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ON THE STATISTICAL THEORY OF PHASE TRANSFORMATIONS
OF THE FIRST ORDER

(K Statisticheskoi Teorii Fazovykh Prevrashchenii
Pervogo Roda)

by

B. T. Geilikman

Translated by

E. Rabkin

OTTAWA
1 June, 1950

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Physics

ON THE STATISTICAL THEORY OF PHASE TRANSFORMATIONS
OF THE FIRST ORDER

by

B. T. Geilikman

(Presented by M. A. Leontovich 31 Aug. 1949)

Translated by Esther Rabkin.

The presently existing theory of the condensation of gases (¹⁻⁴) has, as is known, a number of shortcomings (for example the horizontal section of the curve $p-v$ cannot be converted into a curve for liquids, etc.). We will show that, using this theory, it is possible to develop a general theory of phase transformations of the first order and that the description of the condensation in (¹⁻⁴) is faulty.

If we express the sum of states of a system, consisting of mutually interacting particles, in the form

$Z = \frac{1}{\lambda^{3N}} Q$, $\lambda = \frac{h}{\sqrt{2\pi m k T}}$, then, as is known (¹):

$$Q = \sum_{m_1} \prod_1 \frac{(N v b_1)^{m_1}}{m_1!}, \quad \sum_{l=1}^N l m_l = N, \quad v = \frac{V}{N}. \quad (1)$$

In the classical case for short-range forces:

$$b_1(T) = \frac{1}{1^N V} \int S_1(r_1, \dots, r_1) \prod_{i=1}^1 dV_i;$$

$$S_1 = \sum_{1 \geq i \geq j \geq 1} \prod (e^{-U(r_{ij})/kT} - 1); \quad \frac{\partial b_1}{\partial V} = 0.$$

b_1 is expressed through "irreducible" integrals
 $B_v(T)$:

$$b_1 = \frac{1}{1^2} \sum_{\mu_v} \prod_v \frac{(1\beta_v)^{\mu_v}}{\mu_v!}; \quad \sum_{v=1}^{1-1} v\mu_v = 1 - 1. \quad (2)$$

Considering that (see (3)):

$$\frac{1}{2\pi i} \oint_C \zeta^{n-1} d\zeta = \delta_n, \quad 0 = \begin{cases} 1 & \text{at } n = 0, \\ 0 & \text{at } n \neq 0, \end{cases}$$

we can write (1) in the form:

$$Q = \frac{1}{2\pi i} \prod_1 \sum_{m_1} \frac{(Nvb_1)^{m_1}}{m_1!} \oint_C \zeta^{\sum 1m_1 - N} d\zeta,$$

where the summation with respect to each m_1 now can be carried out independently of each other:

$$Q = \frac{1}{2\pi i} \oint_C \prod_{l=1}^N \sum_{m_l=0}^{[N/l]} \frac{(N v b_1 \zeta^l)^{m_l}}{m_l!} \frac{d\zeta}{\zeta^{N+1}} = \frac{1}{2\pi i} \oint_C \frac{e^{N\phi(\zeta, vb, N, N)}}{\zeta^{N+1}} d\zeta, \quad (3)$$

where $[S]$ --is the whole range of S ;

$$\phi(\zeta, vb, M, L) = \frac{1}{M} \sum_{k=1}^L \ln P_{[L/k]}(M v b_k \zeta^k); \quad P_{[S]}(X) = \sum_{k=0}^{[S]} \frac{X^k}{k!}. \quad (4)$$

$\phi(\zeta, vb, N, N)$ does not have any poles (except $\zeta = \infty$) and branch points (since in (4) $\ln$ is taken as the main branch).

Similarly, for b_1 we obtain from (2):

$$b_1 = \frac{1}{2\pi i l^2} \oint_C \frac{e^{l\phi(\eta, \beta, l, l-1)}}{\eta^l} d\eta. \quad (5)$$

Of the formulae, used earlier and deduced differently ⁽³⁾, (3) and (5) differ by the fact that $N \neq \infty$ ($l \neq \infty$) in the expression

$$\phi\{\zeta, vb, N, N\} \{\phi(\eta, \beta, l, l-1)\}.$$

$$\left(\text{At } N \rightarrow \infty \quad \phi(\zeta, vb, N, N) \rightarrow v \sum_{l=1}^{\infty} b_l \zeta^l \right).$$

Equations (3) and (5) may be calculated either by the contour or by the method of a generating function ⁽⁴⁾ (this function may be selected in the form:

$$F(X) = \sum_{k=1}^{\infty} A_k X^k; \quad A_k = \frac{1}{2\pi i} \oint_C \frac{e^{k\phi(\zeta, vb, N, N)}}{\zeta^{k+1}} d\zeta).$$

Both methods give:

$$\frac{1}{N} \ln Q = \phi(z, vb, N, N) - \ln z + \varepsilon_N, \quad (6)$$

where $\varepsilon_N \rightarrow 0$, and z is the root of the equation
 $N \rightarrow \infty$

$$z \frac{d\phi(z, vb)}{dz} = 1, \quad (7)$$

which gives the largest modulus for $e^{\phi(z, vb)}/z$. The complex and negative roots should be neglected as is evident from (6).

$$b_1 = \frac{e^{l\phi(y, \beta, l, l-1) + l\varepsilon_1}}{l^2 y^{l-1}}, \quad (8)$$

where y is the root of the equation:

$$y \frac{d\phi(y, \beta)}{dy} = 1, \quad (9)$$

giving the largest modulus for $e^{\phi(y, \beta)}/y$.

By the method of contours we find: $\varepsilon_1 \approx -\frac{1}{2} \ln 1/l$.
 From (8) it is evident that (1) the radius of convergence of the z series $\phi(z, vb, \infty, \infty)$ is equal to (for temperatures at which they converge $\phi(y, \beta, \infty, \infty)$):

$$\bar{z} = |y_\infty| e^{-G_0(y_\infty, \beta)},$$

where $y_\infty = \lim_{l \rightarrow \infty} y$ and of the function G_λ are equal to:

$$G_\lambda(y, \beta) = \sum_{k=1}^{\infty} \beta_k y^k k^\lambda. \quad (10)$$

A simple analysis shows that in (6) and (7) we can proceed to the limit $N = \infty$ (for $z > 0$): 1) if all $b_1 > 0$ - only at $z \leq \bar{z}$ $\{\phi(z, vb, N, N) \approx N \ln \bar{z}/z$ at $z > \bar{z}\}$; 2) if b_1 are alternating in sign (this corresponds to $y < 0$ in (9)) - for all cases $z > 0$ (however, for the most interesting case $b_1 \approx y/1^{\frac{3}{2}} \bar{z}^{-1}$); moreover for $z > \bar{z}$ we must use the analytical continuation of the function $G_0(z, vb)$. It is evident that for $b_1 > 0$ a particular point $vG_0(z, b) = \phi(z, vb, \infty, \infty)$ is found on the positive axis, and for alternating in sign b_1 - on the negative axis. In the limit $N = \infty$:

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln Q = vG_0(z, b) - \ln z; \quad (11)$$

$$vG_1(z, b) = 1 \quad (12)$$

$$p = \frac{kT}{N} \frac{\partial \ln Q}{\partial v} = kTG_0(z, b). \quad (13)$$

We will determine the conditions necessary for phase transitions. Q is determined by the root z_1 (12), which gives the smallest value for $ze^{-vG_0(z, b)}$. z_1 appear to be functions of v , T , and if in one region v , T , the smallest value of ze^{-vG_0} , that is the configuration free energy $F_q = NkT(\ln z - vG_0)$, gives a root $z_1(v, T)$, then in another region the smallest value for F_q can give a root $z_2(v, T)$. Since the functional variation of z_1 and z_2 from v , T , is generally speaking, different, then $Q(v, T)$ in these regions will be expressed by different functions v , T , which corresponds to two different phase states (the gaseous phase corresponds to the root of (12) which approaches zero at $v \rightarrow \infty$).

The condition of equilibrium of two phases appears to be the equality of pressures (in addition to the equality of temperatures). Therefore, for the investigation of a phase equilibrium it is more convenient to go over from the general

sum of states $Z(v, T)$ to $Z'(p, T)$, which may be achieved by including a movable piston ($\bar{s}$):

$$Z' = \frac{1}{h} \int dp_v dv \cdot Z(v, T) e^{-p_v^2/2Nm kT - pV/kT}. \quad (14)$$

In correspondence with (6) $Z(v, T)$ may be written as a sum:

$$Z(v, T) = \frac{1}{\lambda^{3N}} \sum_{i=1} e^{N[vG_0(z_i) - \ln z_i + \epsilon_N]}$$

($\phi(z_i, vb, N, N) \approx vG_0(z_i, b)$ in the region of convergence $G_\lambda(z, b)$), which in view of the fact that $N \gg 1$, may be reduced in each region v, T to a single - largest - term;

$$Z' = \frac{1}{N^2 \lambda^{3n+1}} \int_0^\infty \sum_i e^{N[vG_0(z_i) - \ln z_i - pv/kT + \epsilon_N]} dv;$$

$N \gg 1$, therefore the expressions under the integral must have a sharp maximum at $v_1(p, T)$, determined by equating to zero the derivative of the exponent with respect to v :

$$\frac{p}{kT} - G_0\{z_1(v)\} = 0 \quad (15)$$

{(15) coincides with (13)}. In fact, the second derivative

$$\frac{1}{v} \frac{\partial \ln z_i}{\partial v} = kT \left(\frac{\partial p}{\partial v} \right)_T$$

is always negative, if the phase is stable ($\partial p / \partial v < 0$).

Thus: $Z^0(p, T) =$

$$\frac{1}{\lambda^{3N+1}} \sum_1 e^{N[v_1(p, T)G_0\{z_1(p, T), b\} - \ln z_1(p, T) - pv_1(p, T)/kT]} \psi(z_1) \quad (16)$$

In each region p, T the largest value for $e^{v_1 G_0 - \ln z_1 - pv_1/kT}$ gives one of the roots z_1 , that is one term of the sum (16). The equilibrium of two phases is possible only for the condition $v_1 G_0(z_1) - \ln z_1 - pv_1/kT = v_2 G_0(z_2) - \ln z_2 - pv_2/kT$, that is, for the general condition of the chemical potentials being equal: $\mu_1 = \mu_2$ ($\ln z_1 = \ln z_2$). If N is small, then for a small region near the phase curve ($z_1 = z_2$), Z^0 would be determined by both terms of the sum (16), that is, the phase transition would be somewhat diffused. Thus, the sharpness of the phase transition is connected with very large values of N .

A necessary condition of the possibility of phase transitions of the first order is the existence of more than one real positive root of equation (12). It is evident that if at any T all $b_1 > 0$, there exists only one real root. Phase transitions of the first order are possible, therefore, only in the case when b_1 is alternating in sign, which corresponds to the existence not only of forces of attraction but also of forces of repulsion between the molecules.

In the previous works (¹⁻⁴) the mechanism of phase transitions of the first order investigated in them, condensation, is assumed to be completely different. Let all $b_1 > 0$. Since $\partial z / \partial v < 0$ (¹), then z increases when v decreases. At some $v = v_k$ $z = \bar{z}$. It can be easily shown that z remains equal to $\bar{z}$ also at a further decrease in v . Therefore, at $v \leq v_k$ $p = kTG_0(\bar{z})$, that is $p(v) = \text{constant}$, since $\partial \bar{z} / \partial v = 0$ (if b_1 is independent of v).

It was considered that exactly this horizontal section of the curve $p - v$ corresponds to the equilibrium region of two phases: liquid and gaseous. However, it can be shown that $\partial p / \partial v = 0$ not only at $v \leq v_k$, but also at $v = v_k + 0$, that is, in contrast with experiment, the jump $\partial p / \partial v$ does not exist. The possibility of $\partial p / \partial v \neq 0$ at $v = v_k + 0$, which was assumed in (1-4), falls off with a correct consideration of $\phi(z, vb, N, N)$, but not with a consideration of $G_0(z, b)$ in (3). In addition, by calculating the density $\rho(r)$ as a function of coordinates in a weak external field, it can be shown that at $z = \bar{z}$ the subdivision surface between the phases does not exist. Thus, even at $z = \bar{z}$ ($v \leq v_k$) the system consists of one phase - the same as in a similar case of the Einstein condensation of an ideal Bose - gas (in this case $b_1 = \lambda^{3(1-1)} / 1^{\frac{3}{2}}$). That, which was earlier assumed as the point of condensation appears to be, therefore, a point of a transition of the third order

$$\left\{ \Delta \frac{\partial p}{\partial v} = \left(\frac{\partial p}{\partial v} \right)_2 - \left(\frac{\partial p}{\partial v} \right)_1 = 0, \right.$$

therefore, $\Delta C_v = 0$, etc. $\left. \right\}$.

This transition must be investigated in more detail. In the presence of repulsion between molecules located at small distances from each other, this is impossible at high and, apparently, even at fairly low temperatures. It must be noted that at b_1 alternating in sign, the same as in the case of an ideal Fermi-gas $\{b_1 = (-1)^{1-1} \lambda^{3(1-1)} / 1^{\frac{3}{2}}\}$, z , equal to $\bar{z}$, does not correspond to any phase transition (4).

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