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SYSTEMS NEAR THE CRITICAL POINT

By Ya. B. Zel'dovich and O. M. Todes

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THE KINETICS OF FORMATION OF TWO-PHASE SYSTEMS NEAR THE
CRITICAL POINT

[Following is the translation of an article by Ya. B. Zel'dovich and O. M. Todes entitled "Kinetika Obrazovaniya Dvukhfaznykh Sistem Vblizi Kriticheskoy Tochki (English version above) in Zhurnal Eksperimental'noy i Teoreticheskoy Fiziki (Journal of Experimental and Theoretical Physics) Vol. 10, No. 12, 1940, pp 1441 -- 1445.]

The process of stratification of a substance which is in an unstable state relative to small changes near the critical point, is considered. Of importance for the stratification time is the rate of heat exchange, and the distance of heat transfer and the value of the temperature gradient are estimated from the capillarity theory.

Limiting relations for the stratification times are obtained by expanding the thermodynamic quantities in powers about the critical point.

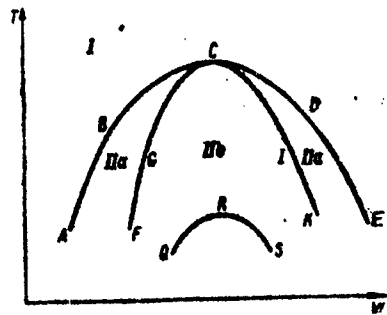


Fig. 1

1. Region of Unstable States

We consider the line ABCDE (Fig. 1), which separates (in the V, T plane) the region I, in which thermodynamic equilibrium corresponds to a single-phase system, from region II, in which the system breaks up in thermodynamic equilibrium into two phases (liquid and vapor).

Going over to an arbitrary point B on this line, we enter near the latter into part of region II, which we shall call region IIa. In this region the single-phase system is unstable relative to the formation of the new phase, which differs essentially in its properties from the initial phase B; in Fig. 1, the second phase thus produced is represented by the point D. The occurrence of an essentially different new phase is connected, as is well known, with the need of consuming surface energy; these considerations have led Gibbs to the concept of the critical dimension of the nucleus of the new phase and to an explanation of the considerable stability of the single-phase system near the boundary curve ABCDE. An experimental disturbance to super cooled vapor or to super heated liquid is actually connected with such extraneous factors as the presence of contaminating dust particles, ions, etc. In the terminology of Gibbs, IIa is the region of states which are stable under small changes in the phase, but are unstable under the occurrence of a new different phase.

In the geometrical treatment, the line ABCDE represents a projection on the plane V, T of the line of intersection of two surfaces of chemical potential. However, on each surface separately, this line of intersection does not correspond to any singularity, from which we see, in particular, the stability of the states which are close to the boundary line ABCDE, relative to small changes in the phase.

Near the critical point, in which the difference between the existing phases in equilibrium vanishes, there is a region IIb of states which have very remarkable properties. Thus, in the region IIb

$$\left(\frac{\partial p}{\partial v}\right)_{T=\text{const}} > 0,$$

whereas on the boundary of the region IIb, along the line FGCIK, and in particular at the critical point C, we have

$$\left(\frac{\partial p}{\partial v}\right)_T = 0.$$

This region is already the region of states which are unstable relative to small changes in phase (Gibbs).

In region IIb, changes in the states, no matter how small, will increase and will lead as a result into the separation of the system into two phases. At the same time, in region IIa, small changes of the state decrease, and ^{disappear} completely as in any stable state I. In the region IIa the stratification takes place, as already indicated, only after the formation of a nucleus, which the parameters that characterize the state (specific entropy, specific volume) differ by

a finite amount from their values in the initial state in the region of finite volume.

The instability with respect to small changes in states, in which

$$\left(\frac{\partial p}{\partial v}\right)_T > 0,$$

is directly obvious, for the reduction in the volume -- compression -- leads to a decrease in the pressure and a further compression.

We consider below specifically the speed of stratification of a system in state IIb, confining our investigation to the only case of physical interest, that of states close to the critical point.

2. The Heat Transfer Determines the Speed of Stratification

A fact which is essential for the question under consideration at the critical point, where $(\partial p / \partial v)_T = \text{const}$ reverses its sign and passes through zero, the value of $(\partial p / \partial v)_S = \text{const}$ experience no essential changes and remains negative.

Thus, an adiabatic compression of certain elements of volume and the expansion of others will lead to an increase in pressure in the compressed parts of the volume and to a drop in pressure in the expanding ones, and consequently, to a reverse equalisation of these changes, relative to which the single-phase system is stable even in region IIb. The instability indicated in the end of the preceding section for the states in region IIb pertains only to isothermal

processes. An isothermal change in the state is connected with a change in the entropy, and consequently, requires heat exchange between the expanding and compressing elements of the volume.

The process of stratification of a system into two phases in region IIb is thus connected with motion of matter and with heat transfer. For a single-component system, the first process does not require any molecular transport, and is realized by molal motion of masses and is therefore quite rapid compared with the second process — heat transfer. (In the case of the critical point for binary mixtures (for example, water-phenol), the appearance of which is connected with the separation of a homogeneous solution into two phases of different composition, one can expect that the limiting factor will be, to the contrary, not heat transfer, but the process of transfer of matter, realized by molecular diffusion.) Therefore, in the process of disintegration of the states in region IIb, one can consider the pressure to be instantaneously equalized in practice. Further calculations of the heat transfer will involve the specific heat at constant pressure. The instability of the system relative to small changes in state is reflected in the singular behavior of the specific heat. According to the relation

$$\frac{C_p}{C_v} = \frac{(\partial p / \partial v)_s}{(\partial p / \partial v)_T} \quad (1)$$

the change in the sign of $(\partial p / \partial v)_T$, passing through zero, implies a change in the sign of C_p with transition through $\pm \infty$. It is

seen therefore that in the region IIB the specific heat C_p is negative. The change in the sign of the specific heat in the equation of heat conduction is formally equivalent to a change in the sign of the time; instead of ordinary exponentially decreasing solutions, describing the equalization of the temperature, we obtain exponentially increasing temperature differences, which lead to a stratification into two phases with subsequent equalization of temperature after the limiting line FGCIK is reached.

The amplitude of the primary fluctuation, the exponential growth of which leads to stratification into two phases, will enter into the expression for the time of stratification logarithmically, and therefore is of no importance in the approximation adopted in our paper.

Let us expand the free energy F , the pressure p , and the thermodynamic potential Φ in powers of the distance to the critical point (in variables V and T) about the critical point.

$$F = F_0(T) - p_k(V - V_k) - a(T - T_k)(V - V_k) + b(T - T_k)(V - V_k)^2 + d(V - V_k)^4 \quad (2)$$

$$p = p_k + a(T - T_k) - (V - V_k)[2b(T - T_k) + 4d(V - V_k)^2] \quad (3)$$

$$\Phi = F_0 + pV_k - b(T - T_k)(V - V_k)^2 - 3d(V - V_k)^4. \quad (4)$$

In the V, T plane, the equation of the boundary line ABCDE is determined from the conditions $p_1 = p_2$ and $\Phi_1 = \Phi_2$. This yields

$$v_{1,2} = v_k \pm \sqrt{\frac{b(T_k - T)}{2d}}. \quad (5)$$

To the contrary, for the line FGCIK, along which $(\partial p / \partial v)_T = 0$, we have

$$v_{\text{sat}} = v_k \pm \sqrt{\frac{b(T_k - T)}{ad}} \quad (6)$$

(6)

Both lines are parabolas near the critical point, tangent to each other at the point C (Fig. 1). The specific heat is

$$C_p = C_v + T_k \frac{[a + 2b(V - V_k)]^2}{2b(T - T_k) + 12d(V - V_k)^2} \approx \frac{a^2 T_k}{2b(T - T_k) + 12d(V - V_k)^2} \quad (7)$$

It actually goes to $\pm \infty$ on the line FGCIK and is negative near this line in the region IIb.

3. Time of Stratification

An estimate of the time of stratification, from a consideration of the equation of heat conduction

$$\rho C_p \frac{\partial T}{\partial t} = K \Delta T \quad (8)$$

($\rho = 1/V$ is the density and K is the coefficient of heat conduction) requires the determination of the characteristic dimension l , i.e., the geometric dimensions of those regions, on which the homogeneous initial system is stratified. The sought time is, in order of magnitude,

$$\tau \approx \frac{F |C_p| l^2}{k} = \frac{F |C_p|}{k v} \quad (9)$$

The stratification is the faster, the farther away we are from the critical point, where $|C_p| \rightarrow \infty$; it is also the faster, the smaller the critical dimension λ . An estimate of the minimum dimension λ requires the use of additional considerations.

We shall use the classical theory of capillarity near the critical point. The law of variation of surface tension on the boundary between liquid and vapor σ near the critical point

$$\sigma = a(T_c - T)^{3/2} \quad (10)$$

is derived from this theory from ideas concerning the term in the thermodynamic potential, dependent on the density gradient. From symmetry considerations it follows that

$$\Phi = \Phi(T, v) + n^2 (\nabla v)^2. \quad (11)$$

It is obvious that the added term insures a continuous change in state on the separation boundary of the two phases. The effect of width of the separation boundary is determined from the condition of minimum of thermodynamic potential of the system $\Psi = \int_0^M \phi \, dm$ (integral over the entire mass of the substance M).

Everywhere, except on the separation boundary between the two phases, $v = v_1$ or $v = v_2$ [see (5)]; $\phi = \phi(v_1, T) = \phi(v_2, T) = \phi_0$.

In a surface layer having a volume $\Omega \lambda$ there is contained a mass

$\Omega \lambda / v_k$; we put there

$$\Phi(V, T) = \Phi\left(\frac{v_1 + v_2}{2}, T\right) = \Phi(v, T) =$$

$$\phi_0 + \frac{b}{d} (T_c - T)^2 \quad [\text{cp. (4), (5)}] \quad \nabla V = \frac{v_1 - v_2}{\lambda} = \frac{2}{\lambda} \sqrt{\frac{b(T_c - T)}{2d}}$$

Denoting $\Psi_0 = \phi_0 M$, we obtain

$$\Psi = \Psi_0 + \frac{\Omega}{v_k} \left[\frac{bl}{d} (T_c - T)^2 + \frac{2n^2 b}{d\lambda} (T_c - T) \right], \quad (12)$$

where Ω is the total area of the separation boundary of the two phases. From this we obtain

$$\tau = \frac{n^2}{b(T_k - T)}, \quad \sigma = \frac{nb^{3/2}}{dv_k} (T_k - T)^{3/2} = a(T_k - T)^{3/2}. \quad (13)$$

By comparison of the obtained limiting laws (5), (7) and (10) with the experimental data on surface tension, specific volume, and specific heat near the critical point, we obtain the coefficients n , b , and d which are involved in the calculation. The relaxation time of interest to us is

$$\tau = \frac{1}{kv_k} \frac{n^2}{b(T_k - T)} \frac{a^2 T_k}{2b(T_k - T) - 12d(V - V_k)^2}. \quad (14)$$

Assume that we obtain a state in the region IIb by adiabatic expansion of the gas such that the adiabat passes exactly through the critical point. Here we have near the critical point along the adiabat

$$\left. \begin{aligned} v - v_k &\sim a(T_k - T), \\ d(V - V_k)^2 &\ll 2b(T_k - T) \end{aligned} \right\} \quad (15)$$

and the stratification time of the system is

$$\tau \sim (T_k - T)^{-2}. \quad (16)$$

4. Estimate of Order of Magnitude of the Stratification Time

Accurate to numerical factors, let us express the coefficients contained in (14) in terms of the critical constants of the substance. As can be seen from the dimensionalities

$$a \cong \frac{P_k}{T_k}; \quad b \cong \frac{P_k}{V_k T_k}; \quad \text{and} \quad d \cong \frac{P_k}{V_k^2} \quad (17)$$

Furthermore, we put approximately

$$a \cong \frac{\sigma_0}{T_k^{3/2}} \quad (18)$$

where σ_0 is the surface tension with $T \ll T_k$. Substituting (17) and (18) in (14), we get

$$\tau \cong \frac{\sigma_0^2 T_k}{k P_k (T_k - T)^2} \quad (19)$$

For water in absolute units $\sigma_0 \cong 80$, $T_k \cong 600^\circ \text{K}$, $P_k \cong 2 \times 10^8$ and $K \cong 10^4$, we obtain

$$\tau \cong \frac{2 \cdot 10^{-8}}{(T_k - T)^2} \quad (20)$$

It must be noted here that in the derivation of (20) we omitted everywhere the numerical factors which, upon accumulation, can considerably increase τ . If we use in the determination of a , b , and d the expansion of the Van der Waals equation near the critical point, we obtain for formulas (19) and (20) a factor $2^{16} \times 3^{-3} \cong 2,000$.

A further refinement of the width λ and determination of the time τ can yield additional numerical factors.

5. Unattainable States

We note that far inside the region IIb one can also imagine states for which not only $(\partial P/\partial V)_T > 0$, but also $(\partial P/\partial V)_S > 0$.

However, such states are not only unstable, but unattainable at all. Actually, according to (1), on the very boundary of this region the specific heat C_p vanishes, and according to (9) the stratification time also vanishes. Thus, as one penetrates deeper into the region II, the time of stratification becomes shorter and shorter and on the line QRS the stratification should occur practically instantaneously.

In the case when the single-phase system is accurately described by the Van der Waals equation of state, the position of the curve QRS was calculated in 1937, at our suggestion, by student A. S. Viglin of the Leningrad Industrial Institute. It was found that the minimum R of the curve QRS is located precisely under the maximum of the boundary curve, i.e.,

$$V_R = V_R; \quad T_R = T_R \frac{C_v}{C_v + R} = T_1 \frac{C_v}{C_v} \quad (21)$$

Leningrad, Institute of Chemical

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