Condensation of a Classical Gas with Long-Range Attraction

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The statistical mechanics of a classical gas of hard spheres with long-range attractive interaction is developed. It is shown that condensation occurs, and the thermodynamic properties of the system are derived. Density fluctuations are also calculated.

1. INTRODUCTION

THE "condensation problem" is the problem of showing how the evaluation of the partition function for a collection of particles may lead to the thermodynamic properties of a condensing system, and of deriving from it the other macroscopic features of a two-phase system. It is generally felt that only rather elaborate mathematics can be expected to extract from statistical mechanics the discontinuities which are characteristic for phase transitions. In fact, both Onsager's treatment of the two-dimensional Ising model[1] and the work of Kac, Uhlenbeck, and Hemmer[2] on the one-dimensional gas require special mathematical methods. In the present paper, however, we treat a simple model of a gas which permits us to derive the familiar features of condensation by means of standard methods of statistical mechanics.

It has often been remarked that the evaluation of the partition function cannot lead to a discontinuous phase transition unless one goes to the limit of an infinite system. This is true for a rigorous mathematical treatment, but the standard methods of statistical mechanics employ asymptotic formulas, which implicitly assume the system to be very large. This is the reason why we shall not need to carry out the limiting process explicitly. The discontinuities enter simply because different asymptotic expressions have to be used for different values of the thermodynamic variables.

The model consists of a gas of small hard spheres, with a two-body interaction consisting of a very long-range, smoothly varying two-body potential. This potential is supposed attractive in the sense that it is everywhere negative or zero. The gas is treated classically and with Boltzmann statistics. This model is similar to the one of Kac, Uhlenbeck, and Hemmer, but the present treatment is three-dimensional and not confined to a special form of the interaction. It is also the picture on which Van der Waals' theory is based, and in fact we shall find the Van der Waals equation of state. In addition, however, it will be shown that the flat part of the isotherm is a necessary consequence of statistical mechanics.

The long-range attraction is, of course, not a realistic

description of an actual gas. However, it is felt that the model correctly describes the essential mechanism of condensation, namely, the competition between the liquid configurations, which are favored by their low energy, and the gaseous configurations, which occupy a large volume in phase space. The long range permits us to disentangle the features that cause condensation from the complications of the geometry of hard spheres in space, which appear to be unessential for condensation. These complications are not eliminated altogether, but we shall be able to deal with them by assuming only some general properties of the hard-sphere partition function. Actually, to simplify the presentation we shall adopt a definite but crude expression for this partition function, and show in Appendix I that the results are more general.

An outline of the method follows. In the canonical partition function the kinetic energy part enters only in a trivial way; for brevity we shall omit it altogether. Hence, we are left with a sum over "*configurations.*" Because of the long-range character of the interaction, the total volume may be subdivided in cells, and the configurations may be identified by the number of particles in each cell. The configuration that gives the maximum term is the stable physical state. To find this maximum term the variation is set equal to zero in the familiar way. However, in this way one finds all configurations for which the magnitude of the term in the partition function is stationary; such configurations will be called "*states.*" The states that correspond to relative maxima which are not absolute maxima are metastable physical states. The states that correspond to minima or saddle points are unstable, and therefore unphysical. *The laws of thermodynamics, however, apply to all states, stable, metastable, or unstable,* because in their derivation only the stationary property is used.

In Sec. 2 all one-phase states are found, i.e., states for which the density is homogeneous. They obey the Van der Waals equation. In Sec. 3 it is shown that above the critical temperature they are stable, and that below the critical temperature they are stable or metastable in the descending parts of the Van der Waals isotherm, but unstable in the ascending part. In Sec. 4 two-phase states are constructed. It is shown in Sec. 5 that they have the expected thermodynamic properties, and that they have a higher probability than the one-phase states with the same number of particles. This establishes the fact that the Van der

[1] L. Onsager, Phys. Rev. **65**, 117 (1944); or, for example, K. Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), Chap. 17.

[2] M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. **4**, 216 and 229 (1963).

Waals isotherm has to be modified by a horizontal line. In Sec. 6 a slightly different method is used to prove that there are no other states, so that the ones we have found are, indeed, the stable physical states. Finally in Sec. 7 the fluctuations in the density are calculated for the one-phase states.

2. ONE-PHASE STATES AND THE VAN DER WAALS EQUATION

The volume of the hard spheres will be measured by δ, the attractive potential is $-w(\mathbf{r},\mathbf{r}') = -w(|\mathbf{r}-\mathbf{r}'|)$. The volume V of the container will be subdivided in cells of volume Δ. It is supposed that Δ is so large that it contains many particles, but so small that the potential $-w(r)$ is practically constant inside Δ. This imposes the condition that the range of $w(r)$ must be very long compared to $\delta^{1/3}$, and that *the density must be so high that many particles interact simultaneously.*

Let the position of the ith cell be $\mathbf{r}_i$, and let N_i be the number of particles in it. The amount of phase space of N_i hard spheres in volume Δ will be called $\omega_i(N_i)$. In one dimension one would have

$$\omega(N_i) = (\Delta - N_i\delta)^{N_i}. \tag{1}$$

For definiteness we shall also use this expression for the three-dimensional case; it is well known that δ should then be taken to be four times the hard-sphere volume. Its precise form is essential for the Van der Waals equation, but it is shown in Appendix I that for condensation only the general form of this function is important. A configuration is defined by the set of numbers $\{N_i\}$. The total number of particles of a given configuration $\{N_i\}$ is

$$\sum_i N_i = N, \tag{2}$$

and its energy is

$$-\tfrac{1}{2}\sum_{ij} w(\mathbf{r}_i,\mathbf{r}_j)N_iN_j = -\tfrac{1}{2}\sum_{ij} w_{ij}N_iN_j.$$

The canonical partition function is (the kinetic energy part being omitted)

$$Q_N = \frac{1}{N!}\sum_{\{N_i\}}'\frac{N!}{\prod_i N_i!}\Big[\prod_i \omega(N_i)\Big]\exp\big[\tfrac{1}{2}\beta\sum_{ij}w_{ij}N_iN_j\big]$$

$$= \sum_{\{N_i\}}' \exp\Phi\{N_i\}. \tag{3}$$

Here $\sum'$ indicates summation over all configurations subject to the condition (2), and

$$\Phi\{N_i\} = \sum_i [N_i\ln(\Delta - N_i\delta) - N_i\ln N_i + N_i]$$
$$+ \tfrac{1}{2}\beta\sum_{ij}w_{ij}N_iN_j. \tag{4}$$

The curly brackets serve to emphasize that Φ is a function of *all* N_i.

According to the standard procedure we have to find the maximum term in (3), that is, we have to find the absolute maximum of (4). This absolute maximum is among the points in which Φ is stationary with respect to variations in the N_i, subject to the condition (2). These points obey the set of equations

$$\ln\frac{\Delta - N_i\delta}{N_i} - \frac{N_i\delta}{\Delta - N_i\delta} + \beta\sum_j w_{ij}N_j = \alpha, \tag{5}$$

where α is a Lagrangian multiplier, to be adjusted to get the desired total number of particles.

One solution of (5) is easily obtained by *postulating a homogeneous density*, so that

$$N_i = N\Delta/V. \tag{6}$$

In this way all equations (5) are satisfied provided that α is taken to be

$$\ln\frac{V - N\delta}{N} - \frac{N\delta}{V - N\delta} + \beta w_0\frac{N}{V} = \alpha, \tag{7}$$

where

$$w_0 = \sum_j w_{ij}\Delta = \int w(r)d^3\mathbf{r}.$$

The corresponding stationary value of Φ is

$$\Phi_s = N\ln[(V - N\delta)/N] + N + \tfrac{1}{2}\beta w_0(N^2/V). \tag{8}$$

If this is also the absolute maximum of Φ, one may write $Q_N = \exp\Phi_s$, so that the free energy is given by $-\beta F = \Phi_s$. On differentiating with respect to V, one finds p, and hence the equation of state

$$\beta p = [N/(V - N\delta)] - \tfrac{1}{2}\beta w_0(N^2/V^2), \tag{9}$$

which is the Van der Waals equation.

Van der Waals' coefficient b is identical with the quantity $N\delta$ in (9) which is, indeed, four times the total volume of the hard spheres. Van der Waals' coefficient a is identical with $\tfrac{1}{2}w_0N^2$; this is also in agreement with his familiar argument, because $\tfrac{1}{2}w_0$ is the work that a particle has to do against the attraction of the surrounding particles in order to reach the boundary. It is true that our homogeneous density solution cannot be quite correct near the wall, but that does not affect the thermodynamical properties of the system provided that it is large enough.

Quantitatively the Van der Waals equation does not agree with experiment; however, quantitative agreement could not be expected in view of our drastic assumptions concerning the hard-sphere partition function (1) and the long range of the attraction.

The present derivation of Van der Waals' equation is essentially the one given by Ornstein in 1908.[3]

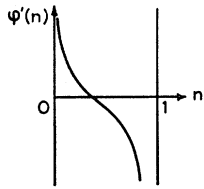[3] L. S. Ornstein, thesis, Leiden, 1908 (unpublished).

Fig. 1. The function $\varphi'(n)$; $\beta w_0 < 27/4$ [see Eq. (10)].

3. STABILITY CONDITIONS FOR ONE-PHASE STATES

Equation (8) may be written $\Phi_s = V\varphi(n)$, where n is the density N/V, and

$$\varphi(n) = n \ln[(1-n)/n] + n + \tfrac{1}{2}\beta w_0 n^2. \tag{10}$$

For convenience we use units in which $\delta = 1$, so that $0 < n < 1$. Equation (5) takes the form $\varphi'(n) = \alpha$. One easily verifies that $\varphi'(n)$ is a decreasing monotonic function when (Fig. 1)

$$\beta w_0 < 27/4, \tag{11}$$

and has one hump when (Fig. 2)

$$\beta w_0 > 27/4. \tag{12}$$

According to the Van der Waals theory, this means above and below the critical temperature, respectively, but we have not yet shown that the hump is actually connected with condensation.

In order to check whether the solution found is a maximum of $\Phi\{N_i\}$ we compute the matrix of the second derivatives

$$\frac{\partial^2 \Phi}{\partial N_i \partial N_j} = -\left[\delta_{ij}\frac{\Delta^2}{N_i(\Delta-N_i)^2} - \beta w_{ij}\right].$$

On substituting (6) one obtains for [ ] a matrix which, according to the first lemma in Appendix II, is positive definite when

$$\frac{V^3}{N\Delta(V-N)^2} > \beta \sum_i w_{ij} = \frac{\beta w_0}{\Delta};$$

that is, when

$$-\frac{1}{n(1-n)^2} + \beta w_0 < 0.$$

Since the left-hand side of this inequality is $\varphi''(n)$, we may state: *Where the curve in Fig. 1 or Fig. 2 has a negative slope, the solution corresponds to a (relative) maximum of* Φ. On the other hand, where the slope is positive, i.e., between A and B in Fig. 2, it corresponds to a configuration for which Φ is stationary, but not a maximum (according to the second lemma in the Appendix II), and therefore not a physical state.

For temperatures obeying (11), the slope is always negative, so that the solution we found is always a relative maximum of $\Phi\{N_i\}$. However, it can also be shown in this case that it is the only relative maximum

of $\Phi\{N_i\}$, so that it must be its absolute maximum and hence a stable physical state. Indeed, one has for any value of N_i the mathematical inequality

$$\frac{\Delta^2}{N_i(\Delta-N_i)^2} \geqslant \frac{27}{4}\frac{1}{\Delta}.$$

Thus, when (11) holds, the matrix of the second derivatives is negative definite for every configuration $\{N_i\}$. Consequently, $\Phi\{N_i\}$ is a convex function of the variables N_i, and can have, therefore, no more than one maximum. This proves that *when (11) holds, the stable state consists of one phase, with homogeneous density in the volume* V.

4. CONSTRUCTION OF TWO-PHASE STATES

When (12) holds there is an interval of values of α for which there are three different densities, $n_{\rm I}$, $n_{\rm II}$, $n_{\rm III}$ (see Fig. 2), but $n_{\rm III}$ is not a physical state. The other two densities $n_{\rm I}$ and $n_{\rm II}$ are at least relative maxima and will give us the densities of the coexisting phases. However, a state with coexisting phases can no longer be described by a homogeneous density, so that we have to go back to (5). What has to be shown is that the absolute maximum of $\Phi\{N_i\}$ obtains for a configuration that has a homogeneous density $n_{\rm I}$ in one part $V_{\rm I}$ of the volume, and another homogeneous density $n_{\rm II}$ in the remaining part $V_{\rm II}$. In this section it will be shown that there actually is such a configuration for which Φ is stationary.

Let $n(\mathbf{r})$ be the space-dependent density, so that $N_i = n(\mathbf{r}_i)\Delta$. Then (4) becomes

$$\Phi\{n(\mathbf{r})\} = \int_V n(\mathbf{r})\left\{\ln\frac{1-n(\mathbf{r})}{n(\mathbf{r})}+1\right\}d^3\mathbf{r}$$

$$+\tfrac{1}{2}\beta \int\int_V w(\mathbf{r},\mathbf{r}')n(\mathbf{r})n(\mathbf{r}')d^3\mathbf{r}d^3\mathbf{r}'$$

$$= \int_V \varphi(n(\mathbf{r}))d^3\mathbf{r}$$

$$-\tfrac{1}{4}\beta \int\int_V w(\mathbf{r},\mathbf{r}')\{n(\mathbf{r})-n(\mathbf{r}')\}^2 d^3\mathbf{r}d^3\mathbf{r}'. \tag{13}$$

Note that $\Phi\{n(\mathbf{r})\}$ is a functional of $n(\mathbf{r})$, while $\varphi(n(\mathbf{r}))$ is simply the function (10) taken at the value $n = n(\mathbf{r})$ of its argument. Differentiation with respect to N_i now takes the form of functional derivation, so that (5)
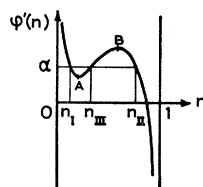

Fig. 2. The function $\varphi'(n)$; $\beta w_0 > 27/4$ [see Eq. (10)].

becomes

$$\frac{\delta\Phi}{\delta n(\mathbf{r})}\equiv\varphi'(n(\mathbf{r}))-\beta\int w(\mathbf{r},\mathbf{r}')\{n(\mathbf{r})-n(\mathbf{r}')\}d^3\mathbf{r}'=\alpha. \quad (14)$$

Rather than analyze this integral equation we make two simplifications. (In Sec. 6 the same results will be obtained without these simplifications.) First, it is assumed that $n(\mathbf{r})$ varies only slowly compared to the range of w, so that $n(\mathbf{r})-n(\mathbf{r}')$ may be expanded to second order in $\mathbf{r}-\mathbf{r}'$. This reduces (14) to the partial differential equation

$$\varphi'(n(\mathbf{r}))+\tfrac{1}{2}\beta w_2\nabla^2 n(\mathbf{r})=\alpha,$$

where

$$w_2=\frac{1}{3}\int \mathbf{r}^2 w(\mathbf{r})d^3\mathbf{r}.$$

Secondly it is assumed that $n(\mathbf{r})$ depends on only one coordinate x, so that we get an ordinary differential equation for $n(x)$,

$$\tfrac{1}{2}\beta w_2(d^2 n/dx^2)=-\varphi'(n)+\alpha. \quad (15)$$

This equation need not be solved exactly, because the relevant features can be deduced by noticing that *it may be interpreted as the equation of motion of a classical point mass* with coordinate n, mass $\tfrac{1}{2}\beta w_2$, time x, moving in the one-dimensional potential

$$\psi(n)=\varphi(n)-\alpha n$$
$$=n\ln[(1-n)/n]+(1-\alpha)n+\tfrac{1}{2}\beta w_0 n^2,$$

(Fig. 3). The maxima of $\psi(n)$ are found from $\varphi'(n)-\alpha=0$, and are therefore n_I and n_{II}, while n_{III} is the minimum. Two solutions of the "equation of motion" (15) are obvious, viz., $n(x)=n_I$ and $n(x)=n_{II}$. They are the homogeneous density solutions obtained in Sec. 2. We are now interested in a solution that tends to n_I for $x\to-\infty$, and to n_{II} for $x\to+\infty$. That is, the point mass is to be initially at rest on top of one potential hill, then move over to the other one, and finally come to rest on top of the other hill. This is a possible solution if and only if both potential hills have the same height,

$$\psi(n_I)=\psi(n_{II}). \quad (16)$$

This condition for coexistence is an implicit equation for α. To show that there is just one solution $\alpha=\alpha_0$, we
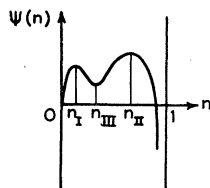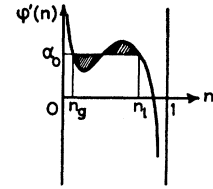

FIG. 3. The function $\psi(n)=\varphi(n)-\alpha n$.

FIG. 4. Determination of α_0.

write it in the form

$$\int_{n_I}^{n_{II}}\varphi'(n)dn=\alpha_0(n_{II}-n_I).$$

This shows that α_0 is determined by the equal area construction applied to the curve for $\varphi'(n)$. (See Fig. 4.) The values of n_I and n_{II} that are determined in this way depend on β alone, and will be denoted by n_g and n_l. To show that (16) is the condition for equal pressures we note that in a one-phase state $\Phi_s=V\varphi(n)$, so that

$$\beta p=\partial\Phi_s/\partial V=\varphi(n)-n\varphi'(n)=\varphi(n)-\alpha n=\psi(n).$$

Remark. In the p-V diagram, the equality of pressures is represented by a horizontal line, while the equality of α's gives rise to the equal area construction. In the present approach the α-n diagram is more natural, and the situation is reversed. Note also that the familiar thermodynamic derivations of the equal area construction are perfectly justified, because thermodynamics applies to all states represented by the Van der Waals curve, even those that are unstable and therefore unphysical.

Let V_g be the volume filled with density n_g, and V_l the volume with density n_l. The volumes V_g and V_l may still be chosen arbitrarily subject to the conditions

$$V_g\geqslant 0, \quad V_l\geqslant 0, \quad V_g+V_l=V. \quad (17)$$

Hence, we have a set of two-phase states, all having the same $\alpha=\alpha_0$. The number of particles in each state is determined by

$$N=V_g n_g+V_l n_l. \quad (18)$$

Thus, there is a state for each value of N in the interval

$$n_g\leqslant N/V\leqslant n_l. \quad (19)$$

To verify that they describe stable two-phase states we shall prove in Sec. 6 that Φ is not just stationary but maximal.

5. PROPERTIES OF THE TWO-PHASE STATES

The densities n_g and n_l are determined by

$$\varphi'(n_g)=\varphi'(n_l),$$
$$\varphi(n_g)-n_g\varphi'(n_g)=\varphi(n_l)-n_l\varphi'(n_l). \quad (20)$$

In a graph of $\varphi(n)$ versus n they are found by drawing the double tangent (Fig. 5), α_0 being the slope of the tangent.
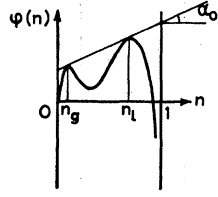
Fig. 5. Determination of n_g and n_l.

For a two-phase state the free energy is given by [see Eq. (13)]

$$-\beta F = \Phi\{n(\mathbf{r})\} = V_g \varphi(n_g) + V_l \varphi(n_l) + \Phi_t ,$$

where Φ_t is an integral over the transition layer, representing the surface free energy. As we are only interested in thermodynamic bulk properties we may omit Φ_t. Hence the free energy is $F = F_g + F_l$, where F_g and F_l are the one-phase free energies corresponding to volumes V_g and V_l and densities n_g and n_l. The pressure is given by

$$\beta p = \frac{\partial \Phi}{\partial V} = \frac{\partial V_g}{\partial V} p_g + \frac{\partial V_l}{\partial V} p_l = \beta p_g .$$

Thus it has a constant value for all two-phase states.

It is easy to prove that in the whole interval (19) *the two-phase state has a higher value of Φ than the one-phase state with the same N and β.* For this purpose one has to show

$$V_g \varphi(n_g) + V_l \varphi(n_l) > V\varphi\left(\frac{V_g}{V}n_g + \frac{V_l}{V}n_l\right).$$

Graphically this inequality states that the double tangent must lie above the curve $\varphi(n)$. It is obvious from Fig. 5 that this is actually the case.

It now remains to show that the one-phase and two-phase states we have constructed are the only possible states, i.e., there are no other configurations for which Φ is stationary and perhaps greater. For the case (11) this has already been proved; in the next section it will be proved for the case (12) by means of a slightly different approach.

6. ALTERNATIVE APPROACH

The expression (13) for $\Phi\{n(\mathbf{r})\}$ consists of two terms, $\Phi = \Phi_1 + \Phi_2$, which are of different character. Φ_1 is an integral over space, whose integrand depends only on the local value of the density. Φ_2 is a double integral depending on the difference of the densities at two points within each others range of interaction. This term is zero if the density is homogeneous, and negative otherwise, all contributions arising from regions where $n(\mathbf{r})$ varies.

First we omit Φ_2 and maximize Φ_1. For this purpose we write

$$\Phi_1\{n(\mathbf{r})\} = \int_V \varphi(n(\mathbf{r})) d^3\mathbf{r} = \int_0^1 \varphi(n)v(n)dn, \quad (21)$$

where $v(n)dn$ is the combined volume of all regions in V where $n < n(\mathbf{r}) < n + dn$. Note that with each density distribution $n(\mathbf{r})$ is associated one function $v(n)$, but, in general, there are many $n(\mathbf{r})$ compatible with each function $v(n)$. Clearly

$$v(n) \geqslant 0, \quad \int_0^1 v(n)dn = V, \quad \int_0^1 nv(n)dn = N. \quad (22)$$

The problem is to find that function $v(n)$ that maximizes (21) with the subsidiary conditions (22).

To solve this variation problem we begin by only taking into consideration functions $v(n)$ of the special type

$$v(n) = \sum_{\lambda=1}^{\Lambda} v_\lambda \delta(n - n_\lambda), \quad (23)$$

so that (21) takes the form

$$\Phi_1\{n(\mathbf{r})\} = \sum_\lambda v_\lambda \varphi(n_\lambda).$$

The number of terms Λ and the quantities v_λ and n_λ may be varied subject to the conditions

$$v_\lambda > 0, \quad \sum_\lambda v_\lambda = V, \quad \sum_\lambda v_\lambda n_\lambda = N. \quad (24)$$

The familiar method now leads to

$$\sum_\lambda \varphi(n_\lambda)\delta v_\lambda + \sum_\lambda v_\lambda \varphi'(n_\lambda)\delta n_\lambda = 0$$

with subsidiary conditions

$$\sum_\lambda \delta v_\lambda = 0, \quad \sum_\lambda (n_\lambda \delta v_\lambda + v_\lambda \delta n_\lambda) = 0.$$

Introducing two Lagrange parameters α, α', one finds

$$\varphi(n_\lambda) = \alpha n_\lambda + \alpha', \quad (25)$$

$$\varphi'(n_\lambda) = \alpha. \quad (26)$$

The meaning of these equations can be visualized if one plots the curve for $\varphi(n)$ as a function of n (Fig. 6). According to (25) the n_λ must be the abscissas of the intersections of this curve with some straight line L. According to (26) L must be tangent to the curve in these intersections. (Not necessarily all intersections of L with the curve need be used.) It is clear from Fig. 6 that these conditions can be met in only two ways.

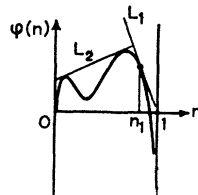(i) $\Lambda = 1$. Any value n_1 between 0 and 1 obeys the

Fig. 6. Graphic solution of Eqs. (25) and (26).

conditions (25) and (26), L being the tangent in the corresponding point $\varphi(n_1)$, for instance L_1 in Fig. 6. Because of (24) one has $v_1 = V$, $n_1 = N/V$, so that $v(n) = V\delta(n - N/V)$. This particular $v(n)$ leaves no choice for the density distribution: $n(\mathbf{r}) = N/V$. These are the one-phase states found in Sec. 2.

(ii) $\Lambda = 2$, so that L has to be L_2 in Fig. 6. In this case n_1 and n_2 are uniquely determined and obey, according to (26) and (25) the equations (20), so that n_1 and n_2 are identical with n_g and n_l. The parameters v_1 and v_2 are determined by (24), which shows that they are identical with V_g and V_l [cf. (17) and (18)]. Hence

$$v(n) = V_g\delta(n - n_g) + V_l\delta(n - n_l). \quad (27)$$

However, there are many density distributions $n(\mathbf{r})$ associated with this $v(n)$, because the two phases may be interlaced.

Thus, we have found all configurations for which Φ_1 is stationary. In the intervals

$$0 < N/V \leqslant n_g \quad \text{and} \quad n_l \leqslant N/V < 1, \quad (28)$$

the one-phase state is the only one, so that it is also the absolute maximum. It is true that only functions of the type (23) were allowed to enter the competition, but that does not affect the result. Indeed, if a function $v(n)$ obeying (22) would exist for which (21) takes a larger value, it would be possible to approximate it by a function of type (23) which also obeys (22), and for which the integral (21) would also be larger than the maximum we found. Moreover, since the one-phase state is not only the absolute maximum of Φ_1, but also of the second term,

$$\Phi_2 = -\tfrac{1}{4}\beta \int\!\!\int_V w(\mathbf{r},\mathbf{r}')\{n(\mathbf{r}') - n(\mathbf{r}')\}^2 d^3r d^3r',$$

it is the absolute maximum of Φ itself. Thus, we have completed the proof that below the critical temperature the one-phase state is the stable physical state in the range (28).

In the remaining interval (19), Φ_1 is stationary for the one-phase state, and for all the two-phase configurations that are associated with (27). It has been proved in Sec. 5 that Φ_1 is greater for the two-phase configurations, hence this is the absolute maximum of Φ_1. If one now includes Φ_2, it is clear that among these two-phase configurations the highest value of Φ_2, and hence of Φ, obtains for that configuration for which both phases are spatially separated, with the smallest possible interface.

This does not yet complete the proof that this configuration is actually the stable physical state, because it is conceivable that the maximum of Φ is reached by another configuration, not included among those that correspond to the absolute maximum of Φ_1. In fact, that may actually occur if the diameter of V is comparable to the range of $w(r)$. However, for large systems, Φ_1 is proportional to V, whereas Φ_2 is of the

order $V^{2/3}$ for the state we have found. Hence, a decrease of Φ_1 cannot be compensated by an increase of Φ_2.

The fact that Φ_2 is of lower order that Φ_1 has another consequence. Although the configuration with the smallest interface is the most probable, the configurations with a somewhat larger interface are not much less probable if the system is large. Hence, two-phase states in which the liquid phase forms a small (compared to 10^{23}) number of droplets may occur. This suggests that one may develop a statistical mechanics of interfaces, as was used by Peierls[4] and by Landau and Lifshitz.[5]

7. DENSITY FLUCTUATIONS

In order to find the probability distribution of the density fluctuations, we compute the second derivatives of $\Phi\{n\}$.

$$\frac{\delta^2\Phi}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} = [\varphi''(n(\mathbf{r})) - \beta w_0]\delta(\mathbf{r} - \mathbf{r}') + \beta w(\mathbf{r},\mathbf{r}'),$$

in agreement with the result in Sec. 3. For a stable one-phase state $\varphi''(n(\mathbf{r})) = \varphi''(N/V)$ is negative and will be denoted by $-|\varphi''|$. Thus, one has to second order of $\nu(\mathbf{r})$

$$\exp[\Phi\{N/V + \nu(\mathbf{r})\} - \Phi\{N/V\}]$$

$$= \exp\left[-\tfrac{1}{2}(|\varphi''| + \beta w_0)\int \{\nu(\mathbf{r})\}^2 d^3r\right.$$

$$\left. + \tfrac{1}{2}\beta \int\!\!\int w(\mathbf{r},\mathbf{r}')\nu(\mathbf{r})\nu(\mathbf{r}')d^3r d^3r'\right]. \quad (29)$$

This is the probability distribution of the fluctuation $\nu(\mathbf{r})$, apart from a constant factor. The exponent is a quadratic form, which can be diagonalized by Fourier transformation

$$\nu(\mathbf{r}) = V^{-1/2}\sum_{\mathbf{k}\neq 0}\nu_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \nu_{\mathbf{k}} = \nu_{-\mathbf{k}}{}^*. \quad (30)$$

The term with $\mathbf{k} = 0$ is to be omitted since the integral of $\nu(\mathbf{r})$ must vanish. Substitution in (29) yields the probability distribution of the $\nu_{\mathbf{k}}$.

$$\exp[-\tfrac{1}{2}\sum_{\mathbf{k}\neq 0}(|\varphi''| + \beta w_0 - \beta w_k)|\nu_{\mathbf{k}}|^2],$$

where

$$w_k = \int e^{-i\mathbf{k}\cdot\mathbf{r}}w(\mathbf{r})d^3r = w_0 - \tfrac{1}{2}w_2 k^2 + O(k^4). \quad (31)$$

It follows (after decomposing $\nu_{\mathbf{k}}$ into real and imaginary parts) that

$$\langle \nu_{\mathbf{k}}\nu_{\mathbf{k}'}{}^*\rangle = (|\varphi''| + \beta w_0 - \beta w_k)^{-1}\delta_{\mathbf{k}\mathbf{k}'}. \quad (32)$$

[4] R. E. Peierls, Proc. Cambridge Phil. Soc. 32, 477 (1936).
[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), Sec. 149.

The covariance of density fluctuations at two points $\mathbf{r}$ and $\mathbf{r}'$ is easily found from (30) and (32):

$$\langle \nu(\mathbf{r})\nu(\mathbf{r}')\rangle = \frac{1}{V}\sum_{k\neq 0}\frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{|\varphi''|+\beta w_0-\beta w_k}$$

$$=\frac{1}{8\pi^3}\int\frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{|\varphi''|+\beta w_0-\beta w_k}d^3\mathbf{k}-\frac{1}{V}\frac{1}{|\varphi''|}$$

$$=\frac{\delta(\mathbf{r}-\mathbf{r}')}{|\varphi''|+\beta w_0}-\frac{1}{V}\frac{1}{|\varphi''|}+\frac{1}{4\pi^2 i}\frac{1}{|\varphi''|+\beta w_0}$$

$$\times\int_{-\infty}^{\infty}\frac{\beta w_k}{|\varphi''|+\beta w_0-\beta w_k}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}kdk.\quad(33)$$

If $|\mathbf{r}-\mathbf{r}'|$ *is large* compared to the range of $w(r)$, only low values of k contribute to the integral, so that w_k may be expanded to second order in k, see (31). The integral may then be computed in the usual way to give

$$\langle\nu(\mathbf{r})\nu(\mathbf{r}')\rangle=\frac{1}{|\varphi''|}\left\{\frac{\kappa^2}{4\pi}\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}-\frac{1}{V}\right\},\quad\kappa^2=\frac{2|\varphi''|}{\beta w_2}.\quad(34)$$

This is the familiar result of Ornstein and Zernike.[6] It is only meaningful if κ^{-1} is larger than the range of $w(r)$, which is conveniently measured by $(w_2/w_0)^{1/2}$. Hence, the condition is

$$2|\varphi''|/\beta w_2 < w_0/w_2.\quad(35)$$

This requires $|\varphi''|$ to be small, which, for stable one-phase states, occurs only near the critical point.

In order to specify further the region where (34) is meaningful, we introduce $f(n)$ by putting

$$\varphi(n)=f(n)+\tfrac{1}{2}\beta w_0 n^2.\quad(36)$$

The function $f(n)$ refers only to the hard spheres (cf. Appendix I), and does not involve β. In the neighborhood of the critical density n_c, one has

$$\varphi''(n)=\tfrac{1}{2}(n-n_c)^2 f''''(n_c).$$

Hence, the condition (35) becomes

$$T(n-n_c)^2<\frac{w_0/k}{|f''''(n_c)|}=\frac{f''(n_c)}{f''''(n_c)}T_c.$$

For the Van der Waals gas this works out to

$$(T/T_c)(n-\tfrac{1}{3})^2<2/27.$$

If $|\mathbf{r}-\mathbf{r}'|$ *is not large* compared to the range of $w(r)$, (34) no longer holds but (33) is still valid, provided that $|\mathbf{r}-\mathbf{r}'|$ is large compared to the average distance

⁶ L. S. Ornstein and F. Zernike, Proc. Koninkl. Akad. Wetenschap. Amsterdam **17**, 793 (1914); or, for example, L. Rosenfeld, *Theory of Electrons* (North-Holland Publishing Company, Amsterdam, 1951), Chap. 5, Sec. 6.

between molecules. Naturally, the result is no longer independent of the special shape of $w(r)$. It is easy to show that when $w(r)$ happens to be a Yukawa potential, $\langle\nu(\mathbf{r})\nu(\mathbf{r}')\rangle$ also has the form of a Yukawa potential, but with longer range. When $w(r)$ is a simple exponential one finds for $\langle\nu(\mathbf{r})\nu(\mathbf{r}')\rangle$ the sum of two Yukawa functions.

As the probability distribution of the Fourier coefficients $\{\nu_k\}$ is known, it is of course also possible to find the probability distribution of $\{\nu(r)\}$. It is more convenient to write down its Fourier transform or "characteristic function," which is found to be

$$\left\langle\exp\left[\int\Lambda(r)\nu(r)d^3r\right]\right\rangle$$

$$=\exp\left[-\tfrac{1}{2}\sum_{k\neq 0}\frac{|\Lambda_k|^2}{|\varphi''|+\beta w_0-\beta w_k}\right].$$

Here $\Lambda(r)$ is an arbitrary function with Fourier coefficients Λ_k.

The same formulas are valid for the electron gas when the appropriate substitutions are made.

$$|\varphi''|+\beta w_0=1/n_0,\quad w_k=-4\pi e^2/k^2.$$

One then finds for (33)

$$\langle\nu(\mathbf{r})\nu(\mathbf{r}')\rangle=n_0\left\{\delta(\mathbf{r}-\mathbf{r}')-\frac{\kappa^2}{4\pi}\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\right\},\quad\kappa^2=4\pi\beta e^2 n_0.$$

APPENDIX I

For the partition function of N hard spheres in a volume Δ, we have used the one-dimensional expression (1). Nevertheless, it is readily seen that the discussion of condensation is more general because it only uses the following features of the function $\omega(N)$:

(i) $(1/\Delta)\ln[\omega(N)/N!]=f(n)$, where $n=N/\Delta$.

(ii) $f(0)=0$, $\lim_{n\to 0}[f(n)/n]=+\infty$.

(iii) $f(n)\to-\infty$ for some value of n, which is taken to be $n=1$.

(iv) $f(n)$ is convex, i.e., $f''(n)<0$ for $0<n<1$.

These properties can be rigorously proved in the limit $N\to\infty$, $V\to\infty$, with constant n. One then has (36), and the critical temperature is determined by the lowest value of β for which $\varphi''(n)$ has a zero. Hence, the critical temperature and the critical density are found by solving the equations

$$f''(n)+\beta w_0=0,\quad f'''(n)=0.$$

In order to be sure that there is only one critical point, one also has to know

(v) $f''(n)$ is convex, i.e., $f''''(n)<0$.

The hard core may be replaced with any other short-range force as long as the features (i)–(v) are maintained. It would also be interesting to find a short-range interaction for which (v) does not hold, because that would lead to a more complicated phase diagram, which could be treated by the same method.

APPENDIX II

First lemma. Let A be a real symmetrical matrix of the form

$$A_{ij} = a_i \delta_{ij} - b_{ij}, \quad b_{ij} = b_{ji} \geqslant 0.$$

This matrix is positive definite if

$$a_i > \sum_j b_{ij} \quad \text{for all } i. \tag{37}$$

Proof. Let λ be an eigenvalue and $\{x_i\}$ the corresponding eigenvector,

$$\lambda x_i = \sum_j A_{ij} x_j = a_i x_i - \sum_j b_{ij} x_j.$$

Let x_1 be the component of $\{x_i\}$ with the largest absolute value and let the arbitrary phase factor in $\{x_i\}$ be chosen such that $x_1 > 0$. Then, if (37) holds,

$$(a_1 - \lambda) x_1 = \sum_j b_{1j} x_j \leqslant x_1 \sum_j b_{1j} < x_1 a_1.$$

Hence, each eigenvalue λ is positive.

Second lemma. A is not positive definite if $a_i \leqslant \sum_j b_{ij}$ for all i.

Proof. It is easily seen that for the vector $\{y_i\} = \{1,1,1,\cdots\}$ one has $\sum_{ij} y_i A_{ij} y_j \leqslant 0$.

Nonlinear Interaction of an Electromagnetic Wave with a Plasma Layer in the Presence of a Static Magnetic Field. III. Theory of Mixing*

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The Boltzmann transport equation coupled with Maxwell's equations has been solved under a small signal, plane-wave assumption for a uniform, weakly ionized plasma layer with a constant collision frequency in the presence of a static magnetic field. The effects of the nonlinear terms in the equations are included. The amplitudes of the sum and difference frequency waves produced within the plasma layer by two incident waves of different frequencies, which propagate in the extraordinary mode in the plasma, are derived as functions of the plasma and incident wave parameters. Resonances in the amplitudes of these waves occur for values of the static magnetic field in the neighborhood of plasma resonance for the waves at the fundamental and combination frequencies. The magnetic-field strength for which a given resonance occurs is a sensitive function of the electron density. This provides a mechanism through which the electron density in a plasma layer can be determined by a measurement of magnetic-field strength.

INTRODUCTION

A NUMBER of authors have discussed the problem of the mixing of two electromagnetic waves in a plasma. Ginzburg[1] has considered two different mechanisms for the generation of combination frequencies in a uniform plasma. In one case, a strong wave at frequency ω_1 traverses a homogeneous, isotropic plasma and produces a variable component of the electron-neutral particle collision frequency at frequency $2\omega_1$, due to the effect of the strong wave on the electron temperature, i.e., $\nu \propto \cos 2\omega_1 t$. A second and weaker wave of frequency ω_2 traversing the plasma results in waves of frequencies $\omega_2 \pm 2\omega_1$. In the second case, in the presence of a dc magnetic field, the stronger wave at frequency ω_1 produces additional ionization, i.e., $n \propto \cos \omega_1 t$. The simultaneous incidence of a weaker wave at frequency ω_2 results in waves of frequency $\omega_2 \pm \omega_1$. Vilenskii[2] discusses the case of an inhomogeneous plasma, in the absence of an external magnetic field, in which the applied electromagnetic field interacts with the electron density gradient to produce a first-order component of the electron density at frequency ω_1. This then interacts with a second, weaker wave at frequency ω_2 to produce waves at frequencies $\omega_2 \pm \omega_1$. The case of an inhomogeneous plasma has been discussed in greater detail by Wetzel.[3,4] Taylor[5] has calculated the effect of the polarizing field in an inhomogeneous plasma upon the mixing of two waves, when the stronger wave is of much lower fre-

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[1] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **35**, 1573 (1958) [English transl.: Soviet Phys.—JETP **35** (8), 1100 (1959)].

[2] I. M. Vilenskii, Zh. Eksperim. i Teor. Fiz. **22**, 544 (1952); **26**, 42 (1954).

[3] L. Wetzel, J. Appl. Phys. **32**, 327 (1961).

[4] L. Wetzel, Phys. Rev. **123**, 722 (1961).

[5] L. S. Taylor, J. Appl. Phys. **33**, 2913 (1962).