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DIFFUSION IN A SOLUTION NEAR THE CRITICAL POINT OF VAPOR FORMATION

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An expression for the diffusion coefficient of dilute solutions near the critical point is derived and discussed on the basis of the general macroscopic diffusion equations and the thermodynamical properties of solutions near the critical point. The nature of the Brownian motion of particles near the critical point is discussed.

A number of interesting experiments in recent years have shown that the diffusion coefficient becomes vanishingly small not only at the critical point for mixing in a two-component liquid solution [1], but also at the critical point for vapor formation in a dilute solution[2]. This result confirms a well known consequence of the general diffusion theory as applied to the critical point.

In view of this it seems reasonable to discuss in greater detail the behavior of the diffusion process near the critical point for vapor formation in a solution by means of the general equation of macroscopic diffusion theory and the thermodynamic properties of the critical point. This is the object of the present paper.

It is well known that there is now experimental evidence that the behavior of the thermodynamic quantities in the neighborhood of the critical point for evaporation is more complicated than was previously believed, as shown by the appearance of a logarithmic rise of the specific heat at constant volume[3,4]. One has to expect a similar behavior for solutions although this problem has not as yet been studied. We shall therefore use in this paper the thermodynamic description of the critical point which was accepted prior to these developments, and which is based on the assumption that the free energy can be expanded in a power series in the neighborhood of the critical point; we shall also use the usual expression for the free energy of a dilute solution, which contains the logarithm of the concentration. One must therefore bear in mind that the formulae derived below may turn out to be inapplicable in the immediate neighborhood of the critical point. For this reason it might be possible to derive further information on this question from an analysis of diffusion experiments and their comparison with the equations derived below.

Finally, we shall consider the question of the significance of our conclusions about the macroscopic diffusion coefficient of dilute solutions in terms of the Brownian motion of individual particles. We shall show that the fact that the diffusion coefficient tends to zero at the critical point does not imply a reduction in the Brownian displacements of the particles, which are determined entirely by their mobility.

1. We start from the general diffusion equations for solutions (at constant pressure and temperature). Denoting by n_0 and n_1 the molecular concentration per unit volume of solvent and solute, by u_0 and u_1 their transport velocities, and by μ_0 and μ_1 their chemical potentials, we can write (for one-dimensional diffusion) a set of four equations for the four functions n_0, n_1, u_0, u_1:

$$\frac{\partial n_1}{\partial t}+\frac{\partial n_1 u_1}{\partial z}=0, \quad \frac{\partial n_0}{\partial t}+\frac{\partial n_0 u_0}{\partial z}=0,$$

$$\frac{u_1-u_0}{b}+\frac{\partial \mu_1}{\partial z}=0, \quad \frac{n_1}{bn_0}(u_1-u_0)-\frac{\partial \mu_0}{\partial z}=0. \tag{1}$$

Here b is the mobility of the solute molecules. From the last two equations one can derive by means of the thermodynamic identity for isothermal changes, $n_0 d\mu_0 + n_1 d\mu_1 = dp$, (in line with our assumption)

$$dp = 0. \tag{2}$$

We can use this equation in place of the last equation in (1).

Using

$$x = n_1/n, \quad n = n_0 + n_1 = 1/v,$$
$$u = u_1 - u_0, \ w = (1-x)u_0 + xu_1,$$

we can transform the set of equations (1) into:

$$\frac{\partial n}{\partial t}+\frac{\partial nw}{\partial z}=0, \tag{3}$$

$$n\left\{\frac{\partial x}{\partial t}+w\frac{\partial x}{\partial z}\right\}=\frac{\partial}{\partial z}\left(nD^*\frac{\partial x}{\partial z}\right), \tag{4}$$

where

$$D^* = bx(1-x)\,(\partial\mu_1/\partial x)_p \tag{5}$$

is the diffusion coefficient for the diffusion equation in terms of the relative concentration x. If we write an equation for n_1, the coefficient is

$$D = bx(1-x)(\partial\mu_1/\partial n_1)_p. \qquad (6)$$

Making use of (2), (3) and (4) we can replace (3) by the equation

$$\frac{\partial w}{\partial z} = -\frac{p_x}{p_v}\frac{\partial}{\partial z}D^* n\frac{\partial x}{\partial z}, \qquad (7)$$

which serves to determine w. The problem is thereby reduced to the three equations (4), (7), and (2) for the three functions x, w, and $n \equiv 1/v$.

The generalization of these equations to the three-dimensional case presents no difficulty; however, some complications may then appear in the study of the phenomenon of diffusion near the critical point.

2. We now quote the necessary thermodynamic equations relating to the critical point of the solution. For this we must use the variables v, x, T, rather than p, x, T since the thermodynamic quantities are not single-valued functions of the variables p, x, T near the critical point. Let f(v, x, T) be the free energy per molecule of solution. The chemical potential μ_1 and the pressure p are then of the form

$$\mu_1 = f - vf_v + (1-x)f_x, \qquad p = -f_v. \qquad (8)$$

We find therefore

$$(\partial\mu_1/\partial x)_p = (1-x)(f_{vv}f_{xx} - f_{vx}^2)/f_{vv}. \qquad (9)$$

The expansion of the thermodynamic potential near some given state v, x (T = const) in a series of powers of Δv and Δx is then:

$$\frac{1}{2}\{f_{vv}\Delta v^2 + 2f_{vx}\Delta v\Delta x + f_{xx}\Delta x^2\} + \frac{1}{6}\{f_{vvv}\Delta v^3 + \ldots\}$$
$$= \frac{1}{2f_{vv}}(f_{vv}\Delta v + f_{vx}\Delta x)^2 + \frac{f_{xx}f_{vv} - f_{vx}}{2f_{vv}}\Delta x^2$$
$$+\frac{1}{6}\{f_{vvv}\Delta v^3 + \ldots\}. \qquad (10)$$

We note that for the further arguments we require only the possibility of an expansion to second order in Δv and Δx i.e., the existence of the derivatives f_{xx}, $f_{vx} = -p_x$ and $f_{vv} = -p_v$.

The critical point represents a stable state. In its neighborhood, however, there exist two stable states rather than one. This is possible only if at that point the quadratic form in the two variables Δv and Δx, which appears in (10), vanishes for certain values of Δx/Δv. This leads to

$$f_{xx}f_{vv} - f_{xv}^2 = 0. \qquad (11)$$

as a necessary condition at the critical point.

Here of course $f_{vv} > 0$ and $f_{xx} > 0$. Furthermore, the third-order terms in (10) (assuming the existence of the third derivatives of f) must vanish for the same values of Δx/Δv; otherwise the state would be unstable. It follows that at the critical point the following condition must apply

$$f_{vvv}f_{vx}^3 - 3f_{vvx}f_{vx}^2f_{vv} + 3f_{vxx}f_{vx}f_{vv}^2 - f_{xxx}f_{vv}^3 = 0,$$

which is equivalent to the equation $(\partial^2\mu/\partial x^2)_p = 0$.

By solving this equation, together with (11), for v and T at given x, we find the critical values of v and T for a given concentration x.

From (11), (9), and (5) we find for the diffusion coefficient the expression

$$D^* = bx(1-x)^2(f_{vv}f_{xx} - f_{vx}^2)/f_{vv}, \qquad (12)$$

which evidently vanishes at the critical point.

We note also that from the well-known equations of fluctuation theory we can write for the rms fluctuations Δv and Δx:

$$\langle\Delta x^2\rangle = \frac{f_{vv}}{f_{xx}}\langle\Delta v^2\rangle = -\frac{f_{vv}}{f_{vx}}\langle\Delta v\Delta x\rangle = \frac{T}{N}\,\frac{f_{vv}}{f_{xx}f_{vv} - f_{vx}^2}.$$

Here N is the total number of particles in the volume for which the fluctuations are considered; the temperature T is here and subsequently expressed in ergs. We can therefore obtain from (12) an equation that connects the diffusion coefficient directly with the fluctuations in the concentration:

$$D^* = bTx(1-x)^2/N\langle\Delta x^2\rangle, \qquad (13)$$

i.e., the diffusion is slower the greater the concentration fluctuations.

3. We consider now dilute solutions. We require an expression for the free energy, which is valid in the neighborhood of the critical point.

We write this equation in the form

$$f(x, v, T) = Tx\ln x + f^*(x, v, T), \qquad (14)$$

and in particular as $x \to 0$

$$\lim f(x, v, T) = f^0(v, T),$$

where $f^0(v, T)$ is the free energy of the pure solvent. In this formulation we do not assume that f* can be expanded in powers of x. The point is that the experimental facts obtained in [3] suggest the possibility that the free energy may, at the critical point, have not only a singularity as a function of v and T (a logarithmic singularity according to [3]), but even a singularity as a function of x beyond that already contained in the term Tx ln x.

Inserting the derivatives of the expression (14)

$$f_{vv} = -p_v, \quad f_{vx} = -p_x, \quad f_{xx} = T/x + f_{xx}^*$$

in (12), we obtain

$$D^* = bT\left\{1 - \frac{x}{T}\left(\frac{p_x^2}{-p_v} - f_{xx}^*\right)\right\}. \tag{15}$$

For a dilute solution with small x the value of p_x may be taken at x = 0. If f_{xx}^* remains bounded as $x \to 0$ it may also be taken at x = 0. In the term with p_x^2/p_v the denominator becomes very small for x near the critical point of the solvent where $p_v = 0$. This term therefore dominates the behavior of D*. Retaining only this term we find

$$D^* = bT\left\{1 - \frac{x}{T}\frac{p_x^2}{-p_v}\right\}. \tag{16}$$

The expression in brackets in (15) is of course always positive. It equals $(f_{xx}f_{vv} - f_{vx}^2)/xTf_{vv}$. At the critical point of the solution it becomes zero; the size of the region of densities and temperatures in which D*/bT is small decreases with decreasing x.

We see from (16) that the solute concentration affects the diffusion coefficient if the equation of state depends on concentration (i.e., $p_x \neq 0$). Assuming (as in [3,4]) that f can at the critical point be expanded in a series of powers of Δv and ΔT, we find the dependence of the diffusion coefficient on the distance from the critical point of the pure solute (T^{0k}, v^{0k})

$$\frac{D^*}{bT} = \frac{\Delta v^2 + \alpha\Delta T + (\beta - \gamma)x}{\Delta v^2 + \alpha\Delta T + \beta x},$$

where

$$\Delta v = v - v^{0k}, \qquad \Delta T = T - T^{0k},$$

$$\alpha = 2p_{vT}^{0k}/p_{vvv}^{0k}, \quad \beta = 2p_{vx}^{0k}/p_{vvv}^{0k}, \quad \gamma = 2(p_x^{0k})^2/Tp_{vvv}^{0k},$$

or at a given pressure $p = p^{0k} + \Delta p$

$$\frac{D^*}{bT} = 1 - x\delta(\Delta p - p_T^{0k}\Delta T - xp_x^{0k})^{-2/3},$$

where

$$\delta = 2^{1/3}(p_x^{0k})^2/3^{2/3}(p_{vvv}^{0k})^{1/3}T.$$

We emphasize that near the critical point and at low concentrations the diffusion equation is nonlinear. Even for an arbitrarily small concentration gradient the transport term $nw\,\partial x/\partial z$ can be shown to be of the order of magnitude of

$$\frac{bT - D^*}{bT}\frac{\partial}{\partial z}D^* n\frac{\partial x}{\partial z},$$

and may therefore be neglected only if D* ~ bT, i.e., far from the critical point. The simple linear diffusion equation applies only if the changes in the concentration are small compared to some constant concentration x_0 (which itself is small). Writing $x = x_0 + \xi$, we have then

$$\frac{\partial\xi}{\partial t} = D^*(x_0)\frac{\partial^2\xi}{\partial z^2}.$$

We note that in the derivation of the diffusion equation in (1) we have taken no account of viscosity, i.e., of terms proportional to the second derivative of the velocity with respect to the coordinates. An estimate shows that these terms contain a factor of the order $(r/L)^2$ by comparison with those taken into account (here r is a measure of the molecular dimensions and L the dimension characterizing the concentration gradient).

In these arguments we have assumed that the free energy depends only on the values of the density and the concentration at a given point and have neglected any dependence on their gradients. As a result, Eq. (1) contains only the first derivatives of μ_1 and μ_0 with respect to z. An attempt to include the gradient terms in the free energy was made by Fisher[6]. Such terms cannot in order of magnitude be greater than $(l/L)^2$ where l is the correlation length. In experiments concerned with macroscopic diffusion they will hardly be observable even very close to the critical point.

4. In cases in which we are concerned with the diffusion of particles which move independently of one another, their concentration will satisfy the usual linear differential equation of diffusion. This is the same equation as that satisfied in this case by the distribution of the displacements of individual particles. The equation for the concentration is then obtained as the equation for the mean density of particles and is a consequence of the equation for the distribution. In this case, therefore, the mean square displacement of an individual particle,

$$\langle(z(t) - z(0))^2\rangle = 2Dt$$

contains the same diffusion coefficient as the equation for the concentration.

This is not the case for the diffusion near the critical point, which is considered in this note. The equation for the concentration is nonlinear. The displacements of different particles are in this case not independent events. We are therefore in this case not justified in identifying the equation for the concentration with that for the probability distribution of individual particle displacements, and therefore it is impossible to draw any conclusions about the displacements of individual particles. The diffusion is slower in these circumstances, not because the particles move more slowly, but because one particle takes the place of another.

The mean-square displacement of the particles in Brownian motion and its time dependence are determined entirely by the mobility of the particles (and the variation of mobility with frequency). This is a consequence of the general fluctuation-dissipation theorem (the Callen-Welton theorem[7]). It is easy to derive from that theorem an expression for the mean square displacement of a particle during a time t

$$\langle (z(t)-z(0))^2\rangle = \frac{4T}{\pi}\int_0^\infty b'(\omega)(1-\cos\omega t)\frac{d\omega}{\omega^2}.$$

Here $b'(\omega) = \operatorname{Re} b(\omega)$ is the real part of the mobility of a particle moving under the influence of a force $F = F_0 e^{i\omega t}$. The quantity $b'(\omega)$ is connected with a "generalized permeability" $\alpha(\omega)$, used in [7]:

$$b'(\omega) = \alpha''(\omega)/\omega = \operatorname{Im}\alpha(\omega)/\omega.$$

If the mobility is independent of frequency, $b'(\omega) = b$, this expression directly leads to the Einstein formula

$$\langle (z(t)-z(0))^2\rangle = 2bTt.$$

For the macroscopic particles of a colloidal solution near its critical point (which is practically that of the solvent) it is not only true that the Brownian motion has no singularities other than those arising from the behavior of the mobility in these conditions, but the same applies also for the diffusion. This follows from the fact that the molecular concentration of the colloid solution is practically zero and in that case the diffusion coefficient equals bT.

The problem of finding the mobility of macroscopic particles moving in a liquid near its critical point reduces to the solution of a hydrodynamic problem. This requires the inclusion of the high compressibility and a correlation length which may be comparable with the dimensions of the particles, and also the behavior of the viscosity of the liquid in this region. This problem will be considered in a separate paper.

The Brownian motion of molecules manifests itself in self-diffusion. As in the case of macroscopic particles, the coefficient of self-diffusion depends only on the mobility of the molecules in the liquid. Noble and Bloom[8] have shown by means of the spin-echo technique that the self-diffusion coefficient of ethane molecules changes near the critical point by amounts of the order of 50% of its magnitude (and not by several orders of magnitude, as the diffusion coefficient of the solution). This change in the diffusion coefficient must be connected with a corresponding behavior of the particle mobility in the critical region.

Krichevskiĭ et al.[5] have shown that the rate of recombination of iodine atoms into molecules in solution (the solvent being carbon dioxide) near the critical point of the solution and the rate of recombination of chlorine atoms in ordinary molecular chlorine (Cl_2) at the critical point are extremely slow. These authors attribute this phenomenon to the fact that the diffusion coefficient is decreased and deduce from this that the Brownian displacement of the individual iodine and chlorine atoms is reduced thereby. Using for the reaction rate ideas similar to the Smoluchowski theory of the coagulation of colloids they then arrive at the conclusion that the time required for two atoms to meet will become exceedingly large, and that therefore the recombination will be slowed down. From the arguments given above it follows however that this explanation of the observed facts cannot be accepted as justified, and that a different explanation is required. One may imagine, for example, that in the conditions near the critical point the foreign atoms in the solution are surrounded by solvent molecules so that their close approach becomes very difficult, while the probability of recombination decreases rapidly with atomic distance (or else one may look for an explanation in the decrease of the atomic mobility).

The hypothesis has been put forward that the reduction of the diffusion near the critical point may lead to an anomalous behavior of the electric fluctuations in solutions of electrolytes in these conditions. This conclusion is however, unjustified. The closeness of the critical point causes no limitations to the applicability of the Nyquist equation and other general equations of the theory of electric fluctuations. Here again everything will depend on the mobility of the ions.

An experimental study of the conductivity of electrolytes, as well as of the Brownian motion of colloid particles near the critical point, is of interest because it could provide information about the behavior of the mobility. For this it is, of course, necessary to know the behavior of the viscosity of the solvent in this region.

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[1] I. P. Krichevskiĭ, N. E. Khazanova, and L. P. Lipshitz, DAN SSSR **99**, 113 (1954),

[2] I. P. Krichevskiĭ, N. E. Khazanove, and L. P. Lipshitz, DAN SSSR **141**, 397 (1961).

[3] M. I. Batatskiĭ, A. V. Voronel', and V. G. Gusak, JETP **43**, 728 (1962), Soviet Phys. JETP **16**, 517 (1963); A. V. Voronel', Yu. R. Chatkin,

V. A. Popov, and V. G. Simkin, JETP **45**, 828 (1963), Soviet Phys. JETP **18**, 143 (1964).

[4] M. Ya. Azbel', A. V. Voronel', and M. Sh. Giterman, JETP **46**, 673 (1964), Soviet Phys. JETP **19**, 457 (1964).

[5] I. P. Krichevskiĭ, D. A. Rott, and Yu. V. Tsekhanskaya, DAN SSSR **163**, 3 (1965).

[6] I. Z. Fisher, DAN SSSR **158**, 1075 (1964), Soviet Phys. Doklady **9**, 906 (1965).

[7] L. Landau and E. Lifshitz, Statisticheskaya Fizika (Statistical Physics) Fizmatiz. 1964, 126, p. 466.

[8] J. D. Noble and M. Bloom, Phys. Rev. Lett. **14**, 250 (1965).

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