that

$$\frac{6\beta_2 D_0}{RT}\left(N_2 - N_{20}\right)(\operatorname{grad} N_2)^2 \ll \frac{\mathbf{v}}{N_2}\operatorname{grad} N_2, \qquad \frac{A}{B} \gg 1.$$

Consider one-dimensional motion. Then

$$\operatorname{grad} N_2 \simeq \frac{N_2 - N_{20}}{\lambda/4}$$

(λ is the wavelength);

$$v = c\frac{\Delta\rho}{\rho}; \qquad \left(\frac{\partial\mu_2}{\partial V}\right)_{T,N_2} = \left(\frac{\partial\mu_2}{\partial P}\right)_{T,N_2}\left(\frac{\partial P}{\partial V}\right)_{T,N_2} = \overline{V}_2\left(\frac{\partial P}{\partial V}\right)_{T,N_2}.$$

Let us estimate the relaxation time in the critical region of stratification. For liquids with $c \sim 10^5$ cm $\cdot$ sec^{-1}, $c_0^2 - c_\infty^2 \sim 10^9$, $N_2 - N_{2,\mathrm{k}} \sim 10^{-2}$, $\Delta\rho \sim 10^{-2}$ g $\cdot$ cm^{-3}. Since

$$\frac{\partial(\mu_{20} - \mu_{10})}{\partial V} = \overline{V}_2\left(\frac{\partial P}{\partial V}\right)_{T,N_2} - \overline{V}_1\left(\frac{\partial P}{\partial V}\right)_{T,N_1},$$

and $\overline{V}_1 - \overline{V}_2 \sim 10$ cm^3, $\partial P/\partial V \sim 10^2$ atm $\cdot$ cm^{-3}, then $\partial(\mu_{20} - \mu_{10})/\partial V \sim 10^2$—$10^3$ atm. With these data and a sound frequency $\omega = 10^7$ Hz,

$$\tau \sim 10^{-7}\text{—}10^{-8} \text{ sec.},$$

which is much greater than the relaxation time outside the critical region. A value of the order of 10^{-7} for τ was obtained in the critical region of pure xenon (5).

The expression (13) obtained makes it possible to trace the dependence of the relaxation time on the properties of the system and the parameters of the sound wave without invoking model assumptions.

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Note: Figure translations are in progress. See original paper for figures.

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