

## On the Stability of a Homogeneous Phase. II Determination of the Limit of Stability

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On the basis of the general theory developed in reference 1, a criterion is given for the stability of a homogeneous phase. An analysis of the basic properties of a system in the vicinity of the limiting points of equilibrium is inquired into. Two examples of the application of the criterion for stability are considered.

### 1. THE CRITERION FOR STABILITY

THE determination of the limits of stability of a homogeneous phase, in particular, of the liquid state, is one of the most important problems of the statistical thermodynamics of molecular systems. This question was considered in connection with the theory of crystallization in the works of Tiablikov<sup>2</sup> and Vlasov<sup>3</sup>. However, the criteria of crystallization given in these works are in error. We will not delay here to consider this matter in detail. It is sufficient to note that Vlasov's theory leads to a positive value of  $dv/dT$  along the crystallization curve (see Fig. 4, p. 198<sup>3</sup>), which is manifestly contradictory to experiment<sup>4</sup>. A similar difficulty arises in Tiablikov's theory.

It will be shown in the present paper that the problem of the limit of the stability of a homogeneous phase can be solved in a general manner, one starting from the theory of the liquid state and based on a study of the radial distribution function. In what follows below we shall use the results and the symbols of the preceding communication<sup>1</sup>.

We shall start from the basic result of our earlier work<sup>1</sup>, according to which the absolute limit of stability of a homogeneous phase for a given temperature  $T$  is determined as the edge of a continuous band spectrum of eigenvalues of the volume parameter  $\lambda$  in Bogoliubov's equation for the radial distribution function under the "boundary condition"  $r(g(r) - 1) \rightarrow 0$  for  $r \rightarrow \infty$ . This leads to the following criterion for the stability of a homogeneous phase: the boundary value  $\lambda = \lambda_0$  is a

value of the parameter  $\lambda$  such that it makes the root of the equation

$$\lambda L(\gamma) = 1 \quad (\lambda > 0) \tag{1}$$

real with the imaginary part vanishing, that is,

$$\text{Im} \{\gamma_1(\lambda_0)\} = 0, \tag{2}$$

but such that there exists a neighborhood  $\delta\lambda$  of the point  $\lambda_0$  in which

$$|\text{Im} \{\gamma_1(\lambda_0 + \delta\lambda)\}| > 0. \tag{3}$$

The phase will accordingly be stable in a neighborhood  $\delta\lambda$  where (3) is fulfilled. There are two possible cases:

1. Condition (3) is fulfilled only on one side of  $\lambda_0$ , that is, only for  $\delta\lambda > 0$  or for  $\delta\lambda < 0$ . Then we have a "normal" boundary point of the type of crystallization, vaporization or condensation of a gas, where a homogeneous phase is possible only for smaller (greater) densities and impossible for greater (smaller) densities.

2. Condition (3) is fulfilled on both sides of  $\lambda_0$ . The point  $\lambda_0$  is an isolated unstable point on the isotherm. This is an instability of the type of the critical point.

In Eq. (1) we have used the designations (see reference 1):

$$L(\gamma) = \int_{-\sigma}^{\sigma} K(z) e^{i\gamma z} dz; \quad \lambda = 2\pi a^3 / v; \tag{4}$$

$$K(z) = 1/2 \int_{|z|}^{\sigma} (e^{-\Phi(t)/kT})' u(t) (z^2 - t^2) dt. \tag{5}$$

Since  $T$  is contained as a parameter in  $L(\gamma)$ , then conditions (2) and (3) determine  $\lambda_0 = \lambda_0(T)$  or, by

<sup>1</sup>I. Z. Fisher, J. Exper. Theoret. Phys. USSR **28**, 171 (1955)

<sup>2</sup>S. V. Tiablikov, J. Exper. Theoret. Phys. USSR **17**, 386 (1947)

<sup>3</sup>A. A. Vlasov, *Many Particle Theory*, Moscow, 1950

<sup>4</sup>P. Bridgman, *Physics of High Pressures*, 1935

means of Eq. (4), determine the limiting line of stability of the system on its  $v - T$  surface:  $v = v_{\text{lim}}(T)$ . Then with the help of the known expression for the pressure<sup>5</sup>, which, in our notation, has the form

$$\frac{pv}{kT} = 1 + \frac{\lambda}{3} \int_0^\sigma (e^{-\Phi(r)/kT})' u(r) r^3 dr, \quad (6)$$

we can also find the limiting line of stability of the system on its  $p - T$  surface:  $p = p_{\text{lim}}(T)$ . These lines on the  $v - T$  and  $p - T$  surfaces of the system determine the absolute limit of the stability of a homogeneous phase (that is, gas or liquid), in other words, determine the limit of its possible existence, including metastable (superheated and supercooled) states. The lines of equilibrium phase transitions, that is, the limits of relative stability, are determined, as always, by the equality of the chemical potentials of the different phases. We wish to remark, however, that for the simplest systems of the type of argon, the only ones to which the theory of liquids in its developed form applies, a knowledge of the absolute limits of the stability of the system gives simultaneously, and with sufficient exactness, a knowledge of the lines of the phase transitions, inasmuch as for these systems the regions of metastable states are comparatively narrow.

It is evident that conditions (2) and (3) lead to the existence of limiting points of two types which are distinguished by whether for  $\text{Im} \{ \gamma_1(\lambda_0) \} = 0$  there appears simultaneously either  $\text{Re} \{ \gamma_1(\lambda_0) \} = 0$ , or  $\text{Re} \{ \gamma_1(\lambda_0) \} \neq 0$ . The analysis of these cases is carried out separately below. As in reference 1, the analysis is limited to that which is possible without an actual solution of Bogoliubov's equation for  $g(r)$ , proceeding only from a knowledge of the behavior of  $g(r)$  for  $r \rightarrow \infty$ .

2. BOUNDARY POINTS OF THE FIRST TYPE

If  $L(\gamma)$  is such that  $L(0) > 0$ , then it may be shown that  $\gamma_1(\lambda_0) = 0$ ; whence, according to Eq. (1),  $\lambda_0$  itself is given by

$$\lambda_0 = [L(0)]^{-1}. \quad (7)$$

This determines  $\lambda_0(T)$  or  $v_{\text{lim}}(T)$ . From this one can readily obtain a general expression for  $p = p_{\text{lim}}(T)$ . Integrating Eq. (4) by parts and taking Eq. (5) into account, we readily obtain the expression

<sup>5</sup>N. N. Bogoliubov, *Problems of Dynamical Theory in Statistical Mechanics*, Moscow, 1946

$$L(0) = -\frac{2}{3} \int_0^\sigma (e^{-\Phi(r)/kT})' u(r) r^3 dr. \quad (8)$$

Hence we have from Eq. (6)

$$pv / kT = 1 - \frac{1}{2} \lambda L(0) \quad (9)$$

and by comparison with (7) we find

$$(pv)_{\text{lim}} = \frac{1}{2} kT. \quad (10)$$

Let us consider now a small neighborhood  $\delta\lambda$  of the point  $\lambda_0$ . In virtue of the evenness of  $K(z)$  we have  $L'(0) = 0$ , and Eq. (1) can be written

$$(\lambda_0 + \delta\lambda) \{ L(0) + \frac{1}{2} L''(0) \gamma_1^2 + \dots \} = 1. \quad (11)$$

We suppose that  $L''(0) \neq 0$ , but this last term we take into account, and we neglect the dependence of  $L(0)$  on  $\lambda$ , which occurs on account of the presence of  $u(t)$  in  $K(z)$ , according to Eq. (5). It will be shown below that for small  $\gamma$  this dependence is unimportant and Eq. (11) is exact. Taking account of Eq. (7), we find for small  $\delta\lambda$  and  $\gamma_1$

$$\gamma_1(\lambda) = \frac{1}{\lambda_0} \sqrt{\frac{2}{L''(0)} (\lambda_0 - \lambda)}. \quad (12)$$

As in reference 1, we use the notation  $\gamma_1 \equiv \beta_1 + i\alpha_1$ . There are then two possible cases:

1.  $L''(0) < 0$ . From Eq. (12) we have

$$\begin{aligned} \beta_1 \equiv 0; \alpha_1 &= \frac{1}{\lambda_0} \sqrt{\frac{2}{L''(0)} (\lambda - \lambda_0)}, & \text{if } \lambda < \lambda_0, \\ \alpha_1 \equiv 0; \beta_1 &= \frac{1}{\lambda_0} \sqrt{\frac{2}{L''(0)} (\lambda_0 - \lambda)}, & \text{if } \lambda > \lambda_0. \end{aligned} \quad (13)$$

In agreement with the remark made in connection with Eq. (3), in accordance with the general theory<sup>1</sup>, we have in Eq. (13) a boundary point of the type of the limit for a supercooled vapor: the phase exists for  $\lambda < \lambda_0$  and the phase is impossible for  $\lambda > \lambda_0$ .

2.  $L''(0) > 0$ . In this case  $\alpha_1$  and  $\beta_1$  exchange places in Eqs. (13) and we have a boundary point of the type of the limit for a superheated liquid: the phase exists for  $\lambda > \lambda_0$  and the phase is impossible for  $\lambda < \lambda_0$ .

Thus boundary points of the type under consideration are such that on one side of them<sup>1</sup>

$$g(r) = 1 + \frac{A_1}{r} e^{-|\alpha_1| r} \quad (r \gg \sigma) \quad (14)$$

(stable states), and on the other side

$$g(r) = 1 + \frac{A_1}{r} \cos(\beta_1 r + \delta_1) \quad (r \gg \sigma) \quad (15)$$

(absolutely unstable states). At the exact boundary point  $\alpha_1 = \beta_1 = 0$ . The function  $g(r)$  in the form (14) is postulated in the theory of critical opalescence<sup>7-9</sup>. To it corresponds the deviation in the density of free energy from the equilibrium value for fluctuations in the number of particles, the deviation being

$$f - f_0 = B \{ (\vec{\nabla}\phi)^2 + \alpha_1^2 \phi^3 \} \quad (16)$$

(see references 1, 9, where  $\phi$  is the relative density, while  $\alpha_1^2 B$  is proportional to  $(-\partial p/\partial v)_T$ . Since for  $\lambda \rightarrow \lambda_0$  we have  $\alpha_1 \rightarrow 0$ , then at the exact boundary point we have  $(-\partial p/\partial v)_T = 0$ , in conformity with the general thermodynamic theory of boundary points (see reference 10).

Thus the limit of stability of a homogeneous phase, determined by Eqs. (2) and (3), coincides with the general thermodynamic definition of the limit of stability, since  $(-\partial p/\partial v)_T = 0$  along the line  $p = p_{\text{lim}}(T)$ .

We shall now show that  $(\partial L/\partial \lambda)_{\lambda_0} = 0$  and, consequently, that Eq. (11) is exact. From Eqs. (4) and (5) we have

$$\begin{aligned} \left( \frac{\partial L}{\partial \lambda} \right)_{\gamma=0} &= 2 \int_0^{\sigma} \left( \frac{\partial K}{\partial \lambda} \right)_{\lambda_0} dz \quad (17) \\ &= \int_0^{\sigma} dz \int_{|z|}^{\sigma} (e^{-\Phi(t)/kT})' \left( \frac{\partial u(t)}{\partial \lambda} \right)_{\lambda_0} (z^2 - t^2) dt \end{aligned}$$

and, integrating by parts, we find [analogous to Eq. (8)]

$$\left( \frac{\partial L}{\partial \lambda} \right)_{\gamma=0} = -\frac{2}{3} \int_0^{\sigma} (e^{-\Phi/kT})' \left( \frac{\partial u(r)}{\partial \lambda} \right)_{\lambda_0} r^3 dr. \quad (18)$$

The right side here is equivalent, by Eq. (6), to the expression

$$\begin{aligned} &-2 \left[ \frac{\partial}{\partial \lambda} \left\{ \frac{1}{\lambda} \left( \frac{pv}{kT} - 1 \right) \right\} \right]_{\lambda=\lambda_0} \quad (19) \\ &= \frac{2}{\lambda_0^2} \left[ \frac{\partial}{\partial v} \left( \frac{pv^2}{kT} - v \right) \right]_{\text{lim}}, \end{aligned}$$

which on calculation turns out to be zero, if we take account of Eq. (10) and the fact that  $(-\partial p/\partial v)_{\text{lim}} = 0$ . Here it is essential that  $(-\partial p/\partial v)_{\text{lim}}$  be zero as a result of Eqs. (14) and (16), independently of whether the member containing  $(\partial L/\partial \gamma)$  is considered in Eq. (11) or not.

Finally, let us consider the special case which occurs for  $L''(0) = 0$ . In this case it is necessary to consider further terms in the expansion in (11), and this gives

$$(\rho_0 + \delta\lambda) \{ L(0) + \frac{1}{24} L^{(IV)}(0) \gamma_1^2 + \dots \} = 1. \quad (20)$$

Taking Eq. (7) into account, we find that

$$\gamma_1(\lambda) = \sqrt[4]{\frac{24}{\lambda_0^2 L^{(IV)}(0)} (\lambda_0 - \lambda)}. \quad (21)$$

Let us suppose for definiteness that  $L^{(IV)}(0) < 0$ . Then for  $\lambda < \lambda_0$  all four values of the root in Eq. (21) will be complex, so that  $\alpha_1(\lambda) \neq 0$  and these states are stable. For  $\lambda > \lambda_0$  there are among the roots of Eq. (21) two which are purely real, for which  $\alpha_1 \equiv 0$ , and two purely imaginary, for which  $\alpha_1(\lambda) \neq 0$ . Consequently the root with imaginary part of smallest absolute value will be the  $\gamma_1(\lambda)$  with  $\alpha_1 \equiv 0$ , and this state is unstable. It is easy to see that an analogous situation arises if  $L^{IV}(0) = 0$  but  $L^{(VI)}(0) \neq 0$ , and so forth.

Thus the boundary points of the first type considered, that is, determined by Eq. (7), are such that they are always boundaries separating two regions of states of a system --- stable and unstable. Isolated points of instability cannot occur here, and consequently a thermodynamic singularity of the type of the critical point (see, above, the end of Section 1) cannot be a boundary point of the first type. The special significance of this circumstance will be considered separately later.

### 3. EXAMPLE OF A SYSTEM WITH BOUNDARY POINTS OF THE FIRST TYPE. SUBLIMATION

As an example of a system leading to boundary points of the type considered, we take a system of mutually attracting point particles, the intermolecular potential of which may be expressed as a rectangular potential well, so that

$$\begin{aligned} \Phi(r) &= -\epsilon \quad \text{for } r < 1; \quad (22) \\ \Phi(r) &= 0 \quad \text{for } r > 1. \end{aligned}$$

The units of length here are dimensionless;  $a$  in Eq. (4) is thus the width of the potential well and

<sup>6</sup> J. Kirkwood, V. Levinson and B. Mann, *J. Chem. Phys.* **20**, 929 (1952)

<sup>7</sup> L. Ornstein and F. Zernicke, *Physik. Z.* **19**, 134 (1918)

<sup>8</sup> L. Ornstein and F. Zernicke, *Physik. Z.* **27**, 761 (1926)

<sup>9</sup> M. A. Leontovich, *Statistical Mechanics*, Moscow, 1944

<sup>10</sup> L. D. Landau and E. M. Lifshitz, *Statistical Mechanics*, Moscow, 1951

$\sigma = 1$  (more precisely,  $\sigma = 1 + 0$ ). Here also

$$(e^{-\Phi(r)/kT})' = -(e^{\epsilon/kT} - 1)\delta(r-1). \quad (23)$$

The kernel  $K(z)$  and its Fourier transform  $L(\gamma)$  are equal, respectively, to

$$K(z) = \frac{1}{2}Eu(1)(1-z^2), \quad (24)$$

$$L(\gamma) = 2Eu(1)\gamma^{-3}(\sin\gamma - \gamma\cos\gamma), \quad (25)$$

where  $E \equiv e^{\epsilon/kT} - 1 > 0$ . By means of a separation into a series in powers of  $\gamma$  we find that

$$L(0) = \frac{2}{3}Eu(1) > 0; \quad (26)$$

$$L''(0) = -\frac{2}{15}Eu(1) < 0.$$

From this it is clear that Eq. (1) has the solution  $\gamma = 0$  of the gaseous condensation point type for

$$\frac{2}{3}\lambda_0 Eu(1) = 1. \quad (27)$$

It will be shown below that all the remaining solutions of Eq. (1) with  $\alpha(\lambda) = 0$  for our system lead to greater magnitudes of the density than Eq. (27) (see Section 5, below). If, therefore, we move along the  $\lambda$  axis from  $\lambda = 0$  in the direction of increasing  $\lambda$ , then the solution  $\gamma(\lambda)$  of Eq. (1), which, according to Eq. (27), goes to zero at the point  $\lambda_0$ , actually possesses its imaginary part of smallest absolute value for  $\lambda < \lambda_0$ , that is,  $\gamma_1(\lambda)$ . Hence  $\lambda_0$  from Eq. (27) actually determines the limit of stability of our system and, taking Eq. (4) into consideration, we have

$$v_{\text{lim}}(T) = \frac{4\pi a^3}{3}(e^{\epsilon/kT} - 1)u(1). \quad (28)$$

The limiting pressure according to Eq. (10) is

$$p_{\text{lim}}(T) = 3kT/8\pi a^3 u(1)(e^{\epsilon/kT} - 1). \quad (29)$$

In order to find out the exact form of  $v_{\text{lim}}(T)$  and  $p_{\text{lim}}(T)$ , it is necessary to know how  $u(1)$  depends on  $\lambda$  and  $T$ , that is,  $u(1; \lambda; T)$ , and for this a knowledge of the exact solution of Bogoliubov's equation for  $g(r)$  or  $u(r)$  is required. But since it has been shown that  $u(r) \sim 1$  always, then in Eqs. (28) and (29) we may discard the factor  $u(1)$ . This is the more accurate for low temperatures, where  $(\epsilon/kT) \gg 1$ . Then  $v_{\text{lim}}(T)$  is large (highly rarefied gas) and the equality  $u(1) \approx 1$  is fulfilled with very great exactness, since for an ideal gas  $u(r) \equiv 1$ . Thus for  $(\epsilon/kT) \gg 1$  we may write

$$v_{\text{lim}}(T) \approx \frac{4\pi a^3}{3}e^{\epsilon/kT}; \quad p_{\text{lim}}(T) \approx \frac{3kT}{8\pi a^3}e^{-\epsilon/kT}. \quad (30)$$

The system under consideration, apart from its extreme schematization, can serve as a model of a real system if the density of the latter is sufficiently small. Actually the neglect of the forces of repulsion between the particles, which forces act only at short range, is allowed if the average distance between the particles is large. A simultaneous neglect of the forces of attraction is not allowed, since then there would be no reason for the loss of stability, and this would contradict the properties of real systems. Since, according to Eq. (28), the case of small densities corresponds to low temperatures, we may then suppose that the relation (30) represents with sufficient accuracy the limiting line of the stability of a real gaseous phase at low temperatures, for example, below the triple point;  $p_{\text{lim}}(T)$  is then the sublimation pressure.

That Eq. (30) is fully admissible quantitatively is evident from the following example. For argon the temperature and pressure at the triple point are, respectively, 83°K and 0.68 atm =  $66.7 \times 10^3$  abs. units. If we then take 1.43 as the magnitude of  $\epsilon/kT$  at the triple point, as follows from the magnitude of the Lennard-Jones potential<sup>11</sup>, then from Eq. (30) the radius of action of the intermolecular forces is found to have the magnitude  $a = 7.7 \times 10^{-8}$  cm, which is more than twice the diameter of an atom of argon and is a fully acceptable result, although perhaps somewhat high. However, we must take into account that the actual pressure at a limiting point on the isotherm  $T = T_{\text{tr}}$  is notably greater than  $p_{\text{tr}}$ , and hence a more exact estimate for  $a$  would be less than the indicated magnitude of  $7.7 \times 10^{-8}$  cm.

We note in conclusion that the pressure  $p_{\text{lim}}$  and volume  $v_{\text{lim}}$  which we have obtained agree well with the corresponding magnitudes calculated for the sublimation equilibrium<sup>12</sup>

$$p_{\text{subl}}(T) = \frac{(2\pi\tilde{\nu}^2)^{3/2}}{V\cdot kT}e^{-\epsilon/kT}; \quad (p\nu)_{\text{subl}} \approx kT, \quad (31)$$

where  $\tilde{\nu}$  is the geometrical mean frequency of the natural oscillations of the crystalline lattice.

<sup>11</sup> Zh. de-Bur, Usp. fiz. nauk 51, 41 (1953)

<sup>12</sup> M. Born and M. Goeppert-Mayer, *Theory of the Rigid Body*, 1933

4. BOUNDARY POINTS OF THE SECOND TYPE

We will call the boundary point  $\lambda = \lambda_0$  determined by (2) and (3) a boundary point of the second type if  $\text{Re} \{ \gamma_1, (\lambda_0) \} \neq 0$ .

Let us consider a certain magnitude  $\lambda$  near  $\lambda_0$  and satisfying condition (3). We use the notation  $\gamma_1 \equiv \beta + i\alpha$  (omitting the index 1). For  $\lambda$  near  $\lambda_0$ ,  $\alpha$  is small and we may write

$$L(\gamma) = \left\{ L(\beta) - \frac{\alpha^2}{2} L''(\beta) + \dots \right\} + i\alpha \left\{ L'(\beta) - \frac{\alpha^2}{6} L'''(\beta) + \dots \right\}. \tag{32}$$

As a consequence of the evenness of the function  $K(z)$ , it turns out, according to Eq. (4), that  $L(\beta)$ ,  $L'(\beta)$ , etc., are purely real. Substituting Eq. (32) into Eq. (1) and separating the real and imaginary parts, we obtain

$$\lambda \left\{ L(\beta) - \frac{\alpha^2}{2} L''(\beta) + \dots \right\} = 1, \tag{33}$$

$$L'(\beta) - \frac{\alpha^2}{6} L'''(\beta) + \dots = 0.$$

At the very boundary point  $\alpha = 0$ , and consequently

$$\lambda_0 L(\beta_0) = 1; \quad L'(\beta_0) = 0. \tag{34}$$

These equations can be regarded as a definition of a boundary point of the second type. Since  $L(\beta)$  contains the temperature  $T$  as parameter, then we find the limiting line of stability of the system on its  $\lambda - T$  or  $v - T$  surfaces:  $\lambda = \lambda_0(T)$  or  $v = v_{\text{lim}}(T)$ ; and with the aid of Eq. (6) we also find the limiting line of stability of the system on its  $p - T$  surface:  $p = p_{\text{lim}}(T)$ .

Let us now consider the behavior of  $\alpha(\lambda)$  and  $\beta(\lambda)$  near a boundary point. Putting  $\lambda = \lambda_0 + \delta\lambda$  and  $\beta = \beta_0 + \delta\beta$  into Eq. (33), we obtain

$$(\lambda_0 + \delta\lambda) \{ L(\beta_0) + (\partial L / \partial \lambda)_0 \delta\lambda + 1/2 L''(\beta_0) ((\delta\beta)^2 - \alpha^2) + \dots \} = 1, \tag{35}$$

$$(\partial L'(\beta) / \partial \lambda)_0 \delta\lambda + L''(\beta_0) \delta\beta - (\alpha^2/6) L'''(\beta_0) + \dots = 0.$$

We will suppose that  $L''(\beta_0) \neq 0$ . Then solving the resulting system of equations for  $\alpha$  and  $\delta\beta$ , we obtain for small  $\delta\lambda$

$$\alpha(\lambda) = \sqrt{\frac{2[1 + \lambda_0^2 (\partial L / \partial \lambda)_0]}{\lambda_0^2 L''(\beta_0)}} (\lambda - \lambda_0); \tag{36}$$

$$\delta\beta = \frac{1}{3\lambda_0^2 [L''(\beta_0)]^2} \left\{ L'''(\beta_0) + i\alpha_0^2 \left[ L'''(\beta_0) \left( \frac{\partial L}{\partial \lambda} \right)_0 - 3L''(\beta_0) \left( \frac{\partial L'}{\partial \lambda} \right)_0 \right] \right\} (\lambda - \lambda_0). \tag{37}$$

Thus in the neighborhood of a boundary point  $\lambda_0$  (on the side of the stable states) we always have

$$\beta(\lambda) = \beta_0 + C(\lambda - \lambda_0). \tag{38}$$

With respect to  $\alpha(\lambda)$  there are two possible cases:

1.  $L''(\beta_0)$  and  $1 + \lambda_0^2 (\partial L / \partial \lambda)_0$  of opposite sign. Then a homogeneous phase is stable for  $\lambda < \lambda_0$  ( $\alpha_1 \neq 0$ ) and a homogeneous phase is impossible for  $\lambda > \lambda_0$  ( $\alpha_1 \equiv 0$ ). We have a boundary point of the type of a gaseous condensation or of crystallization.

2.  $L''(\beta_0)$  and  $1 + \lambda_0^2 (\partial L / \partial \lambda)_0$  of the same sign. Then a homogeneous phase is stable for  $\lambda > \lambda_0$  and a homogeneous phase is impossible for  $\lambda < \lambda_0$ . We have a boundary point of the vaporization type.

Special cases arise when  $L''(\beta_0) = 0$  or  $1 + \lambda_0^2 (\partial L / \partial \lambda)_0 = 0$ . They are connected with the critical point. In view of the importance and special physical interest of these cases, they will be specially studied in a separate communication, and we shall not consider them at present.

Thus boundary points of the second type are such that on one side of them,

$$g(r) = 1 + \frac{A_1}{r} e^{-|\alpha_1| r} \cos(\beta_1 r + \delta_1) \tag{39}$$

$(r \gg \sigma)$

(stable states), and on the other,

$$g(r) = 1 + \frac{A_1}{r} \cos(\beta_1 r + \delta) \tag{40}$$

$(r \gg \sigma)$

(absolutely unstable states). At the very boundary point  $\alpha_1(\lambda_0) = 0$ , but  $\beta_1(\lambda_0) \neq 0$ . Equally possible are the special cases noted above, when the point  $\lambda_0$  is an isolated unstable point and Eq. (39) is correct on both sides.

The question of the thermodynamic properties of a system in the vicinity of a boundary point is very important. But now, unfortunately, in contrast to the case taken up in Sec. 2, our method, which is based only on a study of the behavior of  $g(r)$  for  $r \rightarrow \infty$ , yields almost nothing. If, as is usually done, we make use of the relation

$$\frac{4\pi}{v} \int_0^\infty (g(r) - 1) r^2 dr = \frac{kT}{v^2 (-\partial p / \partial v)_T} - 1, \tag{41}$$

it will then turn out that  $(-\partial p/\partial v)_T = 0$  at the boundary point, in conformity with thermodynamic theory<sup>10</sup>. But, as we have seen in reference 1, Eq. (41) cannot be considered proved in the neighborhood of a boundary point. It is very important that this relation in the form (41), or with slight modifications, actually be correct. However, its proof represents a very difficult problem.

In conclusion we consider the distribution of boundary points on the  $\lambda$  axis. For  $\lambda \rightarrow 0$ , as we have seen, all the  $|\alpha_n| \rightarrow \infty$ . For increasing  $\lambda$  the first boundary point will always be of the type of a gaseous condensation or a crystallization. If subsequently  $\alpha_1(\lambda)$  nowhere ceases to be equal to zero, then we have the case shown in Fig. 1a. A

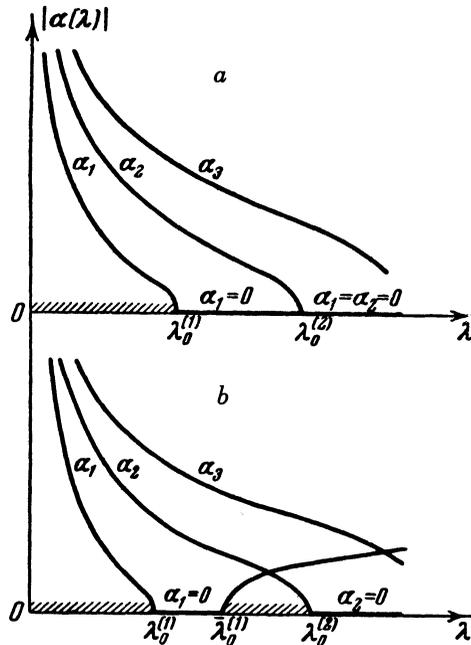


Fig. 1

homogeneous phase is possible only in the interval  $0 \leq \lambda < \lambda_0^{(1)}$  (shown hatched in the figure). This corresponds to the behavior of a real system for  $T > T_{cr}$  or  $T < T_{tr}$ . However, it is possible that  $\alpha_1(\lambda)$ , equal to zero in a certain interval  $\lambda_0^{(1)} \leq \lambda \leq \bar{\lambda}_0^{(1)}$ , may subsequently be different from zero, and in this case  $\lambda_0^{(1)}$  lies on the left side of the first zero of  $\alpha_2(\lambda)$ . This case is shown in Fig. 1b. The spectrum of eigenvalues of the parameter  $\lambda$  now consists of two continuous bands:  $0 \leq \lambda < \lambda_0^{(1)}$  and  $\bar{\lambda}_0^{(1)} < \lambda < \lambda_0^{(2)}$ , where a homogeneous phase is possible. This corresponds to the

behavior of a real system for  $T_{tr} < T < T_{cr}$ . The left band corresponds to a gas, the right to a liquid. Note that in Fig. 1b we have for clarity introduced a notation not in full agreement with the general theory, since for those values of  $\lambda$  where  $|\alpha_1| > |\alpha_2|$  (see the Figure) a larger  $|\alpha_n|$  corresponds to a smaller number  $\gamma_n$ . Strictly speaking, it follows that we should rename  $\alpha_2$  as  $\alpha_1$ , and vice versa.

The positions of the points  $\lambda_0^{(1)}$ ,  $\bar{\lambda}_0^{(1)}$  and  $\lambda_0^{(2)}$  on the  $\lambda$  axis depend on the temperature. On variation of the latter it can happen that the points  $\lambda_0^{(1)}$  and  $\bar{\lambda}_0^{(1)}$  will coincide. This clearly corresponds to the critical temperature and the density  $\lambda = \lambda_0^{(1)} = \bar{\lambda}_0^{(1)}$  is the density of the liquid at the critical point. It may happen also that on variation of the temperature the points  $\bar{\lambda}_0^{(1)}$  and  $\lambda_0^{(2)}$  will coincide, and this clearly corresponds to the triple point (more truly to its analogy on the limiting line of stability, since literally the triple point lies on an equilibrium phase transition line).

#### 5. EXAMPLE OF A SYSTEM WITH BOUNDARY POINTS OF THE SECOND TYPE

Let us consider the problem of the determination of the minimum volume for which a system of a great number of hard noninteracting spheres of diameter  $a$  in "thermal agitation" can be homogeneous (that is, disordered). This problem has been solved earlier by another method<sup>13-15</sup> and is introduced here for the purpose of illustrating the theory developed above. But it must be noted that the correct result was obtained in these researches by a method that was not rigorous: the boundary value  $\lambda_0$  signifying the maximum possible density of the system was obtained from an analysis of an approximate equation which was true only for small densities, and hence one cannot be sure that this  $\lambda_0$  will be conserved at large densities in the more rigorous theory.

In dimensionless units of length we have for  $\Phi(r)$

$$\Phi(r) = +\infty, \quad \text{if } r < 1; \quad (42)$$

$$\Phi(r) = 0, \quad \text{if } r > 1,$$

<sup>13</sup> J. Kirkwood, J. Chem. Phys. 7, 919 (1939)

<sup>14</sup> J. Kirkwood and E. Monroe, J. Chem. Phys. 10, 394 (1942)

<sup>15</sup> J. Kirkwood, B. Mann and B. Alder, J. Chem. Phys. 18, 1040 (1950)

so that

$$(e^{-\Phi(r)/kT})' = \delta(r - 1), \tag{43}$$

and the number  $\sigma$  is equal to 1 + 0. By means of Eqs. (4) and (5) we find further

$$K(z) = 1/2 u(1) (z^2 - 1), \tag{44}$$

$$L(\gamma) = 2u(1)\gamma^{-3}(\gamma \cos \gamma - \sin \gamma). \tag{45}$$

since  $L(0) = -2/3 u(1) < 0$ , then there are no boundary points of the first type, and  $\gamma \neq 0$ . Equations (34), basic for finding  $\lambda_0$ , can be written in the form

$$2\lambda u(1)\beta^{-3}(\beta \cos \beta - \sin \beta) = 1, \tag{46}$$

$$\beta^{-4}((3 - \beta^2) \sin \beta - 3\beta \cos \beta) = 0.$$

The problem comes down to a solution of the transcendental equation

$$\text{tg } \beta = 3\beta/(3 - \beta^2). \tag{47}$$

Its solution is

$$\beta_n = n\pi \left\{ 1 - \frac{3}{(n\pi)^2} - \frac{9}{(n\pi)^4} - \frac{81}{5(n\pi)^6} - \frac{1701}{16(n\pi)^8} - \dots \right\}, \tag{48}$$

with  $n = 2, 3, 4, \dots$ . This leads, according to the first of the Eqs. (46), to the result

$$(2\lambda u(1))_n = (-1)^n \left\{ (n\pi)^2 - \frac{9}{2} - \frac{43}{8(n\pi)^2} - \frac{4991}{112(n\pi)^4} - \dots \right\}. \tag{49}$$

In order to determine the necessary value of  $n$ , we note that all odd  $n$  disappear as negative densities are approached. Among the even  $n$  the

one which gives the smallest  $\lambda_0$  must be chosen (Fig. 1a). This determines the choice  $n = 2$ , so that

$$(2\lambda u(1))_{\text{lim}} = 4\pi^2 - \frac{9}{2} - \frac{43}{32\pi^2} - \frac{4991}{1792\pi^4} - \dots = 34.812. \tag{50}$$

If the results of the direct numerical integration of Bogoliubov's equation for  $g(r)$  for the problem under consideration<sup>15</sup> are used, then it is found that, for  $2\lambda u(1) = 34.8$ , the value of  $u(1)$  is 2.90, which leads, according to Eq. (4), to the following value for the limiting volume:

$$v_{\text{lim}} = (\pi a^3/3) = 2v_0, \tag{51}$$

where  $v_0$  is the volume of a single spherical particle. The limiting volume does not depend on the temperature. By Eqs. (6), (33) and (51) we find the limiting pressure to be

$$p_{\text{lim}}(T) = \frac{3.4}{v_0} kT \tag{52}$$

("fusion curve" of a system of hard noninteracting spheres).

In conclusion we note that if we formally set  $E = -1$  in the equations considered in Sec. 3 of the problem, they go over into the equations just considered. In connection with this the statement made without proof in Sec. 3, namely, that Eq. (27) gives the smallest value of  $\lambda_0$  for which  $\alpha_n = 0$ , becomes evident. If we actually substitute  $n = 3, 5, 7, \dots$  into Eqs. (49), we arrive at values of the density  $\lambda_0$  greater than we obtain from Eq. (27).

Translated by Brother Simon Peter, F.S.C.