On the Stability of a Homogeneous Phase. I
General Theory

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Necessary conditions for thermodynamic stability and sufficient conditions for the thermo-dynamic instability of a homogeneous phase are obtained in terms of the theory of the radial distribution function. The proposed problem of the determination of the radial distribution function is correctly formulated.

INTRODUCTION

THE use of partial distribution functions togeth-with the "superposition approximation" allows the application of the general apparatus of the Gibbs canonical distribution--- which is of very little effectiveness in the case of the liquid state--- to a certain nonlinear problem concerning eigen-functions and eigenvalues[1,2]. Let $F_1(q)$, $F_2(q, q')$, $F_3(q, q', q'')$ be the unitary, binary and ternary distribution functions, respectively. If we consider only a homogeneous phase (that is, a gas or a liquid), then the asymptotic expressions for the first two of these functions, when (by removal of all limits on the volume V up to infinity) the volume V of the system and the number of particles N of the system are allowed to increase without bound [but with $v = \lim (V/N) = \text{const}$], are

$$F_1(q) = 1; \quad F_2(q, q') = g(|q - q'|). \quad (1)$$

The function $g(r)$ is the so-called "radial distribu-tion function". For the sake of simplicity we will assume the absence of strong external fields and will deal only with the simplest type of liquid (or gas), the intermolecular potential of which depends only on the distance between the centers of the two particles. If we allow that with sufficient exacti-tude, we may assume

$$F_3(q, q', q'') = g(|q - q'|) \quad (2)$$

$$g(|q - q''|)\, g(|q' - q''|)$$

("superposition approximation"), then the function $g(r)$ is determined by the intermolecular potential $\Phi(r)$ of the system, its temperature T and density $1/v$, by means of Bogoliubov's equation[1]

$$\cdot - kT \ln g(r) = \Phi(r) \quad (3)$$

[1] N. N. Bogoliubov, *Problems of Dynamical Theory in Statistical Mechanics*, State technical publishing house, 1946.
[2] I. Z. Fisher, Usp. Fiz. Nauk **51**, 71 (1953)

$$+ \frac{\lambda}{r} \int_0^\infty \left\{ \int_{|r-\rho|}^{r+\rho} E(t)\, t\, dt \right\} (g(\rho) - 1)\, \rho\, d\rho,$$

where

$$E(t) = \int_\infty^t \Phi'(t)\, g(t)\, dt, \quad \lambda = 2\pi a^3/v. \quad (4)$$

Here k is Boltzmann's constant, and we have in-troduced the dimensionless unit of length $r' = r/a$, where a is a certain characteristic molecular distance, for example, the diameter of a particle. In (3), as also from here on, the prime on the r has been omitted.

The function $g(r)$ must, moreover, satisfy the normalization condition

$$\lim_{R \to \infty} \frac{1}{R^3} \int_0^R (g(r) - 1)\, r^2 dr = 0, \quad (5)$$

arising from (1) and from the significance of $F_1(q)$ and $F_2(q, q')$ in terms of probability.

Equations (3)---(5), taken together, present the complicated nonlinear problem of the determination of the eigenfunctions $g(r; \lambda)$ and the eigenvalues λ. The question of the spectrum of values λ (for a given temperature T) is very important for the theory of phase transitions from a homogeneous phase, as has already been pointed out by the author[3]. How-ever, the problem of the determination of the spec-trum of values λ for a given $\Phi(r)$ and T is unusually complex on account of the nonlinearity of Eqs. (3) and (4). It will be shown below that this problem can be solved, to a certain extent, by means of an investigation of the behavior of the solutions of Eq. (3) as $r \to \infty$. It will then become apparent that the problem defined by Eqs. (3)--(5) has, in a certain sense, not been formulated altogether correctly, and from this will arise the necessity of correctly formulating "boundary conditions" on Eq. (3). The present communication is devoted to

[3] I. Z. Fisher, J. Exper. Theoret. Phys. USSR **21**, 942 (1951)

the solution of this problem. In the correctly formulated problem the discontinuous character of the spectrum of eigenvalues of the parameter λ arises automatically. In subsequent communications the general theory will be applied to the solution of actual problems of the liquid state.

2. BEHAVIOR OF THE RADIAL DISTRIBUTION FUNCTION AT GREAT DISTANCES

For what follows it is convenient to change over from the function $g(r)$ to the auxiliary function $u(r)$ such that

$$g(r) = e^{-\Phi(r)/kT} u(r). \qquad (6)$$

If, at the same time, in place of $E(t)$ we introduce the function $\bar{E}(t)$ according to the relation

$$\bar{E}(t) = -\frac{1}{kT} E(t) = \int_{\infty}^{t} (e^{-\Phi(t)/kT})' u(t) \, dt, \qquad (7)$$

we then obtain from (3) an equation determining $u(r)$,

$$r \ln u(r) = \lambda \int_{0}^{\infty} \left\{ \int_{|r-\rho|}^{r+\rho} \bar{E}(t) \, t \, dt \right\} \qquad (8)$$

$$\{e^{-\Phi(\rho)/kT} u(\rho) - 1\} \, \rho \, d\rho,$$

which contains only λ as a parameter of the integral equation (to employ the terminology of the theory of integral equations). The temperature enters into (8) in a more complicated manner, in the combination $e^{-\Phi(r)/kT}$, and must be given together with the potential $\Phi(r)$.

We are interested in the behavior of $g(r)$ or $u(r)$ as $r \to \infty$. The potential $\Phi(r)$ is assumed to approach zero sufficiently rapidly for $r \to \infty$. Then from (5) and (6) there follows the requirement that, in any case, $u(r) \to 1$ as $r \to \infty$. Hence we may set

$$u(r) = 1 + \varphi(r) \, r, \qquad (9)$$

where $|\phi(r)/r| \to 0$ as $r \to \infty$. As a consequence of this we may linearize the logarithm in (8) for large r. Moreover, to the extent that $\bar{E}(t)$ rapidly approaches zero with increasing t, only the values of ρ which are near r will be of consequence in the expression under the integral, while for $r \to \infty$ we may replace $e^{-\Phi(\rho)/kT}$ by unity and extend the upper limit of the integral to infinity. If we denote

$$K(z) = \int_{|z|}^{\infty} \bar{E}(t) \, t \, dt \qquad (10)$$

$$= \frac{1}{2} \int_{|z|}^{\infty} (e^{-\Phi(t)/kT})' u(t) (z^2 - t^2) \, dt,$$

where the last expression is obtained by integrating by parts, taking account of (7), we finally arrive at the following equation determining $\phi(r)$ for $r \to \infty$:

$$\varphi(r) = \lambda \int_{0}^{\infty} K(|r-\rho|) \varphi(\rho) \, d\rho \qquad (r \to \infty). \qquad (11)$$

In order to simplify the following discussion we now assume that the intermolecular forces have a finite radius of action, that is, that there exists a number σ such that for $r > \sigma$ we have $\Phi(r) \equiv 0$. This condition, we note, limits the generality of the problem only very slightly, since if $\Phi(r)$ extends to infinity (but falls off sufficiently rapidly), then the "radius of cut-off" may be chosen arbitrarily large. Moreover, in the final results of the theory it is not difficult to go over to the limit $\sigma \to \infty$. So,

$$\Phi(r) \equiv 0; \quad g(r) \equiv u(r) \qquad r > \sigma. \qquad (12)$$

Then $\bar{E}(t) = K(t) = 0$ for $t > \sigma$ and in place of (10) and (11) we have

$$K(z) = \frac{1}{2} \int_{|z|}^{\sigma} (e^{-\Phi(t)/kT})' u(t) (z^2 - t^2) \, dt, \qquad (13)$$

$$\varphi(r) = \lambda \int_{r-\sigma}^{r+\sigma} K(|r-\rho|) \varphi(\rho) \, d\rho \qquad (r \gg \sigma). \qquad (14)$$

In order to find the non-trivial solutions of this equation, we assume

$$\varphi(r) \sim e^{i\gamma r}. \qquad (15)$$

Substitution into (14) leads to the equation for the determination of $\gamma = \gamma(\lambda)$

$$\lambda \mathscr{L}(\gamma) = 1 \qquad (\lambda > 0), \qquad (16)$$

where $\mathscr{L}(\gamma)$ is the Fourier transform of the kernel $K(z)$

$$\mathscr{L}(\gamma) = \int_{-\sigma}^{\sigma} K(z) e^{i\gamma z} dz. \qquad (17)$$

Equation (16), generally speaking, has for every $\lambda > 0$ several, or even infinitely many, roots, complex numbers in general: $\gamma_n = \beta_n(\lambda) + i\alpha_n(\lambda)$ $(n = 1,2,3.....)$. From the nature of λ and $K(z)$ it follows that these roots occur in complex conjugate pairs, and from the evenness of the function $K(z)$ it follows that for every root $\gamma_n(\lambda)$ there is a corresponding root $-\gamma_n(\lambda)$. Hence we conclude that to each number n there correspond four roots: $\pm \beta_n$

(λ) $\pm i\alpha_n(\lambda)$. However, the roots with negative imaginary parts lead, according to (9), (12) and (15), to results for $g(r)$ which manifestly fail to satisfy the normalization condition (5), and therefore must be discarded. The two roots $\pm\beta_n(\lambda) + i|\alpha_n(\lambda)|$ then remain, and the corresponding $\phi(r)$ may be obtained essentially in the form

$$\varphi(r) = A e^{-|\alpha|r} \cos(\beta r + \delta), \qquad (18)$$

where the numbers A and δ remain undetermined in the approximation under consideration. In accordance with (9) and (12), we then arrive at the following general form of the radial distribution function for large distances between particles

$$g(r) = 1 + \frac{1}{r}\sum_n A_n e^{-|\alpha_n|r} \cos(\beta_n r + \delta_n). \qquad (19)$$

This result corresponds to the known behavior of $g(r)$, found from experiments on the scattering of x-rays in liquids: with increasing r the function $g(r)$ approaches unity with an oscillation which diminishes to zero. We wish to emphasize that expression (19) is true for all physically allowed values of λ. Smallness of λ (that is, smallness of the density) was not presupposed in the derivation of (19), and this distinguishes our result from the analogous results of other authors[4,5].

The function $\nu(r) \equiv g(r) - 1$ is the "correlation function" of statistical mechanics (see references 6,7), used in the calculation of fluctuations in the density. As is well known, a very rapid decrease in $\nu(r)$ with increasing r is required for the absence of correlation of the fluctuations in density in adjoining macroscopic volumes. According to (19) this requirement will be met if all the $|\alpha_n|$ are not zero and are sufficiently large. Moreover, the absence of correlation of the fluctuations in density in adjoining macroscopic volumes for a system in a state far from the limit of thermodynamic stability is rigidly derivable from Boltzmann's principle (see Leontovich[6]) and is confirmed by experiments on the scattering of light in liquids and gases. Hence for such states all the $|\alpha_n(\lambda)|$ in (19) are different from zero and we may introduce an enumeration of the roots γ_n of equation (16) in the order of the increasing magnitude of their imaginary parts:

4 J. Kirkwood, J. Chem. Phys. 7, 919 (1939)

5 M. Born and H. Green, Proc. Roy. Soc. A, 189, 455 (1947)

6 M. A. Leontovich, *Statistical Mechanics*, State technical publishing house, 1944

7 L. D. Landau and E. M. Lifshitz, *Statistical Physics*, State technical publishing house, 1951

$$0 < |\alpha_1(\lambda)| < |\alpha_2(\lambda)| < |\alpha_3(\lambda)| < \dots \qquad (20)$$

This enumeration is preserved even in the case of very small $|\alpha_n|$, and we shall hold to it continuously below. Of course, for different values of λ the enumeration of the roots γ_n may be different.

We note that for $\lambda \to \infty$ (that is, in the ideal gas approximation) we have $|\alpha_n| \to \infty$, as is clear from (16).

3. INSTABILITY OF STATES WITH $\alpha_1(\lambda) = 0$

We shall now show that states of the system for which $\alpha_1 = 0$ in (19) are thermodynamically absolutely unstable, that is, they do not correspond to a minimum free energy. As proof of this we need more than the single fact of the presence of correlation of the fluctuations in density in adjoining volumes. It is known, for example, that such correlations occur in the vicinity of the critical point (see references [6,7]), that is, in states which are of themselves stable.

Let us suppose that for a certain value of λ we have $\alpha_1(\lambda) = 0$, but $\alpha_2(\lambda) \neq 0$. Since in the subsequent estimates, due to their thermodynamic character, the behavior of $\nu(r)$ at small distances will not be of consequence, we can neglect the exponential members in (19) and write

$$\nu(r) = \frac{A_1}{r}\cos(\beta_1 r + \delta_1). \qquad (21)$$

We note at once that $\nu(r)$ is Green's function for all space of the linear differential operator

$$L(\varphi) = \Delta\varphi + \beta_1^2\varphi, \qquad (22)$$

where Δ is the Laplace operator.

We now assume that the state of the system with correlation function (21) is thermodynamically stable, so that there exists an equilibrium density of free energy $f_0(\lambda, T)$, the self free energy for which is $F = \int f_0 dV$. Let $f - f_0$ be the deviation of the equilibrium density of free energy from its own equilibrium value as a consequence of local fluctuations in density. Since in our case there is an evident correlation of the fluctuations in density in different regions, then, as is known from the general theory, the magnitude of $f - f_0$ will depend not only on the density itself, but also on the gradient of the density (see[6,7]). If ϕ is the relative density, then $f - f_0$ appears as a certain differential form in ϕ, and for small fluctuations this form will be quadratic: $f - f_0 = K(\phi, \phi)$. Let us use, further, the fundamental result of Leontovich, according to which the correlation function $\nu(r)$ is Green's function for all space of

the Euler-Laplace operator $L(\phi) \equiv$ corresponding to the quadratic differential form $K(\phi, \phi)$ (see[6]). Since we already know the function $\nu(r)$ and the operator $L(\phi)$, then by (22) we can readily set up the quadratic form $K(\phi, \phi)$ and also $f - f_0$. For the latter quantity we obtain

$$f - f_0 = B \{(\overrightarrow{\nabla \varphi})^2 - \beta_1^2 \varphi^2\}, \qquad (23)$$

where B is a certain constant (with respect to ϕ).

Thus to the correlation function (21) there corresponds an expression of indeterminate sign for $f - f_0$, and, consequently, f_0 cannot be a minimum in the density of free energy. The state of the system with $\alpha_1(\lambda) = 0$ is absolutely unstable, since a minimum free energy does not exist there.

4. INCORRECTNESS OF THE PROBLEM OF THE DETERMINATION OF g(r) WITH THE REQUIREMENT OF NORMALIZATION IN EQ. (5)

The results obtained above may be formulated in a way which affirms that the necessary condition for the stability of a homogeneous phase is the absence of purely real solutions of Eq. (16), that is, the condition

$$|\operatorname{Im}\{\gamma_1(\lambda)\}| > 0 \quad \text{for} \quad \lambda > 0. \qquad (24)$$

Correspondingly, the condition

$$\operatorname{Im}\{\gamma_1(\lambda)\} = 0 \quad \text{for} \quad \lambda > 0, \qquad (25)$$

is sufficient for the instability of the system.

The question of the sufficiency of the first condition and the necessity of the second remains open, since it cannot be treated merely by investigation of the behavior of $g(r)$ as $r \to \infty$. If, in spite of this, we confine ourselves to such an investigation, as we are at present compelled to do, then the following circumstance is to be noted. The normalization condition (5) for the function $g(r)$ is somewhat limited, being superimposed on the behavior of the solution of Eq. (3) for $r \to \infty$. It is unsatisfactory that this limitation admits, along with the stable solutions, solutions which are unstable (that is, physically unreasonable) in the sense indicated above. Actually any function (19) with arbitrary $\alpha_n(\lambda)$ satisfies the condition (5), even if some or all of the α_n are zero. Hence we may say that the problem of the solution of Eq. (3) with the supplementary requirement (5) has been set up incorrectly since its answers are not those of the corresponding physical problem. Of course, the question now arises as to whether it is actually

impossible to formulate the question of the solution of Eq. (3) on a physical basis in such a way that physically unreasonable solutions may not occur.

In the works of Born and Green[5], and of Kirkwood and his collaborators[4,8] on the theory of liquids, a more stringent requirement is introduced in place of the normalization condition (5), namely, the requirement of volume integrability of the function $g(r) - 1$:

$$\int_0^\infty [g(r) - 1] r^2 dr < +\infty. \qquad (26)$$

It is readily seen that this requirement is fulfilled only if $|\alpha_1| > 0$ in (19), and, consequently, it permits the separation of the solutions corresponding to stable states from those which are physically unreasonable. However, this requirement appears too strict, and for the purpose of distinguishing the stable solutions it would suffice to require the fulfillment of a less severe condition relative to the behavior of $g(r)$ for $r \to \infty$. What is even more essential is that it is not possible to prove this condition physically without previous knowledge of the solution of Eq. (3) in the form (19). Hence it is not suitable as an initial requirement on the solutions of Eq. (3) and as one capable of replacing condition (5). The latter is connected simply with the fact that the integrability requirement (26) does not arise immediately from the Gibbs canonical distribution, and hence is evidently supplementary— the above superposition approximation—restricted, superimposed on $g(r)$. Cosidering the connection of the left part of condition (26) with the isothermal compressibility of the system, one finds

$$\frac{4\pi}{v} \int_0^\infty [g(r) - 1] r^2 dr = \frac{kT}{v^2(-\partial\rho/\partial v)_T} - 1, \qquad (27)$$

erroneously*. Relation (27) is obtained from the comparison of two well-known equations for the squares of the fluctuations in the numbers of particles in a certain volume G:

$$\overline{(\Delta N_G)^2} = \overline{N}_G \frac{kT}{v^2(-\partial\rho/\partial v)_T}; \qquad (28)$$

$$\overline{(\Delta N_G)^2} = \overline{N}_G \left\{ 1 + \frac{\overline{N}_G}{V_G^2} \int_{(G)} \int_{(G)} \{g(|q_1 - q_2|) \qquad (29) \right.$$
$$\left. - 1\} dq_1 dq_2 \right\},$$

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* The incorrect exposition of this equation is tolerated also by the author of the present paper in the survey[2].

[8] J. Kirkwood, E. Mann and B. Alder, J. Chem. Phys. 18, 1040 (1950)

with the latter having been rewritten in the form

$$\overline{(\Delta N_G)^2} = \overline{N}_G \left\{ 1 + \frac{4\pi}{v} \int_0^\infty [g(r) - 1] r^2 dr \right\}. \quad (30)$$

The erroneousness of Eq. (27), accepted in many works as one of the basic equations of the theory of liquids, is evident. Equation (28) clearly does not hold in the presence of the correlation of the fluctuations in different regions (see Leontovich[6]), and the exact Eq. (29) may be replaced by the approximate Eq. (30) only if the sufficiently rapid tendency of $g(r) - 1$ to zero for $r \to \infty$ is known beforehand. [For example, for a hypothetical function $g(r)$ of form $g(r) \sim 1 + Ar^n e^{-\alpha r}$ the condition (26) will be fulfilled for any $\alpha > 0$, but equations (28) and (27) will not hold for $n > 0$ and small α]. Hence Eq. (26), which does not arise from the general laws of statistical mechanics, is unacceptable as an initial supplementary requirement on the solution of Eq. (3).

The actual solution of the question of the correct presentation of the problem for Eq. (3) lies in an altogether different direction and is connected with the validity of the transition to the limit $N, V \to \infty$, which has already been accomplished in (3). At the basis of Eq. (3) lies the admission of (1), in particular the admission that the system under consideration is such that for removal to infinity of all walls bounding its volume V and the simultaneous preservation of its average density $(N/V) = 1/v$ unchanged, we get asymptotically $F_1(q) \to 1$. It is perfectly clear that a preliminary necessary condition for this must be the finiteness of the size of the walled layer of the system, where as a consequence of surface effects it is certain that $F_1(q) \neq 1$. In the opposite case Eq. (3) is devoid of physical meaning.

5. ON THE SIZE OF THE WALLED LAYER OF THE SYSTEM

Consider a molecular system of volume V and number of particles N, bounded, for example, by plane walls. Then let N and V increase without limit, keeping unchanged the relation $(V/N) = v$ and also the position of one of the walls. We consider the latter situated in the xOy plane, and the system itself extending in the direction of the positive Oz axis. In the limit we obtain a semi-infinite system occupying the entire right half-space. We will assume the wall to be ideal, although the final results would not be altered as long as the potential of the interaction of the wall on the particles had a sufficiently rapid fall-off. Conditions (1) do not hold in the neighborhood of the wall, and it is clear from symmetry considerations that $F_1(q) \equiv F_1(z)$. One may

readily satisfy oneself that in our system the partial distribution functions satisfy equations completely analogous to those of Bogoliubov[1], but in which the integration extends only over the right half-space. For example, for $F_1(z)$ we obtain

$$kT \frac{dF_1(z)}{dz} \quad (31)$$

$$+ \frac{1}{v} \int_{(z'>0)} \frac{\partial \Phi(|q - q'|)}{\partial z} F_2(q,q') dq q' = 0$$

in which the coordinates of the point q may be set equal to $(0,0,z)$. In order to obtain from this an approximate expression for $F_1(z)$, it is necessary to express $F_2(q,q')$ in terms of $F_1(z)$. The superposition approximation, which we are following, corresponds to a relation between F_1 and F_2 of form

$$F_2(q,q') = F_1(z) F_1(z') g(|q - q'|). \quad (32)$$

Actually, if we return to relations (1) and (2), we notice that, for example, $F_3(q,q',q'')$ may be interpreted as the binary distribution function for two particles for a given (and fixed) position of the third: $F_3(q,q',q'') \equiv F_2(q,q' | q'')$. Analogously $g(|q-q''|)$ may be interpreted as the unitary probability density of position of one of the particles for a given and maintained position of the second: $g(|q-q''|) \equiv F_1(q | q'')$. [We note that there is a similar universally prevalent representation of the radial function of the distribution $g(|q|) \equiv F_1(q | 0)$, although according to the definition it is necessary to connect it not with F_1 but with F_2 : $g(|q - q''|) \equiv F_2(q, q'')$; both points of view are equally valid]. Hence relation (2) may be written thus:

$$F_2(q, q' | q'') \quad (33)$$

$$= F_1(q | q'') F_1(q' | q'') g(|q - q'|).$$

That which is given and fixed beforehand in our problem is the position not of the third particle, but of the wall, and (33) is physically transformed into (32). Thus, allowing (32), we remain within the framework of the superposition approximation and do not introduce new limitations on the partial distribution functions.

Inserting (32) and (31), going over again to the dimensionless unit of length, and using relation (4), we easily integrate the resulting equation and obtain

$$kT \ln F_1(z) \quad (34)$$

$$+ \frac{\lambda}{2\pi} \int_{(z'>0)} E(|q - q'|) F_1(z') dq' = C.$$

Since we are considering a homogeneous phase, we must require that $F_1(z) \to 1$ for $z \to \infty$. This determines the constant of integration

$$C = 2\lambda \int_0^\infty E(\rho)\rho^2 d\rho. \tag{35}$$

If, as above, we go over from $g(r)$ and $E(t)$ to $u(r)$ and $\bar{E}(t)$ by means of relations (6) and (7), we obtain an equation for the determination of $F_1(z)$

$$\ln F_1(z) = -2\lambda \int_0^\infty \bar{E}(\rho)\rho^2 d\rho + \frac{\lambda}{2\pi} \tag{36}$$

$$\int_{(z'>0)} \bar{E}(|q - q'|)F_1(z')dq'.$$

The last member may be simplified by introduction of cylindrical coordinates z', ρ, ϕ in place of the cartesian coordinates $q' = (x', y, z')$. Then

$$\int_{(z'>0)} \bar{E}(|q - q'|)F_1(z')dq' \tag{37}$$

$$= 2\pi \int_0^\infty \left\{ \int_0^\infty \bar{E}[\sqrt{\rho^2 + (z - z')^2}]\rho d\rho \right\} F_1(z')dz'$$

$$= 2\pi \int_0^\infty \left\{ \int_{|z-z'|}^\infty \bar{E}(|t|)tdt \right\} F_1(z')dz'$$

$$= 2\pi \int_0^\infty K(|z - z'|)F_1(z')dz',$$

where the kernel $K(z)$ is identical with the kernel $K(z)$ in (10). Thus we have finally

$$\ln F_1(z) = -2\lambda \int_0^\infty \bar{E}(\rho)\rho^2 d\rho \tag{38}$$

$$+ \lambda \int_0^\infty K(|z - z'|)F_1(z')dz'.$$

Now let $z \to \infty$. Setting

$$F_1(z) = 1 + \psi(z) \tag{39}$$

and reckoning $|\psi(z)| < 1$, we readily simplify Eq. (38) and obtain

$$\psi(z) = \lambda \int_0^\infty K(|z - z'|)\psi(z')dz' \quad (z \to \infty). \tag{40}$$

This equation is identical with Eq. (11); whence it follows that the function $r[g(r) - 1]$ for $r \to \infty$ behaves like the function $F_1(z) - 1$ for $z \to \infty$, a result of some importance for the theory of liquids.

If, as above, we allow the intermolecular forces to have a finite radius of action, σ, then, in precisely the same way as in Sec. (2), we find

$$F_1(z) = 1 + \sum_n \bar{A}_n e^{-|\alpha_n|z} \cos(\beta_n z + \bar{\delta}_n), \tag{41}$$

where $\alpha_n(\lambda)$ and $\beta_n(\lambda)$ are the same as in (19), while the numbers $\bar{A}_n$ and $\bar{\delta}_n$ remain undetermined and possibly different from the corresponding A_n and δ_n in (19). Assuming the former enumeration of the $\alpha_n(\lambda)$ according to (20) to be correct, we see at once that the magnitude $|\alpha_1(\lambda)|^{-1}$ is the effective size of the walled layer of the system, in which $F_1(z)$ is notably different from unity. The special case $\alpha_1(\lambda) = 0$ considered in (3) thus corresponds to an infinitely extended "superficial layer".

We consider it necessary to remark, in order to avoid misunderstanding, that the periodic solution $F_1(z) \sim 1 + \bar{A}_1 \cos(\beta_1 z + \bar{\delta}_1)$ appearing in (41) for $\alpha_1(\lambda) = 0$ has no relation to the crystalline state.

6. CONCLUSION

It is not difficult now to formulate the correct requirement which must be satisfied by the behavior of the solution of Eq. (3) for $r \to \infty$. Since Eq. (3) relates only the spatial properties of a homogeneous phase and requires for its correctness the identity $F_1(q) \equiv 1$, this indicates that in the problem of a system bounded by a plane wall the preliminary condition must be $F_1(z) \to 1$ for $z \to \infty$. Since, on the other hand, it appears that the behavior of $F_1(z) - 1$ for $z \to \infty$ in the problem of a system bounded by a wall is identical with the behavior of $r[g(r) - 1]$ for $r \to \infty$ in the problem of the unbounded system, we infer that the preliminary condition required for the correctness of Eq. (3) is that

$$r[g(r) - 1] \to 0 \quad \text{for} \quad r \to \infty. \tag{42}$$

It must be emphasized that this inference is obtained merely from a single comparison of Eqs. (11) and (40) and does not require for its establishment preliminary knowledge of the solutions of (19) and (41).

It is important to note that the nonfulfillment of the first of the conditions (1) necessarily brings with it the nonfulfillment of the second. Hence we may also say that the requirement (42) is a requirement that $g(|q - q'|) = F_2(q, q')$ (exactly, apart from terms which go to zero for $N \to \infty$). Nonfulfillment of condition (42) signifies, then, that $g(|q - q'|) \neq F_2(q, q')$. although $g(r)$, as a solu-

tion of the formally stated problem concerning Eq. (3), that is, of the purely mathematical problem, may possibly exist. However, it is clear that such a solution lacks physical meaning.

Thus we may say that the correctly presented mathematical problem of finding the radial distribution function $g(r)$ for a given intermolecular potential $\Phi(r)$ and given thermodynamic parameters T and λ, adequate to its physical content, is included in the solution of the problem of the eigenvalues λ and eigenfunctions $g(r;\lambda)$ of equation (3) under the additional requirement (42). The normalization requirement (5) is automatically fulfilled at the same time.

The solutions $g(r)$ considered above which correspond to thermodynamically absolutely unstable states do not belong to eigenvalues λ of the problem formulated in the indicated manner. The spectrum of eigenvalues λ now shows itself to be generally speaking, discontinuous, consisting of several continuous bands. The connection of this situation with the theory of phase transitions is evident. We will devote more attention to it in subsequent communications.

In conclusion we wish to remark, in order to avoid misunderstanding, that the states of the system were qualified by us in all the above as stable in a limited sense, that is, such a state may in reality prove to be only metastable. Correspondingly, instability is everywhere understood absolutely.