

# THE PHYSICAL REVIEW

*A journal of experimental and theoretical physics established by E. L. Nichols in 1893*

SECOND SERIES, VOL. 96, No. 2

OCTOBER 15, 1954

## On the Theory of Condensation

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(Received June 9, 1954)

In an attempt to understand why approximations of the van der Waals type can yield semiquantitative results in spite of being qualitatively wrong, we have assumed that the partition function for submacroscopic volumes, as a function of the number of particles, is of the van der Waals type. We have considered, as a model of a real fluid, a cubic array of submacroscopic cells with variable numbers of particles and have assumed an interaction energy between adjacent cells only. Since the van der Waals equation predicts two sharp peaks in the probability function for the occupation numbers, one has then essentially a three-dimensional Ising model. Using some of the known properties of the Ising model (and some which can be safely anticipated), we find that with plausible assumptions about the interaction energy between cells this model exhibits condensation, and that its condensation pressure, its isotherm in the stable states, and its critical temperature, are still essentially determined by those of the individual cell.

### I

APPROXIMATION formulas for the partition function  $Q_N(V)$  of a system of  $N$  interacting particles enclosed in a volume  $V$  are qualitatively wrong for macroscopic systems if they predict (like the van der Waals equation) a violation of the stability condition. It has been shown by van Hove<sup>1</sup> that, with any realistic assumptions concerning the intermolecular forces,  $\partial \ln Q_N(V)/\partial V$  is a nonincreasing function of  $V/N$  in the limit  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V$  finite. In spite of this fact, approximations of this type, when re-interpreted by means of the Maxwell construction, yield a variety of at least semiquantitative results for equilibrium states, and parts of the discarded region of the isotherm can be realized as metastable states. It seems, therefore, reasonable to believe that such expressions of the van der Waals type are approximations to some legitimate physical quantity rather than extrapolations without physical meaning and of merely historical interest. It seems natural to conjecture that they are approximations to the partition function of systems which are very small compared to macroscopic systems. Such a conjecture is not in contradiction with van Hove's theorem. We do not fail to realize that it would probably be very difficult to prove this conjecture

directly from assumptions concerning the intermolecular forces, and we have not attempted to do this. The purpose of the calculations presented here is to carry further the investigation of the consequences of this conjecture and to see what other information would be needed to predict the behavior of a macroscopic system built up of submacroscopic systems, if the partition function of the subsystems were given, e.g., by a machine calculation, and if it turned out to be of van der Waals type.

An earlier attempt in this direction was made by Katsura and Fujita.<sup>2</sup> They consider the total volume  $V$  of the system as divided into small cubical cells of volume  $v$ , and make the conjecture of a van der Waals type partition function for the cells in the form of the assumption that the probability of having  $n$  particles in a cell, as function of  $n$ , has two sharp maxima, at  $n_1$  and  $n_2$  ( $n_1 < n_2$ ), respectively, over a range of values of the temperature and Gibbs free energy. They studied the behavior of the total system, neglecting interaction between particles in different cells, and found that it is similar to that of a real system. The density of the total system is a single-valued function of the pressure and of the Gibbs free energy and shows a rapid rise over a very small range of pressures, at the pressure and Gibbs free energy which would have been obtained by the

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<sup>1</sup> L. van Hove, *Physica* **15**, 951 (1949).

<sup>2</sup> S. Katsura and H. Fujita, *Progr. Theoret. Phys. (Japan)* **5**, 997 (1950).

Maxwell construction. Because of the neglect of interaction, however, the density and pressure which Katsura and Fujita obtain are simply those of the single cell in the grand canonical ensemble. They are analytic functions and thus do not satisfy the accepted definition of phase transitions.<sup>3</sup>

We have kept the basic conjecture for the partition function of the single cells, but have introduced, as a next step, an interaction energy between each pair of adjacent cells, which is a function of their occupation numbers, and which we assume to be small of the order of a surface energy as compared with the product of pressure and volume of the individual cells. We thus have a system of objects (cells) capable of two states ( $n$  close to  $n_1$  or  $n_2$ ) with nearest-neighbor interaction, i.e., a "binary alloy" of cells which is known<sup>4</sup> to be mathematically equivalent to the Ising model of a ferromagnet. Since the three-dimensional Ising model has not yet been treated rigorously it is fortunate that we need only the existence of a phase transition, a rough estimate of its Curie temperature, and some estimates of orders of magnitude of its thermodynamic functions which can be obtained from the series expansions (see reference 4, pp. 379–380). The interesting terms in the pressure and density are the free energy and magnetization, respectively, of the Ising model. The quantity which plays the role of the energy  $\mu H$  of a spin in the magnetic field turns out to be  $(p_2 - p_1)v$  (except for correction terms), where  $p_1$  and  $p_2$  are the pressures formally computed<sup>5</sup> for cells with  $n_1$  and  $n_2$  particles. Except for a small range close to the double point in the graph<sup>6</sup> of the formally computed pressure vs Gibbs free energy, the system therefore corresponds to a magnet in the range  $|\mu H| \gg kT$ . (The system of Katsura and Fujita corresponds, of course, to the paramagnet, and the steep rise of the density which they considered to be condensation corresponds to the change of magnetization of a paramagnet, when the field passes through zero.) The interaction energy  $\epsilon$  of a pair of opposite spins is found to correspond to a linear combination of the interaction energies  $E_{\sigma\sigma'}$  of a pair of cells with  $n_\sigma$  and  $n_{\sigma'}$  particles, and it is plausible that the dominant term in  $\epsilon$  is  $-\frac{1}{2}E_{22}$ , so that  $\epsilon$  is positive (and thus favors parallel spins) if the interaction between "liquid" cells decreases the energy of the pair. The Curie temperature of the model is  $T_c \cong 2\epsilon/k \cong |E_{22}|/k$ .

The interaction energy required to cause condensation is thus very small compared with values which one would consider plausible. This implies that the critical temperature of the system is the critical tem-

perature determined by the van der Waals type partition function of the cell, not the Curie temperature of the Ising model. We find, furthermore, that already for  $\epsilon \geq kT$  quantitative details of the thermodynamic functions of the Ising model become irrelevant, it provides merely the mechanism by which the thermodynamic functions of the total system change from one branch of the thermodynamic functions of the single cell to the other. (There are three branches, but only two correspond to probability maxima.) There are, of course, correction terms to the pressure and density of the individual cell which are of first order in the interaction energies, if pressure and density are written as functions of the Gibbs free energy. In the expression for the pressure as function of the density, however, the first-order correction term appears in the form  $(\partial E_{\sigma\sigma}/\partial n_\sigma - E_{\sigma\sigma}/n_\sigma)$  which reduces it appreciably if the interaction energy between cells in the same state is approximately proportional to the number of particles.

In Sec. 3 we have presented some properties of the hypothetical van der Waals type gas, since the statements found in the literature are often not quite correct.

## II

The total volume  $V$  of the gas is divided into  $\mathfrak{N}$  equal cubical cells of volume  $v$ . The partition function for the  $j$ th cell containing  $n_j$  particles is written as

$$Q_{n_j}(v) \equiv \frac{1}{n_j!} \int_v e^{-\beta U} \prod_1^{n_j} d\tau_k, \quad (2.1)$$

where  $U$  denotes the potential energy of the  $n_j$  particles only and  $d\tau_k$  is the volume element of the  $k$ th particle, and  $\beta = 1/kT$ . We accept as a *conjecture* the assumption of Katsura and Fujita<sup>7</sup> that the relative probability  $y^n Q_n(v)$  of finding  $n$  particles in a cell at fugacity  $y$  has two sharp maxima, at  $n_1$  and  $n_2$  ( $n_2 \gg n_1 \gg 1$ ), in some region of fugacity values and for some volume  $v$  which is large compared to atomic dimensions, but small compared to macroscopic dimensions. The numbers  $n_1$  and  $n_2$  are roots of the equation

$$\ln y + \partial \ln Q_n(v) / \partial n = 0; \quad (2.2)$$

the maxima are furthermore specified by the additional assumption that

$$\sigma^2(n) \equiv -[\partial^2 \ln Q_n(v) / \partial n^2]^{-1} \quad (2.3)$$

is of order  $n_1$  and  $n_2$  at  $n_1$  and  $n_2$ , respectively, and changes only negligibly over a region  $\sqrt{n_1}$  and  $\sqrt{n_2}$  at  $n_1$  and  $n_2$ , respectively. The inequality  $n_2 \gg n_1$  is to be interpreted as  $n_2 - n_1 > \max[\sigma(n_1), \sigma(n_2)]$ .

The intent of these assumptions is to describe a gas of van der Waals type at temperatures below its critical temperature.

Neglecting interaction between particles in different

<sup>7</sup> The proof given by Katsura and Fujita (reference 2) is at best a plausibility argument.

<sup>3</sup> B. Kahn and G. E. Uhlenbeck, *Physica* **5**, 399 (1938).

<sup>4</sup> G. F. Newell and E. W. Montroll, *Revs. Modern Phys.* **25**, 353 (1953); p. 382 ff. and literature quoted there.

<sup>5</sup> These are defined by Eq. (2.4) and must not be confused with the ensemble pressure [Eq. (2.5)].

<sup>6</sup> See J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York and London, 1939), p. 188, Fig. XII-4. The third (short) branch corresponds to a probability minimum.

cells, Katsura and Fujita then obtain the density  $\rho^0$  and pressure  $P^0$  of the total system, which of course are simply the expectation value of the density in the cells in the grand canonical ensemble and its integral with respect to  $\ln y$ , respectively. With the notation

$$p_\sigma \equiv (kT/v)(n_\sigma \ln y + \ln Q_{n_\sigma}) \quad (\sigma=1, 2), \quad (2.4)$$

for the pressure formally computed for cells with  $n_1$  and  $n_2$  particles, these are

$$P^0 = \frac{1}{2}(p_1 + p_2) + v^{-1}kT \ln \cosh[\frac{1}{2}v(p_1 - p_2)/kT], \quad (2.5)$$

$$\rho^0 = v^{-1}\{\frac{1}{2}(n_1 + n_2) + \frac{1}{2}(n_1 - n_2) \tanh[\frac{1}{2}v(p_1 - p_2)/kT]\}, \quad (2.6)$$

where, because of the assumed sharpness of the maxima in the sequence of terms in the grand partition function, the summation has been carried only over the numbers  $n_1$  and  $n_2$  in each cell.

The functions  $P^0$  and  $\rho^0$  are indeed similar to those of a condensing system. They are single-valued monotonically increasing functions of  $\ln y$  and of each other, and the density increases from  $n_1$  to  $n_2$  over a very small region of pressures at that value of  $y$  for which  $p_1 = p_2$ . However, since the density of the total system is the expectation value of the density for the single cell, the density and, *a fortiori*, the pressure are independent of the number of cells and are analytic functions of  $y$ , and thus do not fulfill the specifications of the accepted definition of phase transitions.<sup>3</sup> In terms of the Yang-Lee theory<sup>8</sup> the grand partition function of the  $\mathfrak{N}$  cells is simply the  $\mathfrak{N}$ th power of the grand partition function of the individual cell if interaction is neglected;<sup>9</sup> its roots, therefore, cannot approach the real axis, but remain fixed; only the multiplicity of the roots increases by a factor  $\mathfrak{N}$ .

In view of the fact that the increase of  $\rho^0$  would be experimentally indistinguishable from a discontinuity, one might consider the insistence on the rigorous definition somewhat dogmatic. However, its physical significance is that the neglected interaction could decrease the steepness of the rise of  $\rho^0$  at the transition point. Even if, therefore, the partition function of the individual subsystem (cell) were known (e.g., from a machine calculation) to be of the type specified by the conjecture, some information concerning the interaction between the subsystem would be required to predict the thermodynamic behavior of the total system.

We will, therefore, try to improve on the ensemble model by taking into account the interaction between

adjacent cells (i.e., cells having a surface in common). Instead of the partition function  $Q_N^{(0)}(V)$ ,

$$Q_N^{(0)}(V) = \sum' \prod_i Q_{n_i}(v), \quad (2.7)$$

we then have

$$Q_N(V) = \sum' \prod_i Q_{n_i}(v) \prod_{j \neq k}' q(n_j, n_k), \quad (2.8)$$

where the sum extends over the values  $n_j$  of all cells and the prime denotes the restriction  $N = \sum_j n_j$ , and the prime at the product denotes restriction to adjacent cells. The grand partition function then becomes

$$\begin{aligned} \mathcal{Q}_V(y) &= \sum y^{\sum_j n_j} \prod_i Q_{n_i}(v) \prod_{j \neq k}' q(n_j, n_k) \\ &= \sum \exp\{\sum_j [n_j \ln y + \ln Q_{n_j}] + \sum_{j \neq k}' \ln q(n_j, n_k)\}. \end{aligned} \quad (2.9)$$

Using the conjecture that  $y^n Q_n(v)$  has two sharp maxima, at  $n_1$  and  $n_2$ , respectively, we obtain for the pressure

$$\begin{aligned} P &= kTV^{-1} \ln \mathcal{Q}_V(y) = kTV^{-1} \ln \sum \exp \beta [\mathfrak{N}_1 p_1 v \\ &\quad + \mathfrak{N}_2 p_2 v - \mathfrak{N}_{11} E_{11} - \mathfrak{N}_{12} E_{12} - \mathfrak{N}_{22} E_{22}], \end{aligned} \quad (2.10)$$

where the sum now extends only over the two values  $n_1$  and  $n_2$  for the occupation number of each cell,<sup>10</sup> and where  $\mathfrak{N}_\sigma$  denotes the number of cells with  $n_\sigma$  particles,  $\mathfrak{N}_{\sigma\sigma'}$  the number of adjacent pairs of cells with  $n_\sigma$  and  $n_{\sigma'}$  particles, and where  $E_{\sigma\sigma'}$  is defined by

$$E_{\sigma\sigma'} = -2kT \ln q(n_\sigma, n_{\sigma'}), \quad (2.11)$$

and  $p_\sigma$  by Eq. (2.4). This is the partition function of a binary alloy, which is known<sup>4</sup> to be mathematically equivalent to the three-dimensional Ising model. Since

$$\mathfrak{N}_{11} = 3\mathfrak{N}_1 - \frac{1}{2}\mathfrak{N}_{12} = \frac{3}{2}\mathfrak{N} + \frac{3}{2}(\mathfrak{N}_1 - \mathfrak{N}_2) - \frac{1}{2}\mathfrak{N}_{12}, \quad (2.12)$$

$$\mathfrak{N}_{22} = 3\mathfrak{N}_2 - \frac{1}{2}\mathfrak{N}_{12} = \frac{3}{2}\mathfrak{N} - \frac{3}{2}(\mathfrak{N}_1 - \mathfrak{N}_2) - \frac{1}{2}\mathfrak{N}_{12}, \quad (2.13)$$

one can write

$$P = kTV^{-1} \ln \{ \exp \mathfrak{N} \alpha \beta \sum \exp(-\beta[H(\mathfrak{N}_1 - \mathfrak{N}_2) + \epsilon \mathfrak{N}_{12}]) \}, \quad (2.14)$$

where

$$\alpha = \frac{1}{2}\{(p_2 v - 3E_{22}) + (p_1 v - 3E_{11})\}, \quad (2.15)$$

$$H = \frac{1}{2}\{(p_2 v - 3E_{22}) - (p_1 v - 3E_{11})\}, \quad (2.16)$$

$$\epsilon = E_{12} - \frac{1}{2}(E_{11} + E_{22}), \quad (2.17)$$

and the sum again extends over the two states of each cell. We will denote this sum which is the partition function of the three-dimensional Ising model by  $Z_I$ , and write  $F(H, \epsilon)$  for the free energy,

$$F(H, \epsilon) \equiv -\mathfrak{N}^{-1}kT \ln Z_I, \quad (2.18)$$

<sup>10</sup> The error incurred in this step is estimated in Appendix I.

<sup>8</sup> C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 (1952).

<sup>9</sup> Even if the cells are chosen of macroscopic dimensions, as long as they are of fixed and finite volume, interaction between cells is required for a phase transition in the rigorous sense. Since in that case the probability for the occupation numbers must be already almost flat over a finite interval and practically zero outside this interval, the corresponding ferromagnet consists of classical magnetic dipoles.

$I$  for the normalized magnetization,

$$I \equiv \mathcal{N}^{-1}(\mathcal{N}_2 - \mathcal{N}_1)_{Av} = -\partial F / \partial H, \quad (2.19)$$

and define  $\lambda$  by

$$\lambda \equiv \mathcal{N}^{-1} \langle \mathcal{N}_{12} \rangle_{Av} = \partial F / \partial \epsilon. \quad (2.20)$$

We then have

$$P = v^{-1} \{ \alpha - F(H, \epsilon) \}. \quad (2.21)$$

The density is then

$$\rho = \beta \partial P / \partial \ln y. \quad (2.22)$$

With dots indicating differentiation with respect to  $\ln y$ , and using Eqs. (2.2) and (2.4) to obtain

$$\beta \dot{p}_\sigma v = n_\sigma, \quad (2.23)$$

we get

$$\begin{aligned} \rho &= v^{-1} \beta \{ \dot{\alpha} + I \dot{H} - \lambda \dot{\epsilon} \} \\ &= v^{-1} \{ (n_2 - 3\beta \dot{E}_{22})^{\frac{1}{2}} (1 + I) \\ &\quad + (n_1 - 3\beta \dot{E}_{11})^{\frac{1}{2}} (1 - I) - \beta \lambda \dot{\epsilon} \}. \end{aligned} \quad (2.24)$$

The interaction energy required to change the continuous increase of the density obtained in the grand ensemble into an actual discontinuity is thus extremely small.<sup>11</sup>

It is plausible that  $E_{22} \gg E_{11}$ ,  $E_{12}$  and that  $\epsilon \approx -\frac{1}{2} E_{22}$  is of order  $av^{-\frac{1}{3}} n_2 u$  (where  $a$  is the range of the attractive force and  $u$  is an average potential energy of attraction) and thus of order  $av^{-\frac{1}{3}} n_2 kT$ .

The Curie temperature of the Ising model is, therefore, so high that it has no bearing on the critical temperature of the gas. The latter is given by the critical temperature of the individual cell, i.e., the temperature at which the two roots  $n_1$  and  $n_2$  coalesce, in distinction to the case of the lattice gas, where it is, of course, the same as the Curie temperature.<sup>12</sup> This agrees well with the fact that the van der Waals equation yields  $PV/kT$  at the critical point in rough agreement with experiment.

To estimate the correction terms which are to be applied to the thermodynamic functions of the cell in order to obtain the thermodynamic functions of the total system, we note first that the terms containing  $F(0, \epsilon)$  and  $\lambda$  are irrelevant. The leading term in the expansion of  $F(0, \epsilon)$  is  $-kT \exp[-(9/2)\beta\epsilon]$  [reference 4, p. 380, Eq. (7.5)]. The factor  $\lambda$  can be most readily

<sup>11</sup> This fact and the fast convergence of the low-temperature series suggest an attempt to approximate the partition function with cells of very small size, capable of containing only a few particles, provided that there is a possibility of extending the expansions to more complicated Ising models (with more than two states and less restricted interaction).

<sup>12</sup> T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).

The free energy and magnetization of the paramagnet,  $\ln \cosh$  and  $\tanh$  in Eqs. (2.5) and (2.6), have thus been replaced by the free energy and the magnetization of the Ising model.

Although the three-dimensional Ising model has not yet been treated exactly it seems safe to anticipate the following properties on the basis of approximative calculations (reference 4, p. 379). The model will have a ferromagnetic phase transition at  $H=0$ , if  $\epsilon > 0$ , with a Curie temperature  $T_c \cong 2\epsilon/k$ . At temperatures  $T < \epsilon/k$  the spontaneous magnetization will be unity, with an error of  $\frac{1}{2}$  percent [ $2e^{-6\beta\epsilon}$  according to the low temperature expansion (see reference 4, p. 380)]. This implies that  $\lambda \ll 1$  for  $T < \epsilon/k$ .

If  $\epsilon > kT$ , we have, therefore,

$$I = \pm 1 \quad \text{for } H \gtrless 0, \quad \text{and } F(H, \epsilon) = -|H| + F(0, \epsilon),$$

and thus

$$P = p_2 - [3E_{22} + F(0, \epsilon)]v^{-1} \quad \left\{ \begin{array}{l} \text{for } p_2 - 3E_{22}v^{-1} > p_1 - 3E_{11}v^{-1}; \end{array} \right. \quad (2.25)$$

$$\rho = v^{-1} [n_2 - 3\beta \dot{E}_{22} - \beta \lambda \dot{\epsilon}] \quad (2.26)$$

$$P = p_1 - [3E_{11} + F(0, \epsilon)]v^{-1} \quad \left\{ \begin{array}{l} \text{for } p_2 - 3E_{22}v^{-1} < p_1 - 3E_{11}v^{-1}. \end{array} \right. \quad (2.27)$$

$$\rho = v^{-1} [n_1 - 3\beta \dot{E}_{11} - \beta \lambda \dot{\epsilon}] \quad (2.28)$$

estimated from the identities

$$\mathcal{N}_{12} = 6\mathcal{N}_1 - 2\mathcal{N}_{11} = 6\mathcal{N}_2 - 2\mathcal{N}_{22}, \quad (2.29)$$

which yield

$$\lambda \equiv \mathcal{N}^{-1} \langle \mathcal{N}_{12} \rangle_{Av} \leq 6\mathcal{N}^{-1} \min(\langle \mathcal{N}_1 \rangle_{Av}, \langle \mathcal{N}_2 \rangle_{Av}), \quad (2.30)$$

or

$$\lambda \leq 6 \min[\frac{1}{2}(1 \pm I)] \cong 6e^{-6\beta\epsilon}. \quad (2.31)$$

The thermodynamic functions of the Ising model thus disappear, as they should, from the pressure and density of the total system above and below the transition pressure.

The surface energy terms  $E_{22}$  and  $E_{11}$ , of course, remain, since they express the fact that each cell is surrounded by cells which have (except for the fluctuations specified in the basic conjecture) the same number of particles. (The factor 3 instead of 6 comes from the definition of  $E_{\sigma\sigma}$  as the interaction energy per pair of cells.) The effect of these terms on the isotherm is smaller than would appear on first sight from Eqs. (2.25)–(2.28) because they represent primarily an adjustment of the Gibbs potential for the individual cell. Neglecting terms of second order in the interaction terms one has, in fact, above and below the transition point ( $\sigma=1,2$ ),

$$\begin{aligned} P(\rho) &= p_\sigma(n_\sigma/v) - 3E_{\sigma\sigma}v^{-1} \\ &= p_\sigma(\rho + 3\beta \dot{E}_{\sigma\sigma}v^{-1}) - 3E_{\sigma\sigma}v^{-1} \\ &= p_\sigma(\rho) + 3\beta \dot{E}_{\sigma\sigma}v^{-1} \dot{p}_\sigma(n_\sigma v^{-1}) / \dot{p}_\sigma(n_\sigma v^{-1}) \\ &\quad - 3E_{\sigma\sigma}v^{-1} \\ &= p_\sigma(\rho) + 3n_\sigma v^{-1} [\partial E_{\sigma\sigma} / \partial n_\sigma - E_{\sigma\sigma} / n_\sigma]. \end{aligned} \quad (2.32)$$

The first-order correction to the isotherm is thus caused only by the deviations from linearity of the interaction energy  $E_{\sigma\sigma}$  as a function of  $n_\sigma$ .

### III

In this section we will state some properties of a hypothetical gas of van der Waals type, which is essentially equivalent to the subsystems defined in the basic conjecture of Sec. 2, simplifying and extending the calculations made in an earlier paper.<sup>13</sup> We have chosen the volume-pressure representation because the properties are easier to visualize in this case than in the density-fugacity representation, which we had to use in Sec. 2 in order to have a fixed cell division.

We shall investigate the consequences of the following assumptions: For a certain *finite* range of the number of particles  $N$ , the partition function  $Q$  of a substance has qualitatively the form of the partition function of a van der Waals gas. More precisely, it is analytic and, for a certain finite interval of temperatures  $T$  and volumes  $V$ ,  $\partial^2 \ln Q / \partial V^2$  is positive. In the regions of  $V$  which in the conventional reinterpretation of the van der Waals isotherm are assigned to gas, liquid, undercooled vapor and superheated liquid, we assume  $[-V^2 \partial^2 \ln Q / \partial V^2]$  to be of order  $N$ . Denoting by  $P_c$  the condensation pressure and by  $\Delta V$  the difference between the volumes of liquid and gas which would be obtained from our hypothetical partition function by the conventional construction, we assume  $P_c \Delta V$  to be of order  $NkT$ .

We shall now consider such a substance, together with a mechanical system whose potential energy is  $\Phi(V, V_0)$  (where  $V_0$  is a parameter of the mechanical system) as being in thermodynamic equilibrium with a heat bath.<sup>14</sup> The probability that the substance occupies a volume between  $V$  and  $V+dV$  is then

$$W(V)dV = C^{-1} \exp\{-\beta\Phi + \ln Q\} dV. \quad (3.1)$$

The function  $W(V)$  is stationary at volumes  $V_s$  which are the roots of the equation

$$\partial\Phi/\partial V = \beta^{-1} \partial \ln Q / \partial V. \quad (3.2)$$

A stationary value is a maximum if

$$[-\beta \partial^2 \Phi / \partial V^2 + \partial^2 \ln Q / \partial V^2]_s < 0. \quad (3.3)$$

Since Eq. (3.2) yields

$$\left[ \frac{\partial}{\partial V_0} \left( \frac{\partial\Phi}{\partial V} \right) \right]_s + \left[ \frac{\partial^2 \Phi}{\partial V^2} \right]_s \frac{\partial V_s}{\partial V_0} = \beta^{-1} \left[ \frac{\partial^2 \ln Q}{\partial V^2} \right]_s \frac{\partial V_s}{\partial V_0}, \quad (3.4)$$

this inequality (3.3) is equivalent to the inequality

$$\left[ \frac{\partial}{\partial V_0} \left( \frac{\partial\Phi}{\partial V} \right) \right]_s / \left[ \frac{\partial V_s}{\partial V_0} \right] < 0. \quad (3.5)$$

<sup>13</sup> A. J. F. Siegert, Phys. Rev. **90**, 97 (1953).

<sup>14</sup> Arbitrarily large positive values of  $\partial^2 \ln Q / \partial V^2$  in this region would not essentially affect our conclusions.

The two cases,

$$\Phi = PV \quad (I)$$

and

$$\Phi = \frac{1}{2} \alpha (V - V_0)^2, \quad (II)$$

are of interest since case (I) represents a system under a well-determined force per unit area and case (II) a system for which the relative magnitude of the uncertainty of force and volume can be chosen by an appropriate choice of  $\alpha$ .

In the first case Eq. (3.2) becomes

$$P = \beta^{-1} \partial \ln Q / \partial V. \quad (3.2 I)$$

While this equation is formally the same as the usual equation for the pressure, its derivation shows its correct interpretation as an equation whose roots are the stationary points of  $W(V)$ . The inequality (3.3) shows that only those roots  $V_s$  correspond to maxima for which

$$[\partial^2 \ln Q / \partial V^2]_s < 0, \quad (3.3 I)$$

or—by identification of the parameter  $V_0$  with  $P$  according to (3.5)—

$$\partial V_s / \partial P < 0. \quad (3.4 I)$$

The magnitude of the maxima is obtained from (3.1) as

$$W(V_s) = C^{-1} e^{-\beta g_s}, \quad (3.6)$$

where  $g_s$  is defined by

$$g_s \equiv PV_s - \beta^{-1} \ln[Q]_s, \quad (3.7)$$

and is thus the Gibbs potential, formally computed at  $V_s$ . Under the assumptions stated above, there are two maxima of  $W(V)$ , at  $V_1$  and  $V_2$ . If  $P_c$  denotes the value of  $P$  for which  $g_1 = g_2$ , the ratio of the two maxima of  $W(V)$ , considered as a function of  $P$ , becomes, in the neighborhood of  $P_c$ ,

$$W(V_1)/W(V_2) = \exp\{-\beta(P - P_c)[V_1(P_c) - V_2(P_c)]\}, \quad (3.8)$$

since

$$g_s(P) \cong g_s(P_c) + (P - P_c)[\partial g_s(P)/\partial P]_{P_c}, \quad (3.9)$$

and

$$\begin{aligned} \partial g_s / \partial P &= V_s + [P - \beta^{-1} \partial \ln Q / \partial V]_s \partial V_s / \partial P \\ &= V_s. \end{aligned} \quad (3.10)$$

Defining  $P_l$  and  $P_g$  such that  $W(V_1)/W(V_2)$  equals  $\tau$  for  $P = P_l$  and  $\tau^{-1}$  for  $P = P_g$ , one gets

$$P_l - P_g = 2kT[V_2(P_c) - V_1(P_c)]^{-1} \ln \tau. \quad (3.11)$$

The range of pressures over which the change from one branch to the other occurs is thus of order  $N^{-1}P_c$ .

The two maxima of  $W(V)$  are sharp under the assumptions made, since, in the neighborhood of either  $V_s$ ,  $W(V)$  is of the form

$$\exp[-\frac{1}{2}(V - V_s)^2(-\partial^2 \ln Q / \partial V^2)_s]$$

in the region of interest. The expectation value  $\bar{V}$  of  $V$  can thus be written as

$$\bar{V} = \sum_{s=1,2} V_s e^{-\beta g_s} / \sum_{s=1,2} e^{-\beta u_s}. \quad (3.12)$$

The graph of  $P$  vs  $\bar{V}$  thus follows the curve  $\beta^{-1} \partial \ln Q / \partial V$  practically to  $V_1(P_c)$ , and is practically horizontal between  $V_1(P_c)$  and  $V_2(P_c)$ , where  $P$  changes with increasing  $\bar{V}$  only by a quantity of order  $P_l - P_g$  given by Eq. (3.11), and follows again  $\beta^{-1} \partial \ln Q / \partial V$  for  $\bar{V} > V_2(P)$ . The almost horizontal isotherm must not be ascribed to the individual van der Waals gas, but to the ensemble only.

Under the conditions of case II, the behavior of the van der Waals gas differs even more from the behavior of a macroscopic system. Equation (3.3) becomes

$$\alpha(V - V_0) = \beta^{-1} \partial \ln Q / \partial V. \quad (3.2 \text{ II})$$

If  $\alpha$  is chosen to be larger than  $\max[\beta^{-1} \partial^2 \ln Q / \partial V^2]$  Eq. (3.2 II) has only one root, and, according to (3.3),  $W(V_s)$  is a maximum. In this case, there is thus no phenomenon resembling a phase transition. By an appropriate choice of  $\alpha$ , the "phase transition" can be made to occur between values  $V_1$  and  $V_2$  other than  $V_1(P_c)$  and  $V_2(P_c)$  and any pair of points on the descending branches of  $\partial \ln Q / \partial V$  can thus be reached. Points on the ascending branch can, however, be reached only if  $\alpha$  is chosen large enough so that Eq. (3.2 II) has only one root. The thermodynamic behavior of a van der Waals gas depends thus on the mechanical system with which it is coupled, which means that it is not a thermodynamic system.

By means of a similar argument one can show that the logarithm of the energy level density  $\rho(E)$  as function of the energy  $E$  cannot, for a macroscopic system, have the shape shown as "Actual Curve" in Fig. 16, p. 486, F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York and London, 1940). The analog of van Hove's theorem for this case, that is the theorem that  $\partial \ln \rho(E) / \partial E$  is a nonincreasing function of  $E$  in the usual limit, has not yet been proven directly.

If a macroscopic system is considered as an ensemble of a large number  $m$  of systems with van der Waals type partition function, the behavior of the macroscopic system becomes unique, however, and its isotherm—although still analytic—has almost the shape which one attempts to prove for the limit  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V$  fixed. The probability function  $W_{mN}(V_m)$  for the volume of the ensemble of systems under fixed force is

$$W_{mN}(V_m) = C_m(P) e^{-\beta P V_m} Q_{mN}(V_m), \quad (3.13)$$

where  $mN$  and  $V_m$  are, respectively, the number of particles and the volume of the whole ensemble, and  $Q_{mN}(V_m)$  is its partition function. For sufficiently large

$m$ , the maximum of  $W_{mN}(V_m)$  is located at  $V_m = m \bar{V}(P)$  where  $\bar{V}(P)$  is the expected value of the volume of the subsystem discussed above [Eq. (3.12)]. We thus have

$$\partial \ln W_{mN} / \partial V_m = -\beta P + \partial \ln Q_{mN} / \partial V_m = 0, \quad (3.14)$$

at

$$V_m = m \bar{V}(P).$$

The isotherm of the ensemble is thus the curve of  $P$  vs  $m \bar{V}(P)$ .

In the volume-pressure description, the Laplace transform of  $Q_N(V)$ ,

$$C_N(s) = \int_0^\infty e^{-sV} Q_N(V) dV, \quad (3.15)$$

plays a role similar to that of the grand canonical partition function in the paper of Yang and Lee<sup>8</sup> in the density-fugacity representation. The expected value of the volume,  $\bar{V}_N(s)$  at a pressure  $P = \beta^{-1}s$ , is given by

$$\bar{V}_N(s) = -\partial \ln C_N(s) / \partial s. \quad (3.16)$$

We denote the expected volume per mole by  $\bar{v}_N = N_0 \bar{V}_N / N$ , where  $N_0$  is Avogadro's number. Since  $C_N(s)$  is regular in the open right half-plane  $\text{Re}(s) > 0$ , the only singularities of  $\bar{v}_N(s)$  which can occur in that region are poles of first order. If we think for a moment of  $\text{Re } \bar{v}_N(s)$  as an electrostatic potential, any poles of  $\bar{v}_N(s)$  are to be interpreted as infinite dipole lines perpendicular to the  $s$  plane. A steep decrease of the volume over a small range of pressure at  $P_c$  corresponds to a steep potential drop on the real axis, which occurs if and only if a grating of dipole lines closes in on the real axis at  $s = \beta P_c$ .<sup>15</sup> In order to obtain a finite saltus  $\Delta \bar{v}$  of  $\bar{v}_N$  in the limit  $N \rightarrow \infty$ , the dipole grating must, in this limit, become a dipole layer of dipole strength  $\Delta \bar{v}$ .

The assumption of a van der Waals type partition function for a finite  $N$  yields a dipole grating. We have, writing  $s = t + i\vartheta$ , with  $t$  and  $\vartheta$  real, and using the fact that  $e^{-tV} Q_N(V)$  has one or two sharp peaks as described above,

$$\begin{aligned} C_N(s) &= \int_0^\infty e^{-i\vartheta V} \{p_1(t) \delta(V - V_1(t)) \\ &\quad + p_2(t) \delta(V - V_2(t))\} dV \\ &= p_1(t) e^{-i\vartheta V_1} + p_2(t) e^{-i\vartheta V_2}. \end{aligned} \quad (3.17)$$

The roots of  $C_N(s)$  are thus roots of

$$e^{-i\vartheta(V_2(t) - V_1(t))} = -p_1(t)/p_2(t), \quad (3.18)$$

<sup>15</sup> In order to obtain the theorems of the Yang-Lee theory rigorously one would have to prove the existence of the Gibbs free energy per atom,  $\lim_{N \rightarrow \infty} [N^{-1} \ln C_N(s)]$ , for real values of the pressure only, since the extension into the complex plane is provided by some trivial properties of Laplace transforms and Vitali's theorem [see E. C. Titchmarsh, *The Theory of Functions* (Oxford University Press, London, 1939), second edition, p. 168, Sec. 531].

and, since  $\vartheta$  was to be real, the roots of  $C_N(s)$  are simple roots located at the points defined by

$$p_1(t) = p_2(t) \quad (3.19)$$

and

$$\vartheta = \pm \frac{(2l+1)\pi}{V_2(t) - V_1(t)} \quad (l=0, 1, 2, \dots). \quad (3.20)$$

Our assumptions thus yield a grating of dipole lines on the line  $t = \text{Re } s = \beta P_c$ , spaced with separation  $2\pi/(V_2 - V_1)$ . The roots of  $C_N(s)$  are of first order and each pole of  $\bar{V}(s)$  is, therefore, of the form  $-(s - s_l)^{-1}$ , which corresponds to a dipole of moment  $2\pi$ ; the dipole grating has thus a dipole moment per unit length of  $[V_2(t) - V_1(t)]$ .

In the ensemble the position of the roots remains unchanged. In order to consider interaction we used the density-fugacity representation in Sec. 2 since there is no equivalent to the Ising model available for the irregular array of cells of variable volume which one would have to deal with in the volume-pressure representation.

The author would like to thank Professor L. van Hove for some very interesting discussions, Professor J. R. Oppenheimer for the hospitality of the Institute for Advanced Study, The John Simon Guggenheim Memorial Foundation for a fellowship, and Northwestern University for a leave for research.

#### APPENDIX I

In order to estimate the effect of fluctuations in the occupation numbers around their most probable values we write the (unnormalized) probability function for the occupation numbers in the form

$$\exp(n_j \ln y + \ln Q_{n_j}) = \sum_{n_{j\sigma}=n_1, n_2} \exp[n_{j\sigma} \ln y + \ln Q_{n_{j\sigma}} - (n_j - n_{j\sigma})^2 / 2\sigma^2(n_{j\sigma})], \quad (A1)$$

where  $\sigma^2(n)$  is defined by Eq. (2.3), and expand the interaction terms to first order in the fluctuations:

$$\sum'_{j \neq k} \ln q(n_j, n_k) = \sum'_{j \neq k} \ln q(n_{j\sigma}, n_{k\sigma}) + 2 \sum_j (n_j - n_{j\sigma}) \sum'_k \frac{\partial \ln q(n_{j\sigma}, n_{k\sigma})}{\partial n_{j\sigma}}. \quad (A2)$$

Instead of Eq. (2.10) we then have

$$\mathcal{Q}_V(y) = \sum \exp\left\{\sum_j [n_{j\sigma} \ln y + \ln Q_{n_{j\sigma}}] + \sum'_{j \neq k} \ln q(n_{j\sigma}, n_{k\sigma}) + \ln J\right\}, \quad (A3)$$

where the sum extends again over  $n_{j\sigma} = n_1, n_2$  only, for each cell. The correction term  $J$  is defined as

$$J = \int \cdots \int \exp \sum_j \left\{ - (n_j - n_{j\sigma})^2 / 2\sigma^2(n_{j\sigma}) + 2(n_j - n_{j\sigma}) \sum'_k \partial \ln q(n_{j\sigma}, n_{k\sigma}) / \partial n_{j\sigma} \right\} \prod_j dn_j, \quad (A4)$$

where the summation over  $k$  extends only over nearest neighbors of  $j$ . The integration yields

$$\ln J = \frac{1}{2} \sum_j \ln(2\pi\sigma^2(n_{j\sigma})) + 2 \sum_j \sigma^2(n_{j\sigma}) \left[ \sum'_k \ln q(n_{j\sigma}, n_{k\sigma}) / \partial n_{j\sigma} \right]^2. \quad (A5)$$

The logarithmic terms are irrelevant and we thus have

$$\ln J = 2 \sum_j \sigma^{-2}(n_{j\sigma}) \times \left[ \sum'_k \sigma^2(n_{j\sigma}) \partial \ln q(n_{j\sigma}, n_{k\sigma}) / \partial n_{j\sigma} \right]^2. \quad (A6)$$

Since  $\sigma^2(n)$  was assumed to be of order  $n$ , the terms  $\sigma^2(n) \partial \ln q / \partial n$  are of the order of the surface terms  $\ln q$ , and the terms of  $\sum_j$  become of lower order than the surface terms  $\ln q$ .