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I. R. Krichevskii, L. A. Rott, Yu. V. Tsekhanskaya

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Abstract

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I. R. Krichevskii, L. A. Rott, Yu. V. Tsekhanskaya

Autocorrelation of Thermal Fluctuations in a Double Dilute Solution Near Its Critical Point

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The critical point of a pure substance is in itself a very curious phenomenon (for a pure substance only the liquid-gas equilibrium critical point is known). No less, if not more, interesting are the liquid-gas equilibrium critical points in binary dilute (infinitely dilute) solutions. The existence of such critical points is a firmly established experimental fact (see, for example, (1)).

In binary dilute solutions experiment has not found critical points of other equilibria: liquid-liquid, gas-gas, crystal-crystal. Here there is complete agreement with the theory of phase equilibria developed by van der Waals (2).

According to the principle of continuity, the temperature, pressure, and density of the liquid-gas equilibrium critical point of a binary dilute (infinitely dilute) solution differ little from the temperature, pressure, and density of the critical point of the pure substance.

According to Gibbs'thermodynamic theory of critical phenomena (3), the critical point of a binary solution is characterized by the equations

$$(\partial\mu_2/\partial N_2)_{T,P,\kappa} = 0; \qquad (1)$$

$$(\partial^2\mu_2/\partial N_2^2)_{T,P,\kappa} = 0; \qquad (2)$$

μ is the chemical potential of a component, N its mole fraction; T the thermodynamic temperature, P the pressure. The subscript 2 refers to the dissolved substance, and the subscript κ denotes the critical phase.

Equations (1) and (2) can, of course, also be rewritten for the solvent (subscript 1). But these will no longer be equations independent of (1) and (2).

Equations (1) and (2) are valid for the critical point of any composition, of any type of equilibrium. For the liquid-gas equilibrium critical point, equations (1) and (2) are also valid in the limit as $N_{2,\kappa} = 0$:

$$\lim_{\substack{T_\kappa \to T_{1,\kappa} \\ P_\kappa \to P_{1,\kappa} \\ N_{2,\kappa} \to 0}} (\partial \mu_2 / \partial N_2)_{T,P,\kappa} = 0; \tag{3}$$

$$\lim_{\substack{T_\kappa \to T_{1,\kappa} \\ P_\kappa \to P_{1,\kappa} \\ N_{2,\kappa} \to 0}} (\partial^2 \mu_2 / \partial N_2^2)_{T,P,\kappa} = 0. \tag{4}$$

Equations (3) and (4) show that even to infinitely dilute solutions at the liquid-gas equilibrium critical point the ordinary equations for chemical potentials (containing only a logarithmic term) are not applicable (these latter equations were substantiated by Gibbs (3)). Equations (3) and (4) show that Raoult' s and Henry' s laws are not obeyed even in the limit as $N_{2,\kappa} \to 0$.

Equations (1) and (2) have repeatedly been used to justify large fluctuations of composition at the critical point of a binary solution (see,

for example, (4)). The authors wish here to emphasize that large fluctuations of composition are necessarily associated with a low rate of dissipation of these fluctuations (and a low rate of their establishment) at the critical point of any binary solution. Indeed, according to Onsager' s theory, the rate of dissipation of composition fluctuations obeys the equation of macroscopic diffusion (see, for example, (5)). The driving force of isothermal diffusion in a binary solution is the gradient of the chemical potential of the component (5). According to equation (1) (and also (3)), this gradient becomes zero at the critical point of a binary solution.

The cessation of diffusion at the critical point of a binary solution has been confirmed experimentally for the systems studied (6). The diffusion flux practically falls to zero even at a considerable concentration gradient.

The cessation of diffusion was specifically demonstrated for the critical point of liquid-gas equilibrium in a very dilute solution of iodine (J_2) in carbon dioxide (7) (the mole fraction of iodine in the solution was of the order of 10^{-5}).

Equation (2) (and also (4)) explains why experiments detect a very low diffusion rate also in the neighborhood of the critical point of a binary solution, at N_2 noticeably different from $N_{2,\mathrm{k}}$ (6, 7). The diffusion rate is low also at T, P in the neighborhood of $T_\mathrm{k}, P_\mathrm{k}$ (6, 7).

Classical thermodynamics and the thermodynamics of irreversible processes readily explain the cessation of diffusion at the critical point of a binary solution, even one as dilute as a solution of iodine in carbon dioxide. But the molecular-statistical picture of the phenomenon remains unclear.

Diffusion is a macroscopic manifestation of Brownian motion. The cessation of diffusion of iodine in carbon dioxide means that the Brownian motion of iodine molecules is reduced to their "jostling" in place (8). The iodine molecules behave as though they had acquired a "memory." The material carrier of the "memory" is, of course, carbon dioxide. But one can only put forward hypotheses about the mechanism of the "memory."

In a stochastic scheme, the displacement of a particle must contain an aggregate of steps. Among them there must be steps with unequal probabilities of displacement to the left and to the right. This corresponds to the necessity for the particle to overcome stable condensations and rarefactions of the medium, characteristic only of the critical point of a pure substance. The probability of displacement of a particle, in contrast to motion in a homogeneous (i.e., rapidly relaxing) medium, decreases sharply (8).

In connection with the problem of "memory," the authors consider it interesting to repeat Perrin' s famous experiments, but with one essential difference. The Brownian motion of a colloidal particle should occur not in water but, for example, in carbon dioxide at its critical point. The mole fraction of colloidal particles will, of course, be many orders of magnitude smaller than the mole fraction of iodine. But it has already been pointed out that, for the critical point of liquid-gas equilibrium, equation (1) is valid in the limit (see equation (3)). Equation ($2'$) is also valid in the limit (see equation (4)). Therefore there is reason to expect that the colloidal particle will be "jostled" in place not only at the critical point of carbon dioxide itself, but also in the neighborhood of this point.

In repeating Perrin' s experiments it is important to trace how the dependence between the mean-square displacement of the colloidal particle and time changes as the experimental conditions approach the critical parameters of carbon dioxide.

Fluctuations in the number of molecules of the dissolved substance in a fixed volume are also an expression of Brownian motion. In consequence of the validity of equations (1) and (2), these fluctuations should be large at the critical point of a binary solution (see, for example, (4)), but

because, owing to the very long "trampling" of molecules in place, these fluctuations occur very slowly and rarely.

Hence there follows the general proposition: where large fluctuations are possible, there they are established slowly and dissipate slowly.

At the critical point of liquid-gas equilibrium in a very dilute solution of iodine (J_2) in carbon dioxide, illumination with ultraviolet light causes photodissociation of iodine molecules into atoms ([9]). The energy of an ultraviolet-light quantum is greater than the energy of the $J—J$ bond. The iodine atoms acquire excess kinetic energy (in comparison with thermal energy) and fly apart. Then, having given up the excess kinetic energy to the solvent, the iodine atoms become Brownian particles and "trample" in place.

As a result of photodissociation, the binary system $CO_2—J_2$ is transformed into a ternary (metastable) system $CO_2—J_2—J$. The ternary system has a different critical temperature (it was measured) than the original binary system. The displacement of the critical temperature slowly (over 1 hour, over 2 hours) disappears as a consequence of recombination of iodine atoms into iodine molecules (under noncritical conditions recombination occurs practically instantaneously). Thus, at the critical point the probability of encounter of iodine atoms is sharply reduced.

It seems interesting, in addition to Perrin's experiments, also to repeat Svedberg' s experiments on fluctuations in the number of colloidal particles in a fixed volume (again at the critical point of carbon dioxide). One may expect that these fluctuations, like fluctuations of iodine atoms, will occur slowly and rarely. If this assumption is correct, then coagulation of smoke (fog) at the critical point of carbon dioxide should proceed very slowly.

There is a great analogy between Brownian motion and thermal electrical noise ([10]). The mechanism of energy exchange is similar in both cases. Using this analogy, one can derive Nyquist' s formula. It is known to be analogous to Einstein' s equation for the mean-square displacement of a Brownian particle ([10]).

Einstein' s equation, in the authors' opinion, should change at the critical point (and in the vicinity of the critical point). Will the critical point of a binary solution introduce changes also into Nyquist's formula? What will these changes consist of (if they occur at all)?

A conductor for measurements could be, for example, a dilute solution of ammonium chloride in ammonia near the critical point of liquid-gas equilibrium for this solution.

The critical point of a binary solution has a sharply expressed influence on fluctuations: the rate of fluctuations falls strongly; a strongly expressed temporal autocorrelation of thermal fluctuations arises. An experimental study of fluctuations at the critical point of a binary solution by various methods appears interesting to the authors.

Belorussian Technological Institute
named after S. M. Kirov

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