

Lower critical point for the stratification of a liquid solution: dependence on the energy and lifetime of intermolecular bonds

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A non-Markov process of the formation and rupture of hydrogen bonds leads to stratification of a solution at high temperatures if the product of the energy and lifetime of a hydrogen bond exceeds a certain threshold. This threshold is calculated.

A fairly large number of solutions behave in the opposite way compared to their usual behavior as their temperature T changes: The stratification into two phases, rich in different components, occurs during heating rather than cooling (see, for example, Ref. 1). The T - x phase diagram of such solutions (x is the concentration of one component) typically has a minimum stratification temperature $T_L(x_L)$, at which concentration fluctuations grow anomalously (there is a second-order phase transition with a lower critical point). In certain solutions the stratification region is closed; i.e., there is also an upper critical point $T_H(x_H) > T_L(x_L)$, above which the solution becomes uniformly mixed again. There are grounds for believing that in both cases the solution has—in addition to the region with a lower critical point—a low-temperature stratification region with an upper critical point, which cannot be observed because it lies below the melting point.

Infrared absorption spectra clearly show that essentially all solutions which have a lower critical point are comprised of molecules which form relatively strong intermolecular bonds H...O, H...F, and H...N, and which form associations that survive for a finite time. This point gives rise to difficulties in constructing a theory for solutions with a lower critical point. The only success which has been achieved so far in this direction has been to work from a phenomenological expansion of the Landau type for a thermodynamic potential, i.e., to postulate the existence of a lower critical point.² At the moment, the difficulties in constructing a theory of associated solutions from first principles look quite formidable (suffice it to say that constructing such a theory will require, in particular, solving a nontrivial percolation problem). It is therefore worthwhile to develop intermediate-level models. We present one such model below.

We start from a virial expansion of the mixing free energy:¹

$$F_m = T[N_1 \ln N_1 + N_2 \ln N_2 - (N_1 + N_2) \ln(N_1 + N_2)] \\ - (u_{11}N_1^2 + 2u_{12}N_1N_2 + u_{22}N_2^2)/2(N_1 + N_2), \quad (1)$$

where $N_{1,2}$ are the number of molecules of the two species, and $u_{i,j}$ are their interaction energies. A variation of (1) describes a stratification curve with an upper critical point. Assuming $u_{11} \approx u_{22} = u$, $u_{12} = v$ for simplicity, we find the binodal $\mu_1 - \mu_2 = \partial F_m / \partial N_1 - \partial F_m / \partial N_2 = 0$:

$$\Theta_b = 1 - y^2/3, \quad (2)$$

where $\Theta = T/T_c$, $T_c = (u - v)/2$, $y = 2x - 1 \ll 1$, and the concentration is $x = N_1/(N_1 + N_2)$. The relaxation equation corresponding to a variation of (1) near the critical value of the concentration, $x_c = 1/2$, is

$$\gamma_x \dot{y} = (T_c - T)y - Ty^3/3, \quad (3)$$

where $\gamma_x \sim \tau_x T_c$ is a generalized viscosity constant, and τ_x is a diffusion time.

To take the effects of hydrogen bonds into account, we introduce a dichotomic noise³ in the energy (v) of the cross interaction (a typical example is an N...H bond between molecules of water and pyridine compounds). For simplicity we assume that u is a constant (a complete analysis will be the subject of a comprehensive paper). This assumption means that we have $v = v_f + \xi$, where v_f is a long-range energy, and the quantity ξ takes on the two values $\xi = 0$ and $\xi = v_b$, where v_b is the binding energy. The average value is $\langle \xi \rangle = qv_b$, where q is the bond-formation probability (we assume that this probability is independent of T , so that we can pursue our approximate analysis to completion). We assume a correlation energy

$$\langle \xi(t)\xi(t - \tau) \rangle = q(1 - q)v_b^2 \exp(-\tau/\tau_b). \quad (4)$$

Here τ_b is the lifetime of the hydrogen bond (the time interval between spontaneous ruptures of the bond). A stochastic equation corresponding to Eqs. (3) and (4) is

$$2\gamma_x \dot{y} = (u - v_f - 2T)y - 2Ty^3/3 - \xi y. \quad (5)$$

The stochastic process introduced here is very non-Markovian.³ The corresponding Fokker-Planck equation contains nonlinear operators of the $\exp(-\partial/\partial x)$ type.

We construct a complete time-dependent Fokker-Planck equation corresponding to Eq. (5) on the basis of the theory of Ref. 3 [see Eq. (9.33) of that paper]. From the steady-state limit ($t \rightarrow \infty$; to save space, we omit the clear but lengthy expression for the steady-state distribution function) we find a stratification curve: an equation which relates the concentration y and the temperature Θ for an extremum of the steady-state distribution function. This equation contains as parameters q , $\epsilon = v_b/(u - v_f)$, and $\nu = \tau_b/\tau_x$:

$$y^2 \approx [\nu\Theta^2 - (1 + 2\nu - \epsilon\nu)\Theta + (1 + \nu - q\epsilon - \epsilon\nu)]/[\Theta(1/3 + 2\nu - \epsilon\nu - 2\nu\Theta)]. \quad (6)$$

This equation, with separable variables, explicitly determines the square concentration y^2 as a rational function of the temperature Θ which can easily be tabulated. We therefore construct the stratification curve $\Theta(y)$ simply for the function which is the inverse of $y^2(\Theta)$ from (6).

Under the conditions $\nu \ll 1$ and $q \ll 1$ (a transition to a regular problem: a short-lived weak bond), we find Eq. (2) from (6). Here we have a realization of a stratification region with an upper critical point (Fig. 1). The nature of the phase diagram changes in a qualitative way at a threshold value of the parameter $\epsilon\nu$. At

$$\epsilon\nu \geq 1 - 2q - 2(1 - 9q + 9q^2)^{1/2}/3, \quad (7)$$

a lower critical point arises, and the stratification region becomes closed. We wish to repeat that the rupture and formation of bonds constitute a non-Markovian process: A

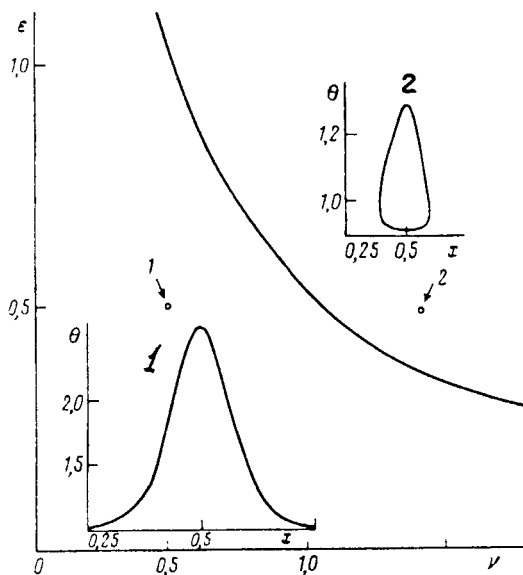


FIG. 1. Transition to stratification with a lower critical point as the parameter $\epsilon\nu$ increases. The stratification curves in the insets are plotted for $q=0.1$ and either $\epsilon=0.5$ (1) or 1.43 (2). Curve (7) ($q=0.1$) separates characteristic regions of (ϵ, ν) .

calculation with a white noise analogous to that carried out above with a dichotomic noise leads to an ordinary diagram with an upper critical point for all values of the parameters of the white noise.

Estimate (7) shows that the effect of the mechanism described here for a "floating" of the stratification region on the $T-x$ diagram is completely realistic for known association solutions, for which typical values of the hydrogen-bond energy ν_b are 8–40 kJ/mole (ranging from the relatively weak H...N bond to the strongest bond, H...F) (Ref. 4). The diffusion time for a solution is on the order of $\tau_x \sim a^2/D$, where $a \sim 3 \text{ \AA}$ is the average distance between molecules, and $D \sim 10^{-5} \text{ cm}^2/\text{s}$ is the diffusion coefficient. In other words, we have $\tau_x \sim 10^{-10} \text{ s}$. This figure is one or two orders of magnitude longer than the bond lifetime, which is comparable to the time scale for dielectric relaxation. The parameter $\epsilon\nu$ is therefore greater than one in nearly all association solutions, which accounts for a lower critical point.

¹A. A. Vedenov, *Physics of Solutions* [in Russian] (Nauka, Moscow, 1984).

²A. A. Sobyenin, *Usp. Fiz. Nauk* **149**, 325 (1986) [*Sov. Phys. Usp.* **29**, 570 (1986)].

³W. Horsthemke and R. Lefever, *Noise-Induced Transitions* (Springer-Verlag, New York, 1983).

⁴D. Eisinger and W. Kauzmann, *Structures and Properties of Water* (Oxford Univ. Press, London, 1969).

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