Reports of the Academy of Sciences of the USSR

PHYSICS

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 158, No. 5

PHYSICS

I. Z. FISHER

ON THE LAYERED NATURE OF A DIFFUSION FLUX NEAR THE CRITICAL POINT OF A BINARY SOLUTION

(Presented by Academician M. A. Leontovich on May 6, 1964)

In papers ([1,2]) it was found that, near the critical point of demixing of a binary liquid solution, diffusion proceeds not only extremely slowly, as had been noted earlier, but also possesses qualitatively new properties in comparison with ordinary diffusion. The most interesting finding was the discovery of a layered structure of the diffusion flux: the relative concentration of the components of the solution changes along the direction of the flux in an oscillatory manner. In the present paper a theory of this phenomenon will be given.

Let there be a binary solution at constant temperature and pressure, but whose relative concentration of components can undergo local fluctuations: $c(\mathbf{r}) = c_0 + \delta c(\mathbf{r})$. From the theory of light scattering by solutions it is known ([3]) that, near the critical point of demixing, concentration fluctuations are strongly developed and strongly correlated in space. In the generally accepted theory of light scattering, this corresponds to the following expression for the deviation of the entropy density from its equilibrium value, equal to ([3,4])

$$\delta s(\mathbf{r}) = -\frac{1}{2}\{a(\delta c)^2 + b(\vec{\nabla}\delta c)^2\}, \tag{1}$$

where a, b are positive constants. The quantity a is proportional to the derivative of the appropriately chosen chemical potential with respect to the concentration c: $a \sim (\partial\mu/\partial c)_{p,T}$, and at the critical point itself it vanishes. Differentiating (1) with respect to time and using the continuity equation for the concentration:

$$\dot{\delta c} + \operatorname{div}\mathbf{j} = 0, \tag{2}$$

where $\mathbf{j}$ is the vector of diffusion-flux density, we obtain, by the usual method ([5]), the expression for the density of entropy production in the form

$$\sigma = -\mathbf{j}\vec{\nabla}(a\delta c - b\Delta\delta c), \tag{3}$$

where Δ is the Laplace operator. Consequently, the vector factor multiplying $\mathbf{j}$ is the thermodynamic force conjugate to the flux $\mathbf{j}$, and we may write the linear law (see [5])

$$\mathbf{j} = -L\vec{\nabla}(a\delta c - b\Delta\delta c), \tag{4}$$

where L is a constant coefficient. Denoting $La = D$, $Lb = H$, from (2) and (3) we obtain the generalized Fick laws in the form

$$\mathbf{j} = -D\vec{\nabla}\delta c + H\vec{\nabla}\Delta\delta c, \tag{5}$$

$$\dot{\delta c} = D\Delta\delta c - H\Delta\Delta\delta c. \tag{6}$$

At the critical point itself $D = 0$. Therefore, sufficiently close to the critical point, the differential diffusion equation is written as

in the form

$$\frac{\partial n}{dt} + H\Delta\Delta n = 0, \tag{7}$$

where, for brevity, $\delta c \equiv n$. It is assumed here not only that proximity to the critical point is ensured at $n = 0$, but also that n itself is sufficiently small. Otherwise, in equation (7) terms nonlinear in n, as well as terms with still higher spatial derivatives, would have to be taken into account.

Let us now find the solution of equation (7), idealized to correspond to the conditions of the experiments described in [1,2]. Suppose there is an unbounded tube located along the Ox axis, and suppose that at the initial instant $t = 0$ to the right and to the left of the cross section $x = 0$ there were constant, but mutually unequal, distributions of concentration close to the critical value:

$$n = n_0' > 0 \quad \text{for } x < 0 \text{ and } t = 0,$$

$$n = n_0'' < 0 \quad \text{for } x > 0 \text{ and } t = 0. \tag{8}$$

This leads to the following problem for equation (7):

$$\frac{\partial n}{\partial t} + H\frac{\partial^4 n}{\partial x^4} = \delta(t)\{\theta(-x)n_0' - \theta(x)|n_0''|\}, \tag{9}$$

where $\delta(t)$ is the Dirac δ-function and $\theta(x)$ is the unit step. Equation (9) is solved by a double Fourier transform, in t and x. It is not difficult to verify that the solution is

$$n(x,t) = \delta c(x,t) = \theta(t)\{\tfrac{1}{2}(n_0' - |n_0''|) - (n_0' + |n_0''|)F(u)\}, \tag{10}$$

$$F(u) = \frac{1}{\pi}\int_0^\infty e^{-\frac{1}{4}s^4}\sin(us)\,\frac{ds}{s}, \qquad u = \frac{x}{\sqrt[4]{4Ht}}. \tag{11}$$

The function $F(u)$ is odd and, for small values of u, has the rapidly convergent expansion

$$F(u) = \frac{1}{2\pi\sqrt{2}}\sum_{n=0}^{\infty}\frac{(-1)^n 2^n}{(2n+1)!}\,\Gamma\!\left(\frac{n}{2}+\frac{1}{4}\right)u^{2n+1} \tag{12}$$

and for $u = \pm\infty$ is equal, respectively, to $\pm\frac{1}{2}$. These limiting values are approached nonmonotonically. The asymptotic expression for $F(u)$ at large positive u, obtained by the method of steepest descent, is

$$F(u) \simeq \frac{1}{2} - \frac{4}{2^{1/6}}\sqrt{\frac{3}{\pi}}\,u^{-2/3}e^{-\frac{3}{8}u^{4/3}}\cos\left(\frac{3\sqrt{3}}{8}u^{4/3}+\frac{\pi}{6}\right). \tag{13}$$

For $u < 0$ we obtain $F(-u) = -F(|u|)$.

Thus, the distribution of the excess concentration $n \equiv \delta c$ for $t > 0$, in contrast to ordinary diffusion, proves to be nonmonotonic and has an oscillating, or layered, structure. With time the layers slowly move in both directions from the middle cross section $x = 0$ according to the law $x \sim \sqrt[4]{4Ht}$. Obviously, the same oscillating behavior will also occur for the optical refractive index: $\delta\varepsilon = (\partial\varepsilon/\partial c)\,\delta c$, and this layered structure of the solution can be observed visually, as was done in ([1,2]).

The expression for the diffusion flux is obtained from (5) and (10) at $D = 0$ and proves to be equal to

$$j = \frac{\theta(t)H(n_0' + |n_0''|)}{\pi(4Ht)^{3/4}}\int_0^\infty e^{-\frac{1}{4}s^4}\cos(us)s^2\,ds. \tag{14}$$

The flux is also nonmonotonic. For example, for large positive u we have, analogously to (13),

$$j \simeq \frac{4}{2^{1/6}}\sqrt{\frac{3}{\pi}}\,\frac{H\theta(t)}{(4Ht)^{3/4}}(n_0' + |n_0''|)u^{1/3}e^{-\frac{3}{8}u^{4/3}}\cos\left(\frac{3\sqrt{3}}{8}u^{4/3}-\frac{5\pi}{6}\right). \tag{15}$$

However, the mean flux is invariably directed in the positive direction of the Ox axis, as is seen, for example, from the expression for the flux in the middle section: at $x = 0$, from (14) we have

$$j_{x=0} = \frac{\theta(t) H^{1/4}}{4\pi t^{3/4}} \Gamma\left(\frac{3}{4}\right) (n_0' + |n_0''|) > 0. \tag{16}$$

The asymptotic estimates (13) and (15) are in fact valid down to comparatively very small values of u. If this is used for approximate estimates of the layered structure, then for the positions of the extrema of the function $F(u)$ we obtain

$$u_n \cong 3.2616\,(^2/_3 + n)^{3/4}, \qquad n = 0, 1, 2, \ldots, \tag{17}$$

with even n corresponding to maxima of $F(u)$, and odd n to minima, so that the distance between an adjacent pair of layers of concentration excess turns out to be approximately equal to

$$\Delta x \cong 3.2616 \left\{(^8/_3 + n)^{3/4} - (^2/_3 + n)^{3/4}\right\} \sqrt[4]{4Ht}; \tag{18}$$

it slowly increases with time and is slightly different for different layers. The thicknesses of the first few layers are

$$\Delta x_1 \cong 4.40 \sqrt[4]{4Ht}, \qquad \Delta x_2 \cong 3.54 \sqrt[4]{4Ht}, \qquad \Delta x_3 \cong 3.18 \sqrt[4]{4Ht}. \tag{19}$$

These expressions may be used for experimental determination of the magnitude of the coefficient H.

Unfortunately, the experiments described in ([1],[2]) were qualitative in character, and they cannot be used for reliable estimates. Very roughly it follows that, near the upper critical point of demixing of the solution CH_3OH-n-C_6H_{12}, according to ([2]), $H \sim 10^{-11} \div 10^{-12}$ cm^4/sec. The quantity $a \sim (H/D)^{1/2}$, where D is the diffusion coefficient far from the critical point, is a certain characteristic length connected either with the correlation radius of the fluctuations or with the linear dimensions of a typical fluctuation. In our case, for $D \sim 10^{-5}$ cm^2/sec, one obtains $a \sim 10^{-3} \div 10^{-4}$ cm, which appears satisfactory.

Thus, the layered nature of the diffusion flux near the critical point observed in works ([1],[2]) is a natural consequence of the strong correlation of fluctuations of the solution concentration and can be approximately estimated from the same differential quadratic form (1) that is also used in the theory of critical opalescence.

Odessa State University
named after I. I. Mechnikov

Received
25 III 1964

REFERENCES

1. B. A. Smirnov, in: *Critical Phenomena and Fluctuations in Solutions*, Publishing House of the Academy of Sciences of the USSR, 1960, p. 137.

2. B. A. Smirnov, *Zh. Fiz. Khim.* **35**, No. 10, 2249 (1961).

3. M. V. Vol' kenshtein, *Molecular Optics*, Moscow, 1951.

4. Landau, Lifshitz, *Statistical Physics*, Moscow, 1951.

5. C. De Groot, *Thermodynamics of Irreversible Processes*, Moscow, 1956.

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