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SINGULARITY OF THERMODYNAMIC QUANTITIES AT A FIRST ORDER PHASE TRANSITION POINT

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It is shown that the thermodynamic potential of a liquid has a singularity at the boiling point. This singularity, however, is such that all derivatives of the thermodynamic potential with respect to temperature remain finite. Fluctuation formation of gas bubbles is the mechanism which causes the singularity.

It is well known that the chemical potentials of the two phases of a substance are equal at a first-order phase-transition point. Let us consider for definiteness a transition between liquid and gaseous phases. The boiling temperature of the liquid T_b is defined by the relation

$$\mu_1(T_b) = \mu_2(T_b), \tag{1}$$

where $\mu_1(T)$ and $\mu_2(T)$ are the chemical potentials of the liquid and gaseous phases, respectively, considered as functions of the temperature T for fixed pressure. When $T < T_b$ the chemical potential of the liquid is smaller than the chemical potential of the gas; therefore the liquid phase is absolutely stable. For a transition in the region $T > T_b$ the gaseous phase is energetically more favorable, and the liquid becomes metastable. The metastable phase is not, strictly speaking, stable since it goes over into the more favorable phase, although with a very long relaxation time. As is well known, this transition takes place because once the gas bubbles produced in the liquid as the result of fluctuations appear, they do not disappear but become evaporation centers of the liquid.

It is natural that gas bubbles should also form in the liquid when $T < T_b$, except that any such bubble will eventually disappear. Therefore a certain average number of bubbles per unit volume of the liquid exists at temperatures below the boiling temperature, and these give a certain completely definite contribution to thermodynamic quantities. Thus the bubbles introduce a finite contribution to the thermodynamic potential of the liquid when $T < T_b$, and cause instability of the liquid phase when $T > T_b$. The point $T = T_b$ is therefore a singular point for thermodynamic functions of the liquid (derivatives of certain order of the thermodynamic potential with respect to temperature could, for example, become infinite at $T = T_b$). The question arises of elucidating the nature of this singularity.[1]

The probability for the formation of a bubble is determined by the minimum amount of work

$$\Delta W = \Delta E - T\Delta S + P\Delta V, \tag{2}$$

which must be expended for its creation. Expression (2) for ΔW can be transformed into the form (see [1]):

$$\Delta W = (4\pi/3v)\,[\mu_2(T) - \mu_1(T)]\,R^3 + 4\pi\sigma R^2, \tag{3}$$

where R is the radius of the bubble, σ is the coefficient of surface tension at the gas-liquid boundary, v is the volume of one particle in the gas.

μ_2 will be less than μ_1 for $T > T_b$; therefore the derivative $\partial\Delta W/\partial R < 0$ for sufficiently large values of R, i.e., sufficiently large bubbles will eventually increase in size. Conversely, for $T < T_b$ any bubble will eventually disappear. Evidently, for the average number n(R) of bubbles of radius R per unit volume we have when $T < T_b$

$$n(R) \sim \exp[-\Delta W(R)/T]. \tag{4}$$

Each bubble of radius R introduces the following contribution to the thermodynamic potential:

$$\varphi(R) = a(T_b - T)R^3 + bR^2, \tag{5}$$

where a and b are positive constants. We have taken into account that near T_b the difference

$$\mu_2(T) - \mu_1(T) = q(T_b - T)/T_b, \tag{6}$$

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[1] The notion that a first-order phase-transition point must be singular for thermodynamic quantities was expressed by L. P. Pitaevskiĭ.

where q is the latent heat of the transition.

Now we obtain for the total contribution of the bubbles to the thermodynamic potential $\Delta\Phi$

$$\Delta\Phi = V\int_0^\infty 4\pi R^2 dR\varphi(R)\,n(R), \qquad (7)$$

where V is the volume. It is evident from Eqs. (4) and (7) that $\Delta\Phi$ is determined by an integral of the form

$$\int_0^\infty R^m \exp\left\{-a\frac{T_b - T}{T_b}R^3 - \frac{b}{T_b}R^2\right\} dR. \qquad (8)$$

If $T > T_b$ this integral diverges because the liquid state is unstable in this region. As $T \to T_b - 0$, the derivatives (of all orders) of $\Delta\Phi$ with respect to temperature approach finite limits. Let us calculate $d^n\Phi/dT^n$ $(T = T_b - 0)$ for large values of n. (The derivatives with $n \sim 1$ cannot be calculated on the basis of (8) because values of R of the order of an atomic distance give the major contribution to the corresponding integrals.) With the aid of (8) it is easy to obtain, using the well-known asymptotic representation of the Γ-function for large values of the argument,

$$d^n\Phi\,(T_b - 0)/dT^n \approx (-aT_b^{1/2}/b^{3/2})^n \sqrt{n}\,(3n/2e)^{3n/2}. \qquad (9)$$

This means that the Taylor series for Φ in powers of $T - T_b$ is an asymptotic, and not a convergent series.

The function of the complex variable $\tau = T_b - T$ which appears upon analytic continuation of the integral (8) has an essential singularity at the point $\tau = 0$. In particular, for $\tau = i\eta$ $(\eta \to \pm 0)$ this function increases exponentially like $\exp(\mathrm{const}/\eta^2)$.

Thus the thermodynamic potential and also the other thermodynamic quantities along with it have a singularity at $T = T_b$. This singularity, however, is very weak (all derivatives of Φ with respect to temperature remain finite) and apparently cannot be observed experimentally.

In conclusion I express my gratitude to L. P. Gor'kov, L. P. Pitaevskiĭ and I. M. Khalatnikov for a helpful discussion.

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[1] V. G. Levich, Vvedenie v statisticheskuyu fiziku (Introduction to Statistical Physics), Gostekhizdat, 1954, p. 347.

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