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The Imperfect Gas*

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The partition function of the classical imperfect gas is approximated by means of a generalized cell model in which the number of particles in a cell is taken as the statistical variable. The limiting free energy per particle exhibits critical phenomena, and, for temperatures less than the critical temperature, the p-v isotherm is a nonanalytic function of v consisting of three pieces. These properties depend only on the interparticle potential energy having the general features usually assigned to it. However, the condensation pressure is not constant, and, for temperatures sufficiently low, the isotherm shows thermodynamic instability. The model allows the calculation of the limiting free energy per particle for all values of the temperature and specific volume.

1. INTRODUCTION

It is believed that the partition function of classical statistical mechanics is capable of completely describing the equilibrium behavior of an imperfect gas from its ideal gas behavior at large specific volumes, down through the liquid-solid transition. It is nevertheless true that a theoretical description of the whole mechanism of condensation does not exist.

Several aspects of the condensation problem seem clearly established. (1) All gases condense. The essential molecular property involved here is the general shape of the potential energy of interaction between a pair of particles. (2) The p-v isotherm is a nonanalytic function of v, the specific volume, for temperatures below a critical temperature. Condensation occurs at a constant value of p. Above the critical temperature, p is an analytic function of v. For all (T, v), $dp/dv \leqslant 0$. (3) The nonanalytic behavior of the isotherm can only appear as the result of a limiting process. The process considered is $V, N \to \infty$, $V/N = v$ fixed, where N is the total number of particles in the volume V.

The established difficulty of an exact approach to the condensation problem justifies the consideration of models. We have therefore devised an approximation which retains some of the pertinent physical features of an imperfect gas and which is capable of representing a good part of the behavior just described. The model is described by a partition-like function which is susceptible to analysis. We believe that the model is of interest in that the limiting partition-like function has the following properties: (1) It exhibits critical phenomena; (2) for temperatures below the critical temperature, the p-v isotherm is a nonanalytic function of v consisting of *three* pieces; (3) these properties depend only on the intermolecular potential energy having the general features usually assigned to it. The model is, of course, not without drawbacks. The disadvantages are: (1) The condensation region is not characterized by constant pressure; (2) for temperatures sufficiently low, the isotherm shows thermodynamic instability. The most serious disadvantage is the lack of a constant condensation pressure. In fact, the model is unable to suggest to us how the constant pressure part of the isotherm comes about.

2. THE CLASSICAL PARTITION FUNCTION

The configurational partition function for an imperfect gas is

$$Z_N = \frac{1}{N!}\int\cdots\int_V d\tau_1\cdots d\tau_N \exp[-\beta W(\mathbf{r}_1\cdots\mathbf{r}_N)], \quad (2.1)$$

with W the total potential energy of a configuration of particles and $\beta = 1/kT$. The total free energy of the system, supposed to consist of a single type of particle is

$$\exp[-\beta\Psi] = (2\pi m/\beta h^2)^{3N/2} Z_N. \quad (2.2)$$

Suppose that the volume V is divided into K cells of equal volume τ, $K\tau = V$, and that the cells are numbered from 1 to K. Let n_j denote the number of particles in the jth cell. We may then write

$$Z_N = \frac{1}{N!}\sum_{\{n_j\}}\left(N!\Big/\prod_{j=1}^{K} n_j!\right)\int\cdots\int_V d\tau_1\cdots \times d\tau_N \exp[-\beta W], \quad (2.3)$$

where, in the integral, n_j particles are confined to cell j. The sum is over all sets of integers $\{n_j\}$, $n_j \geqslant 0$, subject to the restriction

$$\sum_{j=1}^{K} n_j = N.$$

In principle, the specific subdivision of the space into cells is irrelevant for the final result if a consistent calculation is carried through. Therefore, we make the choice $\tau = v$ the specific volume, so that $K = N$. Then $\langle n_j\rangle = 1$ for all v, β. This specific choice of τ is discussed in Sec. 7.

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The limiting free energy per particle is defined by

$$\psi(v,\beta)=\lim_{\substack{V,N\to\infty\\ V/N=v}}\Psi(N,v,\beta)/N. \tag{2.4}$$

Furthermore, the thermodynamic quantities are supposed to be defined in the usual way. For example,

$$p=-\partial\psi/\partial v;\quad \lim_{\substack{V,N\to\infty\\ V/N=v}}\langle E\rangle/N=\partial(\beta\psi)/\partial\beta, \tag{2.5}$$

where E is the total energy of the system.

3. AN APPROXIMATION TO THE IMPERFECT GAS

The model is derived by approximating (2.3). We will proceed to list the assumptions and their direct consequences for (2.3). Each of the assumptions will be discussed in Sec. 7.

(1) $$W(\mathbf{r}_1,\cdots\mathbf{r}_N)=\sum_{1\leqslant i<j\leqslant N}U(r_{ij}), \tag{3.1}$$

where r_{ij} is the distance between particles i and j and $U(r)$ is the potential energy of interaction between a pair of particles.

(2) When two particles i and j are in different cells k and m, we assume that $U(r_{ij})=U(R_{km})$, where R_{km} is the distance between centers of the kth and mth cells.

The total interaction energy with respect to particles in different cells is

$$\sum_{1\leqslant k<m\leqslant N}n_k n_m U(R_{km}). \tag{3.2}$$

This energy is now independent of the coordinates of the particles and it can be taken outside of the integral.

We define an average interaction energy within a cell by

$$\exp[-\beta W_k]\equiv v^{-n_k}\int\cdots\int_v d\tau_1\cdots \times d\tau_{n_k}\exp[-\beta W(\mathbf{r}_1,\cdots\mathbf{r}_{n_k}]. \tag{3.3}$$

W_k is a function of v, β, and n_k.

(3) Let W_0 be defined by

$$W_k\equiv\tfrac{1}{2}n_k(n_k-1)W_0. \tag{3.4}$$

In general W_0 will be a function of v, β, and n_k. It is assumed that the dependence of W_0 on n_k can be neglected so that it is independent of the cell number k.

The consequence of assumptions (1), (2), and (3) is that

$$Z_N=\sum_{\{n_j\}}\left(v^N\Big/\prod_{j=1}^N n_j!\right)\times\exp[\tfrac{1}{2}N\beta W_0-\beta\sum_{j,k}a_{jk}n_jn_k], \tag{3.5}$$

where

$$a_{jk}=\tfrac{1}{2}U(R_{jk}),\quad j\neq k,$$
$$a_{jj}=\tfrac{1}{2}W_0,\quad j=k,$$

and $\sum_{j,k}$ is over all cells.

(4) The sum over the set $\{n_j\}$, where the n_j are integers $\geqslant 0$ and

$$\sum_{j=1}^N n_j=N,$$

is a sum over lattice points, in an N-dimensional Euclidean space, bounded by an $N-1$ dimensional figure, a "hyperhedron." The center of the hyperhedron is the point $(1, 1, \cdots, 1)$ which describes the configuration with one particle in each cell. This is the average configuration, since $\langle n_j\rangle=1$.

Our next assumption is to replace the sum over the lattice points by an integration throughout the volume Ω of the hyperhedron. We write

$$Z_N=A(N)v^N\exp[\tfrac{1}{2}N\beta W_0]\int\cdots\int_\Omega dn_1\cdots dn_N \times\left(\prod_{j=1}^N\Gamma(n_j+1)\right)^{-1}\exp[-\beta\sum_{j,k}a_{jk}n_jn_k], \tag{3.6}$$

where $A(N)$ is a normalization constant.

(5) The division of physical space into cells of volume v implies that the fluctuation in the number of particles per cell, $\sigma=\langle(n_j-1)^2\rangle$, is finite for all v, β; unless, of course, purely attractive forces are present. This suggests that a significant contribution to the above integral arises from points which lie on the intersection of the hyperplane $\sum_{j=1}^N n_j=N$ with the N-dimensional sphere $\sum_{j=1}^N(n_j-1)^2=R^2$, where $R^2=N\sigma$. The intersection is the surface of an $(N-1)$ dimensional sphere with center the center of the hyperhedron. The volume of the intersection is of the order of magnitude of the volume of the hyperhedron.

Now, the volume integral in (3.6) may be written

$$\int\cdots\int_\Omega dn_1\cdots dn_N =\int_0^N dR\int_{\sum_{j=1}^N(n_j-1)^2=R^2,\ \sum_{j=1}^N n_j=N}\cdots\int dn_1\cdots dn_N. \tag{3.7}$$

The difficulty here is that for $R>1$, a good part of the surface of the $(N-1)$ dimensional sphere lies outside the hyperhedron. However, integration becomes feasible if the whole surface of the sphere is an allowed region. We allow this extended region but introduce a weighting factor to compensate for the additional unwanted states. A factor is needed which is 1 for $R<1$, which is of order e^{-N} for $R\sim N^{\frac{1}{2}}$, and which is negligible with respect to e^{-N} for $R\sim N$. It is therefore assumed that

$$\int\cdots\int_{\Omega} dn_1\cdots dn_N \approx \int_0^{\infty} dR \exp\left[-\frac{\alpha}{2N}R^4\right] \times \int_{\sum_{j=1}^{N}(n_j-1)^2=R^2,\ \sum_{j=1}^{N}n_j=N} \cdots \int dn_1\cdots dn_N, \quad (3.8)$$

where α is a finite constant.

(6) Since in both the gas and liquid regions we can expect that $\sigma\sim1$, the $\Gamma(n_j+1)$ will mostly be of order 1. We approximate the gamma function by $\exp[an_j(n_j-1)]$ where we choose $a=\frac{1}{2}\ln2$ to fit the point $n_j=2$.

(7) The final assumption is to set the Born-von Karman periodic boundary conditions on the physical space. A one-dimensional gas would be confined to a ring, and a two-dimensional gas to the surface of a torus. The mathematical analogy is extended to the three-dimensional gas. The effect of this assumption is to cyclize the interaction matrix (a_{jk}).

The partition function of our approximation to the imperfect gas is

$$Z_N = Av^N \exp[\tfrac{1}{2}N\beta W_0] \int_{\sum_{j=1}^{N} n_j=N} \cdots \int dn_1\cdots dn_N \times\exp\left[-\frac{\alpha}{2N}\left\{\sum_{j=1}^{N}(n_j-1)^2\right\}^2 - a\sum_{j=1}^{N} n_j(n_j-1) - \beta\sum_{j,k} a_{jk}n_jn_k\right]. \quad (3.9)$$

The constants A and α will be fixed by comparison with the ideal gas.

4. LIMIT FUNCTIONS OF THE EIGENVALUES OF THE MATRIX (a_{ij})

Before evaluating the partition function, it is convenient to have an understanding of the properties of the eigenvalues of the interaction matrix (a_{ij}).[1]

Since the matrix is cyclic, it is easy to show that the eigenvalues are given by

$$\Lambda_k = a_{11} + 2\sum_{p=2}^{\frac{1}{2}(N+1)} a_{1p}\cos\left[\frac{2\pi}{N}(k-1)(p-1)\right], \qquad k=1,2,\cdots N. \quad (4.1)$$

The subscript p refers to the cell number with respect to cell 1. [(4.1) is exactly true for N odd. The extra term for N even does not influence the analysis in any significant way.] With the exception of Λ_1, the eigenvalues are doubly degenerate because $\Lambda_k=\Lambda_{N-k+2}$, $k\neq1$.

Let z be a complex variable and consider a function

$$F_n(z) = \operatorname*{Lim}_{N\to\infty} N^{-1}\sum_{j=1}^{N} f(z+\lambda_j). \quad (4.2)$$

The subscript n denotes the number of spatial dimensions of the physical system, and $\Lambda_k - a_{11} = \lambda_k$ defines λ_k.

It is not difficult, although the analysis is lengthy,[2] to show that

$$F_n(z) = \frac{1}{(2\pi)^n}\int_0^{2\pi}\cdots\int d\omega_1\cdots d\omega_n f(z+\lambda(\boldsymbol{\omega})), \quad (4.3)$$

where

$$\lambda(\boldsymbol{\omega}) = 2\sum_{\mathbf{r}} a_{1\mathbf{r}}\cos\left(\frac{\mathbf{r}\cdot\boldsymbol{\omega}}{v^{1/n}}\right),$$

and $\boldsymbol{\omega}$, $\mathbf{r}$ are n-dimensional vectors having components $(\omega_1, \cdots, \omega_n)$ and $(x, y, z, \cdots)$, respectively. The sum $\sum_{\mathbf{r}}$ is over all the cell centers in the physical space including cell 1; $v^{1/n}$ is the unit of length, v denoting the specific volume; and the components of r are integral multiples of $v^{1/n}$. The vector $\mathbf{r}$ has its origin at the center of cell 1. The degeneracy of $\lambda(\boldsymbol{\omega})$ is evidenced by $\lambda(\omega_1, \cdots, \omega_n) = \lambda(2\pi-\omega_1, \cdots, 2\pi-\omega_n)$.

Considering the case $n=3$, it is a convenience to assume that

$$a_{1\mathbf{r}}\cos\left(\frac{\mathbf{r}\cdot\boldsymbol{\omega}}{v^{\frac{1}{3}}}\right) \simeq \frac{1}{v}\int\int_{\mathbf{r}}\int d\mathbf{r}' a_{i\mathbf{r}'}\cos\left(\frac{\mathbf{r}'\cdot\boldsymbol{\omega}}{v^{\frac{1}{3}}}\right), \quad (4.4)$$

where the integral is over the volume of the cell with center at $\mathbf{r}$. Then,

$$\lambda(\boldsymbol{\omega}) \simeq \frac{2}{v}\int\int\int' d\mathbf{R}a(\mathbf{R})\cos\left(\frac{\mathbf{R}\cdot\boldsymbol{\omega}}{v^{\frac{1}{3}}}\right), \quad (4.5)$$

where the prime signifies that the integration is over all space excluding a volume v centered at the origin. Note, however, that the use of the integral has destroyed the degeneracy of $\lambda(\boldsymbol{\omega})$. Consequently, the degeneracy must be preserved by definition.

If we suppose that $2a(R)=U(R)$ is a function of R only,

$$\lambda(\boldsymbol{\omega}) = \lambda(\omega) = \frac{4\pi}{v}\int_{R_0}^{\infty} U(R)\frac{\sin(R\omega/v^{\frac{1}{3}})}{(R\omega/v^{\frac{1}{3}})}R^2dR, \quad (4.6)$$

where we take $v=R_0^3$.

Since the qualitative behavior of a gas should not depend on the details of $U(R)$, we shall represent $U(R)$ by the potential shown in Fig. 1.

The integration is readily performed and we find that

$$v \geqslant v_2: \qquad \lambda(\omega)=0;$$

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[1] G. Kowaleski, *Determinantentheorie* (Chelsea Publishing Company, New York, 1948), third edition, p. 105.

[2] T. H. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952).

$v_2 \geqslant v \geqslant v_1$:

$$\lambda(\omega) = -4\pi U_a\{H[\omega] - (v_2/v)H[(v_2/v)^{\frac{1}{3}}\omega]\}; \quad (4.7)$$

$v_1 > v > 0$: $\lambda(\omega) = \infty$;

where

$$H[q] = (q\cos q - \sin q)/q^3 = -(\pi/2)^{\frac{1}{2}} q^{-\frac{3}{2}} J_{\frac{3}{2}}(q). \quad (4.8)$$

5. EVALUATION OF THE PARTITION FUNCTION

Let us first transform from the variables $\{n_j\}$ to the variables $\{y_j\}$ by a translation and rotation such that

$$\sum_1^N (n_j-1)^2 = \sum_1^N y_j^2;$$

and (5.1)

$$\sum_{j,k} a_{jk}(n_j-1)(n_k-1) = \sum_1^N \Lambda_j y_j^2.$$

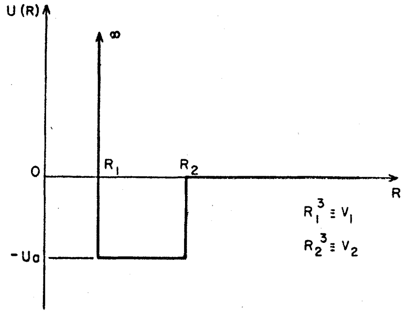

FIG. 1. A representation of $U(R)$, the potential energy of interaction between two particles.

The transformation matrix t can be taken as

$$t_{jk} = N^{-\frac{1}{2}}\left\{\cos\left[\frac{2\pi}{N}(j-1)(k-1)\right] + \sin\left[\frac{2\pi}{N}(j-1)(k-1)\right]\right\}, \quad (5.2)$$

where the characteristic vectors are normalized to unity and the Λ_k are given by (4.1). The hyperplane is described by $y_1=0$.

The partition function (3.9) may now be written as

$$Z_N = B\int_0^\infty dR \exp\left[-\frac{\alpha}{2N}R^4\right] \underset{\sum_2^N y_j^2 = R^2}{\int\cdots\int} dy_2\cdots dy_N \times \exp\left[-\sum_2^N (a+\beta\Lambda_j)y_j^2\right], \quad (5.3)$$

$$B = Av^N \exp[N\beta(\tfrac{1}{2}W_0 - \Lambda_1)].$$

Relaxing the restriction on the region of integration of the variables $\{y_j\}$ by means of the delta function, using the representation

$$\delta\left(R - \left[\sum_2^N y_j^2\right]^{\frac{1}{2}}\right) = \frac{2R}{2\pi i}\int_{s_0-i\infty}^{s_0+i\infty} ds \exp\left[s\left(R^2 - \sum_2^N y_j^2\right)\right], \quad (5.4)$$

and because R is positive, we may write

$$Z_N = \frac{B}{2\pi i}\int_{s_0-i\infty}^{s_0+i\infty} ds \exp(Ns^2/2\alpha)\int_{-Ns/\alpha}^{\infty} dw \times \exp[-(\alpha/2N)w^2]\left\{\prod_{j=2}^N \pi^{\frac{1}{2}}(s+a+\beta\Lambda_j)^{-\frac{1}{2}}\right\}. \quad (5.5)$$

This result is obtained by multiplying the integrand of (5.3) by (5.4) and allowing $-\infty < y_j < \infty$ all j; interchanging the s and $\{y_j\}$ integrations by choosing s_0 real, positive, and large enough to make $s_0 + a + \beta\Lambda_j > 0$ for all j; and finally interchanging the s and R integrations, which is permissible for all s. It is to be understood that the normalization constant A in B is to be determined at our convenience.

We are interested in the limit $N\rightarrow\infty$, and the limiting form of the integrand in (5.5) is required. The product may be written

$$\prod_{j=2}^N (s+a+\beta\Lambda_j)^{-\frac{1}{2}} = \exp\left[-\frac{1}{2}\sum_2^N \ln(s+a+\beta\Lambda_j)\right].$$

Let

$$G_n(s) = \operatorname*{Lim}_{N\rightarrow\infty} N^{-1}\sum_{j=2}^N \ln(s+a+\beta\Lambda_j). \quad (5.6)$$

From (4.3) we have

$$G_n(s) = f_n(s) = \frac{1}{(2\pi)^n}\int_0^{2\pi}\cdots\int d\omega_1\cdots d\omega_\Omega \times \ln(s+a+\beta\Lambda(\omega)), \quad (5.7)$$

where $\Lambda(\omega) = a_{11} + \lambda(\omega)$. However, some care is now necessary.

Let $\tilde{S}$ denote the algebraically smallest value of $a+\beta\Lambda(\omega)$. If the s plane is cut from $s=-\infty$ to $s=-\tilde{S}$ along the real axis, then the integrand in (5.7) is analytic in the cut plane. The behavior of the integral in the neighborhood of $s=-\tilde{S}$ is characterized by the density of eigenvalues $\Lambda(\omega)$ in the neighborhood of the algebraically smallest eigenvalue. This behavior incompletely describes the behavior of (5.6) in the neighborhood of $s=-\tilde{S}$ because the singular nature of the integral in (5.7) has in general nothing to do with the singular nature of a single term in the sum in (5.6). Consequently, we more accurately write,

$$G_n(s) = \frac{2}{N}\ln(s+\tilde{S}) + f_n(s). \quad (5.8)$$

The 2 arises because the algebraically smallest eigenvalue is doubly degenerate.

In the integral over w in (5.5), the important values of w are of order $N^{\frac{1}{2}}$. For finite s, the lower limit of integration is of order N. In this situation the integral over w may be replaced by $(2\pi N/\alpha)^{\frac{1}{2}}$ if s is positive. Therefore we must evaluate

$$Z_N=\frac{B}{2\pi i}\pi^{\frac{1}{2}(N-1)}\left(\frac{2\pi N}{\alpha}\right)^{\frac{1}{2}}$$

$$\times\int_{s_0-i\infty}^{s_0+i\infty}\frac{ds}{(s+\tilde{S})}\exp[Ng_n(s)], \quad (5.9)$$

where $g_n(s)=s^2/2\alpha-\frac{1}{2}f_n(s)$.

Applying the method of steepest descent to the integral, we find that

$$Z_N=\frac{B\pi^{\frac{1}{2}(N-1)}\exp[Ng_n(s_s)]}{(s_s+\tilde{S})[\alpha(\partial^2g_n/\partial s^2)_{s_s}]^{\frac{1}{2}}}, \quad (5.10)$$

if a saddle point s_s can be found such that s_s is real, positive, to the right of the singularities of the integrand, and with

$$[\partial g_n/\partial s]_{s_s}=0; \quad [\partial^2g_n/\partial s^2]_{s_s}>0. \quad (5.11)$$

The constant A shall be determined by normalizing to the ideal gas, for which $Z_N=V^N/N!$ For the ideal gas $a_{jk}=0$ for all j, k, so that $\Lambda_j=0$ for all j. Then

$$g_n(s)=\frac{s^2}{2\alpha}-\frac{1}{2}\ln(s+a); \quad \left(\frac{\partial g_n}{\partial s}\right)_{s_s}=\frac{s_s}{\alpha}-\frac{1}{2(s_s+a)}=0;$$

$$\left(\frac{\partial^2g_n}{\partial s^2}\right)_{s_s}=\frac{1}{\alpha}+\frac{1}{2(s_s+a)^2}>0.$$

The solution of the saddle point equation that meets the requirements is

$$s_s=s_{id}\equiv+\tfrac{1}{2}(a^2+2\alpha)^{\frac{1}{2}}-\tfrac{1}{2}a. \quad (5.12)$$

It is found that, for $N\rightarrow\infty$,

$$\frac{1}{N}\ln A=\ln(e/\pi^{\frac{1}{2}})-g_n(s_{id}). \quad (5.13)$$

This yields for the limiting free energy per particle,

$$-\beta\psi_n=\frac{n}{2}\ln(2\pi m/\beta h^2)+\ln(ev)+\beta(\tfrac{1}{2}W_0-\Lambda_1)$$

$$+g_n(s_s)-g_n(s_{id}). \quad (5.14)$$

We now investigate the existence of a saddle point, and we shall get to a real gas by considering first a repulsive potential only, second an attractive potential only, and finally the usual molecular potential.

For a three-dimensional system, $n=3$, the saddle point equation is

$$\frac{2s_s}{\alpha}=\frac{1}{(2\pi)^3}\int\int_0^{2\pi}\int\frac{d\omega_1d\omega_2d\omega_3}{s_s+a+\beta\Lambda(\boldsymbol{\omega})}\equiv I(s_s,v). \quad (5.15)$$

It is easy to see that if a solution s_s exists, then s_s is real. It follows that $[\partial^2g_3/\partial s^2]_{s_s}>0$. We also recall that $\Lambda(\boldsymbol{\omega})$ is double degenerate, that is $\Lambda(\omega_1,\omega_2,\omega_3)=\Lambda(2\pi-\omega_1, 2\pi-\omega_2, 2\pi-\omega_3)$, the point (π,π,π) being a center of symmetry. The integral representation of $\lambda(\boldsymbol{\omega})$ destroys this symmetry and, therefore, the symmetry is maintained by definition.

A Repulsive Potential

We represent a repulsive potential by Fig. 1 except that $U_a=0$. Then for

$$\begin{aligned} v\geqslant v_1: &\quad \lambda(\omega)=0;\\ v_1>v>0: &\quad \lambda(\omega)=\infty. \end{aligned} \quad (5.16)$$

Recall that $\Lambda(\omega)=a_{11}+\lambda(\omega)$, where $2a_{11}=W_0$ is an average energy of interaction among particles within a cell. a_{11} is independent of ω and for a repulsive potential monotonically increases to ∞ as v decreases to $v_1/8$.

In the range $\infty>v\geqslant v_1$, (5.15) becomes $2s_s/\alpha=(s_s+a+\beta a_{11})^{-1}$. Therefore as v decreases to v_1, s_s monotonically decreases from s_{id} to 0. Hence, the gas does not exhibit any transition and the limiting value of the free energy per particle is given by (5.14) for all v, β.

An Attractive Potential

The attractive potential is represented by Fig. 1 except that $R_1=0$. Then for

$$v\geqslant v_2: \quad \lambda(\omega)=0$$

$$v_2\geqslant v>0: \lambda(\omega)=-4\pi U_a\left\{H[\omega]-\frac{v_2}{v}H[(v_2/v)^{\frac{1}{3}}\omega]\right\} \quad (5.17)$$

a_{11} monotonically decreases to $-\frac{1}{2}U_a$ as v decreases to $v_2/8$ and for $v<v_2/8$, a_{11} is constant at this value.

In the range $v>v_2$, $2s_s/\alpha=(s_s+a+\beta a_{11})^{-1}$; and as v decreases, s_s increases.

In the range $v<v_2$, something new occurs. The algebraically smallest value of $\lambda(\omega)$ occurs for $\omega=0$, $\lambda(0)=-(4\pi/3)U_a(v_2/v_1-1)$, and $\tilde{S}=a+\beta(a_{11}+\lambda(0))$.

The qualitative behavior of $\lambda(\omega)$ is shown in Fig. 2.

It is easily shown that $I(-\tilde{S},v)$ is finite, and the qualitative behavior of $I(s,v)$ is shown in Fig. 3.

The saddle point is the point of intersection of the straight line $(2/\alpha)s$ with the curve $I(s,v)$ for given v. From Fig. 3, we see that for fixed β, a v_β will exist such that for $v<v_\beta$ a saddle point will not exist. Consequently, there exists a transition point for which the temperature and volume are related by

$$-(2/\alpha)\tilde{S}=I(-\tilde{S},v). \quad (5.18)$$

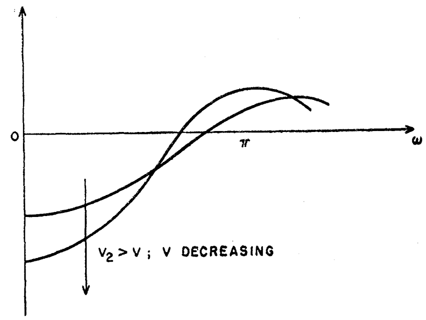

FIG. 2. $\lambda(\omega)$ for $v<v_2$.

The variation of the transition temperature with volume is sketched in Fig. 4. There is no critical temperature above which a transition fails to take place.

No transition exists for the one and two-dimensional gases because then the integral $I(-\tilde{S}, v)$ diverges. The divergence is easy to see because the "volume" element goes to zero as $\omega^{n-1}d\omega$ where n is the dimensionality, whereas the denominator goes to zero as ω^2 when $s=-\tilde{S}$.

For a given temperature there is the transition volume $v_\beta<v_2$. We must now find Z_N for $v<v_\beta$ since the partition function must exist.

The integrand in (5.9) has a pole at $s=-\tilde{S}$. To determine if a path of steepest descent exists in the neighborhood of the pole, which is also a branch point of $g_3(s)$, the behavior of $g_3(s)$ near the pole is required. After some analysis we find that

$$\begin{gathered} g_3(s)=g_3(-\tilde{S})+\gamma(s+\tilde{S}) \\ +(1/48)(\pi\delta^{\frac{3}{2}})(s+\tilde{S})^{\frac{3}{2}}+O[(s+\tilde{S})^2], \\ \gamma=-\frac{\tilde{S}}{\alpha}\frac{1}{2}\left(\frac{\partial f_3}{\partial s}\right)_{s=-S};\quad \delta=\frac{1}{2}\left(\frac{\partial^2\lambda(\omega)}{\partial\omega^2}\right)_{\omega=0}. \end{gathered} \tag{5.19}$$

On setting $s+\tilde{S}=\epsilon$, it is plain that the integrand of (5.9) falls off rapidly from its value at $\epsilon=0$ for real part of ϵ negative *if* $\gamma>0$. From Fig. 3, it is easy to see that γ is >0 for $v<v_\beta$. Finally a path, qualitatively shown in Fig. 5, does exist for which the imaginary part of $g_3(s)=0$, and which does not cross the branch cut. Therefore, we note that the contributions to the integral from the partial paths on opposite sides of the cut cancel in the limit $N\rightarrow\infty$ and that it is only the residue at the pole that contributes to the integral. Hence

$$Z_N=B\pi^{\frac{1}{2}(N-1)}\left(\frac{2\pi N}{\alpha}\right)^{\frac{1}{2}}\exp[Ng_3(-\tilde{S})],\quad v<v_\beta. \tag{5.20}$$

This provides

$$\begin{aligned} -\beta\psi_3=\tfrac{3}{2}\ln(2\pi m/\beta h^2)+\ln(ev)+\beta(\tfrac{1}{2}W_0-\Lambda_1) \\ +g_3(-\tilde{S})-g_3(s_{id}),\quad v<v_\beta. \end{aligned} \tag{5.21}$$

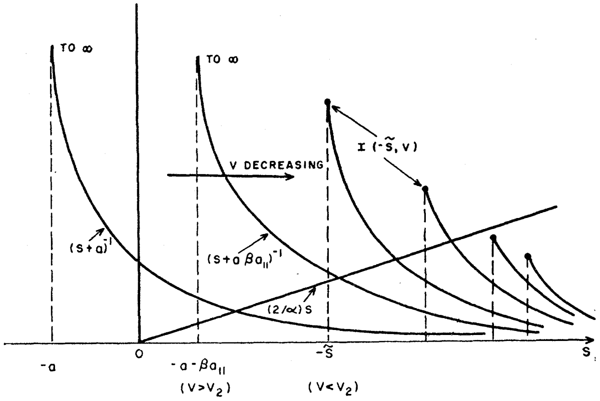

FIG. 3. The qualitative behavior of $I(s, v)$ as a function of s and v.

We will forego a discussion of the nature of the transition until the normal molecular potential is considered.

It would be expected that a gas with purely attractive molecular forces would collapse to a point. In the model, however, a restriction has been placed on the fluctuations in n_j, the number of particles in a cell, and as a consequence this limitation to finite fluctuations plays the role of a repulsive force.

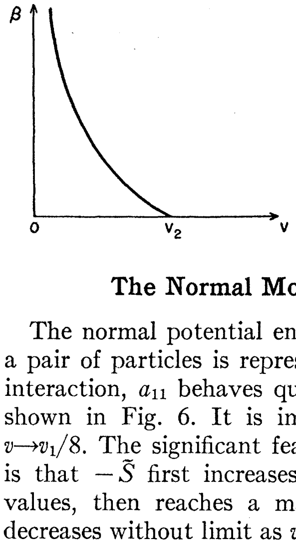

FIG. 4. The qualitative relation between the transition temperature and specific volume for an attractive potential.

The Normal Molecular Potential

The normal potential energy of interaction between a pair of particles is represented by Fig. 1. With this interaction, a_{11} behaves qualitatively on v in the way shown in Fig. 6. It is important that $a_{11}\rightarrow+\infty$ as $v\rightarrow v_1/8$. The significant feature of the behavior of a_{11} is that $-\tilde{S}$ first increases as v decreases from large values, then reaches a maximum value, and finally decreases without limit as $v\rightarrow v_1/8$.

In the range $\infty>v>v_2$ a normal saddle point exists. The possibility for a transition only develops when neighboring cells get into the range of the attractive forces.

As v decreases from v_2, $I(-\tilde{S}, v)$ becomes finite. Figure 3 illustrates this behavior. Now $I(-\tilde{S}, v)$ is proportional to temperature. We can then see the possibility that if T is large enough (β small enough), the minimum value of $I(-\tilde{S}, v)$ as a function of v is above the line $(2/\alpha)s$ when the maximum value of $-\tilde{S}$ is reached. Consequently, a normal saddle point exists for all v under the circumstance that T is large enough, and this means that no transition occurs. We are thus able to define a critical temperature T_c, β_c, and volume

v_c by means of the equations

$$-2\tilde{S}_c/\alpha = I(-\tilde{S}_c, v_c);$$

$$-\tilde{S}_c \text{ as a function of } v \text{ is maximum at } v_c \text{ for } \beta=\beta_c. \quad (5.22)$$

This critical behavior is described in Fig. 7.

Now for $\beta>\beta_c(T<T_c)$, a volume v' exists for which

$$-2\tilde{S}'/\alpha = I(-\tilde{S}', v'); \quad v_1<v'<v_2; \quad \beta>\beta_c. \quad (5.23)$$

Furthermore, as v decreases still further, the repulsion pulls I to the left as shown in Fig. 7, and a volume v'' exists for which

$$-2\tilde{S}''/\alpha = I(-\tilde{S}'', v''); \quad v_1<v''<v'<v_2; \quad \beta>\beta_c. \quad (5.24)$$

We will show below that v' and v'' correspond to the onset and completion of a condensation phenomenon. This phenomenon does not occur in either one or two dimensions because $I(-s, v)$ diverges. It is, therefore, concluded that

$$-\beta\psi_n = \frac{n}{2}\ln(2\pi m/\beta h^2) + \ln(ev) + \beta(\tfrac{1}{2}W_0 - \Lambda_1) + g_n(s_s) - g_n(s_{id}), \quad (5.25)$$

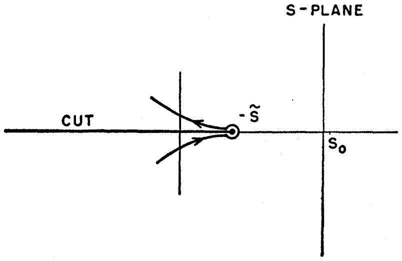

FIG. 5. Path of steepest descent for $v<v_\beta$.

where

$$2s_s/\alpha = I(s_s, v),$$

for

$$n=1,2; \quad 0<\beta<\infty, \quad v_1<v<\infty,$$

$$n=3; \quad \begin{cases} \beta>\beta_c, \\ v_1<v<\infty, \end{cases} \quad \begin{cases} \beta<\beta_c, \\ \infty>v>v';\ v''>v>v_1. \end{cases}$$

The normal region is defined by the above conditions.

For volumes v such that $v'>v>v''$, the normal saddle point does not exist. However, the path of steepest descent described by Fig. 5 exists, the saddle point sticking at the pole. Then

$$-\beta\psi_3 = \tfrac{3}{2}\ln(2\pi m/\beta h^2) + \ln(ev) + \beta(\tfrac{1}{2}W_0 - \Lambda_1) + g_3(-\tilde{S}) - g_3(s_{id}), \quad (5.26)$$

for $\beta<\beta_c$, $v'>v>v''$. This region we call the transition region.

This completes the evaluation of the partition function for all v, β for the normal molecular potential.

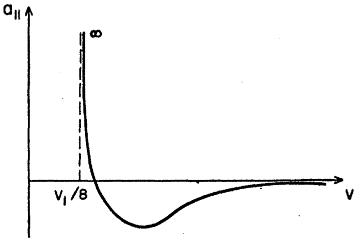

FIG. 6. Qualitative dependence of a_{11} on specific volume.

6. ISOTHERMS, FLUCTUATIONS, AND CORRELATIONS

The equation of state can now be obtained from Eqs. (5.25) and (5.26) by the relation $p=-(\partial\psi/\partial v)_T$. For a three-dimensional gas this gives in the normal region

$$p = \frac{1}{\beta v} + \frac{1}{2}\frac{\partial W_0}{\partial v} - \frac{\partial \Lambda_1}{\partial v} - \frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi} \frac{d\omega}{s_s + a + \beta\Lambda(\omega)}\frac{\partial\Lambda(\omega)}{\partial v}, \quad (6.1)$$

where s is determined by the saddle point equation (5.15). In the transition region the pressure is given by

$$p = \frac{1}{\beta v} + \frac{1}{2}\frac{\partial W_0}{\partial v} - \frac{\partial \Lambda_1}{\partial v} + \frac{\partial\Lambda_1}{\partial v}\left[\frac{\tilde{S}}{\alpha} + \frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{d\omega}{[-\tilde{S}+a+\beta\Lambda(\omega)]}\right] - \frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{d\omega\partial\Lambda(\omega)/\partial v}{[-s+a+\beta\Lambda(\omega)]}. \quad (6.2)$$

At the transition points v' and v''; $s=-\tilde{S}$, and the term in the brackets of (6.2) vanishes as can be seen from Eq. (5.15) by a differentiation. Consequently the pressure is continuous at the transitions. The first derivative of the pressure with respect to volume is

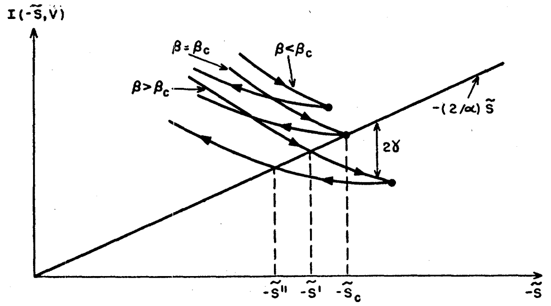

FIG. 7. Qualitative behavior of $I(-\tilde{S}, v)$ as a function of β, v, and $-\tilde{S}$. Arrows on the curves show direction as v decreases. These curves are the locus of end points of curves which could be drawn to correspond to curves in Fig. 3 where $I(s, v)$ is shown as a function of s.

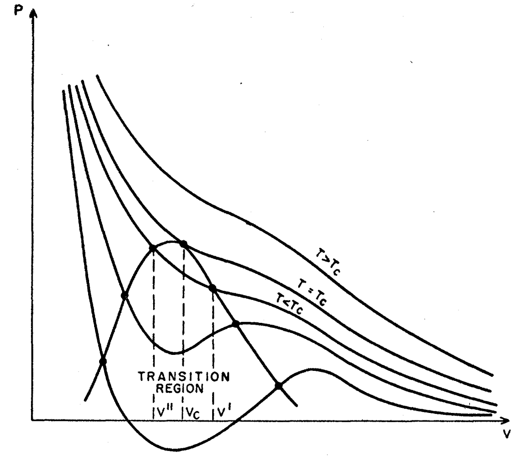

FIG. 8. Qualitative features of the equation of state.

also continuous at the transition points; however, there is a discontinuity of the second derivative. These statements are proved in the appendix.

Qualitative investigation and numerical estimates using typical Lenard-Jones potential energy curves to deduce the behavior of W_0 and $\lambda(\omega)$ give results for the equation of state summarized in Fig. 8. These estimates give critical temperatures and volumes which are of the same order of magnitude as experimental results for the potentials considered. Below the critical temperature T_c, the isotherms consist of three analytically different pieces while above T_c the isotherms are everywhere analytic. The discontinuities are located and described by the analysis without further thermodynamic considerations.

It is immediately obvious that the isotherms are not flat in the transition region. For all temperatures above T_c, and for temperatures immediately below T_c, $\partial p/\partial v$ is everywhere negative; this means that for these temperatures the states described by the theory are all stable. For lower temperatures $\partial p/\partial v$ becomes positive for a part of the range of the isotherms and the theory has admitted unstable states. At these temperatures there is no obvious relation between the location of the transition points and the position of the loop in an isotherm. It can easily be shown that for very low temperatures the maximum in the isotherm occurs at larger volumes than the transition volume v' adjacent to the gaseous phase. Similarly, the states in the liquid phase are everywhere stable, $\partial p/\partial v<0$, for all temperatures. At low temperatures also, the pressures are allowed by the theory to become negative. The edifying features of the equation of state are thus the existence of a critical temperature with the accompanying analyticity for higher but not lower temperatures and the stability of all states for temperatures immediately below the critical.

The correlation between numbers of molecules n_j, n_k situated in the jth and kth cells, respectively, is defined as

$$C_{jk}=\frac{\langle n_jn_k\rangle}{(\langle n_j^2\rangle)^{\frac{1}{2}}(\langle n_k^2\rangle)^{\frac{1}{2}}}. \tag{6.3}$$

The average value of a function F is defined, after transformation to the variable s and after using (5.9) for the partition function, to be

$$\langle F\rangle=\int_{s_0-i\infty}^{s_0+i\infty} ds(s+\tilde{S})^{-1}F(s)\exp[Ng_n(s)]\Big/ \int_{s_0-i\infty}^{s_0+i\infty} ds(s+\tilde{S})^{-1}\exp[Ng_n(s)]. \tag{6.4}$$

Expressed in terms of the variables $x_j=n_j-1$, the correlation is

$$C_{jk}=(1+\langle x_jx_k\rangle)/(1+\langle x_j^2\rangle). \tag{6.5}$$

The correlation function, $\langle x_jx_k\rangle$, expressed in terms of the variables $\{y_i\}$ is

$$\langle x_jx_k\rangle=\sum_{l=2}^{N}\sum_{m=2}^{N} t_{jl}t_{km}\langle y_ly_m\rangle. \tag{6.6}$$

However, $\langle y_ly_m\rangle=0$ unless $l=m$ because the integrand in Eq. (5.3) is an even function of y_l and y_m and the limits of integration are symmetric. Thus,

$$\langle x_jx_k\rangle=\sum_{m=2}^{N} t_{jm}t_{km}\langle y_m^2\rangle. \tag{6.7}$$

It is clear from (5.3) and (5.5) that we can express $\langle y_m^2\rangle$ as

$$\langle y_m^2\rangle=\frac{1}{2}\left\langle\frac{1}{s+a+\beta\Lambda_m}\right\rangle, \tag{6.8}$$

so that

$$\langle x_jx_k\rangle=\frac{1}{2}\left\langle\sum_{m=2}^{N}\frac{t_{jm}t_{km}}{s+a+\beta\Lambda_m}\right\rangle. \tag{6.9}$$

Using (5.2) for the components of the characteristic vectors,

$$\langle x_jx_k\rangle=\left\langle\frac{1}{N}\sum_{m=2}^{\frac{1}{2}(N+1)}\frac{\cos[(2\pi/N)(k-j)(m-1)]}{s+a+\beta\Lambda_m}\right\rangle. \tag{6.10}$$

The term with $m=1$ does not appear in the sum due to the restriction $\sum_{i=1}^{N} n_i=N$. Because this term is omitted, we have for all j,

$$\sum_{k=1}^{N}\langle x_jx_k\rangle=0. \tag{6.11}$$

Write (6.10) in the form

$$\langle x_jx_k\rangle=\left\langle\frac{\cos[(2\pi/N)(k-j)]}{N(s+\tilde{S})}\right\rangle + \left\langle\frac{1}{N}\sum_{m=3}^{\frac{1}{2}(N+1)}\frac{\cos[(2\pi/N)(k-j)(m-1)]}{s+a+\beta\Lambda_m}\right\rangle. \tag{6.12}$$

Consider the second term. Since all the singularities of the sum are to the left of $-\tilde{S}$, the presence of this sum will not influence the existence or position of the saddle point, so that

$$\left\langle\frac{1}{N}\sum_{m=3}^{\frac{1}{2}(N+1)}\frac{\cos[(2\pi/N)(k-j)(m-1)]}{s+a+\beta\Lambda_m}\right\rangle$$

$$=\frac{1}{N}\sum_{m=3}^{\frac{1}{2}(N+1)}\frac{\cos[(2\pi/N)(k-j)(m-1)]}{s_s+a+\beta\Lambda_m}. \quad (6.13)$$

Define $H(r_{jk};s)$ by

$$H(r_{jk};s)=\lim_{N\to\infty}\frac{1}{N}\sum_{m=3}^{\frac{1}{2}(N+1)}\frac{\cos[(2\pi/N)(k-j)(m-1)]}{s+a+\beta\Lambda_m}. \quad (6.14)$$

When a normal saddle point exists, the correlation function in the limit $N\to\infty$ is

$$\lim_{N\to\infty}\langle x_jx_k\rangle=H(r_{jk};s_s). \quad (6.15)$$

In the transition region, $s_s=-\tilde{S}$, and

$$\lim_{N\to\infty}\langle x_jx_k\rangle=\gamma\lim_{N\to\infty}\cos(2\pi/N)(k-j)+H(r_{jk};-\tilde{S}), \quad (6.16)$$

where γ is defined in (5.19). If we put $j=k$, we then have the fluctuations in the number of particles in a cell, σ. In the normal region,

$$\sigma=\langle x_j^2\rangle=s_s/\alpha. \quad (6.17)$$

In the transition region

$$\sigma=\langle x_j^2\rangle=\gamma+\frac{1}{2}\left(\frac{\partial f_3}{\partial s}\right)_{s=-\tilde{S}}=-\tilde{S}/\alpha. \quad (6.18)$$

For the ideal gas, it follows directly from Eq. (2.3) for the configuration sum that $\sigma=1$. This fixes the saddle point for the ideal gas; $s_{id}=\alpha$. From (5.12) it follows that

$$\alpha+a=\tfrac{1}{2}. \quad (6.19)$$

Since $a=\frac{1}{2}\ln 2$, α is positive.

The qualitative dependence of σ on volume and temperature is obtained from Fig. 7 which shows how the saddle point s_s depends on these variables. In Fig. 9 we show the general features of σ.

The function $H(r_{jk};s_s)$ defined in (6.14) can be shown[2] to be

$$H(r_{jk};s_s)=\frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{\cos[\boldsymbol{\omega}\cdot(\mathbf{r}_j-\mathbf{r}_k)/v^{\frac{1}{3}}]}{s_s+a+\beta\Lambda(\boldsymbol{\omega})}d\boldsymbol{\omega}. \quad (6.20)$$

This is true in the limit as $N\to\infty$, for fixed r_{jk}. Because of this restriction the $\langle x_jx_k\rangle$ obtained using $H(r_{jk};s_s)$ will no longer satisfy the condition

$$\sum_{k=1}^{N}\langle x_jx_k\rangle=0.$$

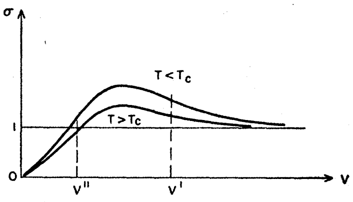

FIG. 9. The qualitative dependence of $\sigma=s_s/\alpha$ on volume and temperature.

According to (6.20), the $H(r_{jk};s_s)$ are Fourier coefficients for $\frac{1}{2}[a+\beta\Lambda(\omega)+s_s]^{-1}$, and from (4.3) the $U_1\mathbf{r}$ are Fourier coefficients of $\lambda(\omega)$. If one represents $\frac{1}{2}[a+\beta\Lambda(\omega)+s_s]^{-1}$ by its Fourier series, and then expresses $\Lambda(\omega)=a_{11}+\lambda(\omega)$ in terms of the $U_1\mathbf{r}$, one can get, after some manipulation, the following integral equation for $H(r_{jk};s_s)$:

$$H(r_{jk};s_s)=\frac{\delta(r_{jk}v^{\frac{1}{3}})}{2(a+\beta a_{11}+s_s)}-\frac{\beta}{v(a+\beta a_{11}+s_s)}\int\int\int' U(r_k)H(r_{jl};s_s)d\tau_l, \quad (6.21)$$

where the prime signifies that the integration is over all space excluding the volume v of a cell centered at $\mathbf{r}_l$, and

$$\delta(r_{jk}/v^{\frac{1}{3}})=\begin{cases}1 \text{ if } r_{jk}/v^{\frac{1}{3}}\leqslant 1,\\ 0 \text{ otherwise.}\end{cases}$$

The asymptotic behavior of $H(r_{jk};s_s)$ is considered in Appendix II.

In the transition region the correlation function is

$$\lim_{N\to\infty}\langle x_jx_k\rangle=\gamma\lim_{N\to\infty}\{\cos[(2\pi/N)(k-j)]\}+H(r_{jk};s_s). \quad (6.22)$$

For any two cells for which $r_{jk}/v^{\frac{1}{3}}$ is not of order N, the first term equals γ and is independent of r_{jk}. Thus the correlation function between two cells does not approach zero for large separation distances, but approaches the value $-\tilde{S}/\alpha-I(-\tilde{S},v)/2$. In Fig. 7, γ is one-half the vertical distance between $I(-\tilde{S},v)$ and the line $-2\tilde{S}/\alpha$. As the volume is decreased through the transition region along an isotherm, γ goes from zero at the beginning of the transition region to a maximum value and back to zero as we come to the end of the transition.

The existence of this constant correlation is to be expected for the condensation process. To interpretate the significance of the constant correlation we investigate a more detailed distribution function, namely, the average number of particles in the kth cell for a fixed number of particles in the jth cell. The correlation function $\langle x_jx_k\rangle$ is related to this quantity, which we denote by $\langle n_k\rangle_{n_j=n}$,

$$1+\langle x_jx_k\rangle=\langle n_jn_k\rangle=\sum_{n=1}^{N} n\langle n_k\rangle_{n_j=n}. \tag{6.23}$$

In this work, the occupation numbers $\{n_i\}$ are treated as continuous, and allowed to become negative, so that $\langle n_jn_k\rangle=\int_{-\infty}^{\infty}n\langle n_k\rangle_{n_j=n}dn$.

After a straightforward calculation, using the technique described in Sec. 5, we obtain,

$$\langle n_k\rangle_{n_j=n}=(2\pi\sigma)^{-\frac{1}{2}}\exp[-(n-1)^2/2\sigma]\times[1+(n-1)\langle x_jx_k\rangle/\sigma]. \tag{6.24}$$

Inspection of (6.24) reveals the following facts. If there is one particle in the jth cell, then the average number in all other cells is independent of their location. If the correlation function $\langle x_jx_k\rangle$ were zero then this would also be true for every value of n. The effect of positive $\langle x_jx_k\rangle$ is to increase $\langle n_k\rangle_n$ if $n>1$, and to decrease $\langle n_k\rangle_n$ if $n<1$. The important difference between the behavior of $\langle n_k\rangle_n$ in the normal and in the transition regions is due to the existence of the constant term γ for $\langle x_jx_k\rangle$ in the transition region. For the same n and k, $\langle n_k\rangle_n$ in the transition region is everywhere larger than $\langle n_k\rangle_n$ in the normal region, if $n>1$. If $n<1$, then $\langle n_k\rangle_n$ in the transition region is everywhere less than $\langle n_k\rangle_n$ in the normal region, for the same n and k. For very large distances in the normal region, $\langle n_k\rangle_n\rightarrow(2\pi\sigma)^{-\frac{1}{2}}\times\exp[-(n-1)^2/2\sigma]$, while in the transition region

$$\langle n_k\rangle_n\rightarrow(2\pi\sigma)^{-\frac{1}{2}}\exp[-(n-1)^2/2\sigma][1+(n-1)\gamma/\sigma].$$

Thus the presence of the term in the transition region shows that a deviation from the average number of particles in a cell induces deviations of the same sign even in cells which are very distant.

7. DISCUSSION

We shall attempt to analyze, at least briefly, each of the approximations made in Sec. 3.

(1) It is assumed that the total potential energy is the sum of pair interactions and that the potential energy of interaction between a pair of particles depends only on the distance between the pair. Although it is obvious that this assumption is not generally true, it is very nearly true for the noble gases. The status of the condensation problem being what it is, it is unnecessary to introduce any further complication of the force law.

(2) It is assumed that $U(r_{ij})=U(R_{km})$ when two particles i and j are in cells k and m and R_{km} is the distance between cell centers. This assumption becomes poor when R_{km} is in a range where $U(R_{km})$ is a rapidly varying function of R_{km}. We believe, nevertheless, that the particles will feel an average potential which will have the same qualitative behavior as the molecular potential. In other words, it is a mistake to pick the value of $U(R_{km})$ from the molecular potential if quantitative agreement is desired, but quantitative agreement might be possible by reasonable adjustment of the molecular potential. Such adjustment would be dependent on cell size. We do not believe that this adjustment would qualitatively damage the conclusions of our approximation.

The choice of the specific volume as the cell size was made to effect a compromise between this approximation (2) and approximation (4). Approximation (2) is favored by $\tau\ll v$ and approximation (4) is favored by $\tau\gg v$.

The choice of the cell size may play a really important role. For example, the van der Waals' loop is in part due to choosing v as the cell size. It is necessary to develop a more accurate description of a rapidly varying $U(R)$ in order to lessen, and perhaps remove, the instability in our approximate partition function. Furthermore, this choice of v may also have destroyed the liquid-solid transition. The consequences of an arbitrary cell size are being closely studied.

(3) It is assumed that if W_k, the average interaction energy for n_k particles in a cell of volume equal to the specific volume is represented as $W_k=\frac{1}{2}n_k(n_k-1)W_0$, then W_0 is independent of n_k. The definition of W_k (3.3), shows that this is qualitatively possible for specific volumes sufficiently small so that the potential energy between two particles in the cell is always positive. For large specific volumes, the cell diameter is equal to, or larger than, the range of the forces. Then this relation still holds for small n_k, when W_k is negative. However, W_k must become positive for large n_k, and therefore W_0 is not qualitatively independent of n_k. To assign to W_0 the value obtained for small n_k does not properly account for the repulsion due to close packing. However, it can be demonstrated that for these large volumes, W_k can be more closely represented with a slightly different quadratic dependence on the n_k, but with no significant changes in the behavior of the gas. Since W_0 becomes important for small volumes when our approximation is a good one, this assumption is not considered as affecting the general results obtained.

(4) This assumption replaces the sum over lattice points by a continuous integral. This is a serious approximation in that this can change the nature of the transition. As evidence for this statement, we can point to the relation between the Ising model and spherical model of a ferromagnet.[2] This means that the entropy may play a singular role that is not present in our model. A further consequence of this assumption may be the nonappearance in the model of the liquid-solid transition.

(5) The replacement of the hyper-hedron by the hyper-sphere as a region of integration is again a serious assumption. The advantage of this assumption is that it enables us to evaluate the multidimensional integral. The reasonableness of the assumption is based on the view that a very large number of important occupational configurations are included. The significant defect in the assumption is that many configurations having negative occupation numbers are also included. The

obvious effect is that the sign of the interaction energy is reversed for two different cells having occupation numbers of opposite sign. This aspect may not be too damaging, for it gives rise to a repulsion when particles are in attractive range and so it is not likely that this assumption is responsible for the instability of the van der Waals' loop obtained at sufficiently low temperatures when the particles are essentially attractive. In fact, a purely repulsive potential does not lead to any instability, which we would expect if negative occupation numbers played a spectacular part. The damaging aspect is that it spoils the configurational entropy. This is seen by the fact that use of the hyper-sphere requires the introduction of a weighting factor. We believe that any simple-minded use of a weighting factor will not change the qualitative nature of our results. We also believe, however, that the exact problem implies a complicated, probably singular, configurational entropy which could easily modify the mathematically delicate transition mechanism.

(6) The approximation $\Gamma(n+1)\simeq\exp[an(n-1)]$ is not qualitatively significant. If we choose $a=0$ we uniformly weight all configurations and if we choose $a=\frac{1}{2}\ln 2$ to fit $n=2$ in addition to $n=0$ and 1, then we reduce the weight of configuration involving large n. The latter choice of a is equivalent to a weak repulsive force and cannot qualitatively influence the condensation phenomena.

(7) The assumption of periodic boundary conditions eliminates the possibility of discussing surface behavior. Since we expect the condensation phenomena to be a volume phenomenon, this assumption does not introduce a qualitatively significant influence.

The main idea of this work was to show that a not entirely unreasonable approximation to the exact partition function of an imperfect gas can be made which exhibits some of the very general aspects of condensation. An important point of the approximation was to preserve, at least in part, the cooperative nature of the phenomenon.

We are of the opinion that it will be difficult, in our approach, to improve assumptions (4) and (5), and this greatly handicaps further progress along the lines set down here. We think that some progress can be made by refining the cell size. This will give a better estimate of the interaction energy and it is possible that stability will be achieved. It is also possible that the solid may appear. We think that the lack of a mechanism yielding a constant pressure during condensation is a serious defect of our approach, and one which we are presently unable to illuminate.

Since the approximation yields a partition function for the liquid which is stable and otherwise qualitatively proper, it is our view that useful applications to the liquid state are not improbable.

APPENDIX I: ANALYTIC BEHAVIOR AT TRANSITION POINTS

This appendix shows that $\partial^2 p/\partial v^2$ is discontinuous at the transition points. Complete mathematical rigor is lacking but can obviously be supplied where needed. Define $\Delta p(v_1, v_2)\equiv -p(v_1)+p(v_2)$, where v_1, v_2 are volumes close to a transition point, v'; v_1 is in the transition region, v_2 is outside. We are interested in $\Delta p(v', v')$ which is the limiting behavior of Δp as $v_1, v_2\rightarrow v'$ from their respective sides of v'. From (6.1) and (6.2),

$$\begin{aligned}\Delta p(v_1, v_2) &= \left\{-\frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{d\omega}{s_s+a+\beta\Lambda(\omega)}\frac{\partial\Lambda(\omega)}{\partial v}\right\}_{v_2} \\ &\quad+\frac{1}{\beta}\left(\frac{1}{v_1}-\frac{1}{v_2}\right)+\frac{1}{2}\left(\frac{\partial W_0}{\partial v_1}-\frac{\partial W_0}{\partial v_2}\right)-\left(\frac{\partial\Lambda_1}{\partial v_1}-\frac{\partial\Lambda_1}{\partial v_2}\right) \\ &\quad+\left\{\frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{d\omega}{-\tilde{S}+a+\beta\Lambda(\omega)}\frac{\partial\Lambda(\omega)}{\partial v}\right. \\ &\quad\left.-\frac{\partial\Lambda_1}{\partial v}\left[\frac{\tilde{S}}{\alpha}+\frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{d\omega}{-\tilde{S}+a+\beta\Lambda(\omega)}\right]\right\}_{v_1}. \end{aligned} \tag{I.1}$$

Let $\Lambda\equiv\Lambda_1+F(w, v)$. For small w, $F(w, v)=f(v)w^2+O(w^4)$, which defines f. Let Ω be a value of w for which the term $O(w^4)\ll f(v)w^2$. At v_2, the saddle point is s_s; as $v_2\rightarrow v'$, $s_s\rightarrow -\tilde{S}$. Regard v_2 sufficiently close to v' so that we can express $s_s=-\tilde{S}+\epsilon(v)$ with $\epsilon(v)\ll\beta f(v)\Omega^2$. Considering the first bracket in (I.1)

$$\begin{aligned}&-\frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{d\omega}{s_s+a+\beta\Lambda(\omega)}\frac{\partial\Lambda(\omega)}{\partial v} \\ &\quad=-\frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{d\omega}{\epsilon+\beta F}\left(\frac{\partial\Lambda_1}{\partial v}+\frac{\partial F}{\partial v}\right) \\ &\quad=\frac{\partial\Lambda_1}{\partial v}\frac{s_s}{\alpha}-\frac{1}{2}\frac{1}{(2\pi)^3}\int\int\int_0^{2\pi}\frac{d\omega}{\epsilon+\beta F}\frac{\partial F}{\partial v} \\ &\quad\simeq\frac{\partial\Lambda_1}{\partial v}\left(\frac{-\tilde{S}+\epsilon}{\alpha}\right)-\frac{1}{2}\frac{1}{(2\pi)^3}\left\{4\pi\frac{\partial f}{\partial v}\int_0^{\Omega}\frac{w^4dw}{\epsilon+\beta fw^2}\right. \\ &\qquad\left.+\int\int\int_{\Omega}^{2\pi}\frac{d\omega}{\beta F}\frac{\partial F}{\partial v}\right\}.\end{aligned}$$

In the above we have split the integration $\int\int\int_0^{2\pi}d\omega$ into two regions, $4\pi\int_0^{\Omega}w^2dw+\int\int\int_{\Omega}^{2\pi}d\omega$. In the first region the integrand was spherically symmetric and we neglected a term in the denominator $O(w^4)$. In the second region we neglect ϵ in the denominator since $\epsilon\ll\beta f\Omega^2$.

Treating the second bracket in (I.1) in a similar way gives

$$\Delta p(v',v')=\operatorname*{Lim}_{\epsilon\to 0}\left[\left(\frac{\partial\Lambda_1}{\partial v}+\frac{1}{2}\frac{1}{(2\pi)^3}\frac{\partial f}{\partial v}\frac{\Omega}{\beta f^2}\right)\epsilon-\left(\frac{1}{2}\frac{1}{(2\pi)^3}\frac{\partial f}{\partial v}\frac{J}{\beta f^2}\right)\epsilon^{\frac{3}{2}}\right],\qquad(\text{I.2})$$

where

$$J=\int_0^{\Omega/\sqrt{\epsilon}}\frac{dq}{1+\beta f q^2}.$$

Calling the two parentheses A, B, respectively,

$$\frac{\partial}{\partial v}\Delta p(v',v')=\operatorname*{Lim}_{\epsilon\to 0}\left(A\frac{\partial\epsilon}{\partial v}-\frac{3}{2}B\epsilon^{\frac{1}{2}}\frac{\partial\epsilon}{\partial v}\right),\qquad(\text{I.3})$$

$$\frac{\partial^2}{\partial v^2}\Delta p(v',v')=\operatorname*{Lim}_{\epsilon\to 0}\left(A\frac{\partial^2\epsilon}{\partial v^2}+\frac{3}{4}B\frac{1}{\epsilon^{\frac{1}{2}}}\left(\frac{\partial\epsilon}{\partial v}\right)^2-\frac{3}{2}B\epsilon^{\frac{1}{2}}\frac{\partial^2\epsilon}{\partial v^2}\right),\qquad(\text{I.4})$$

where A, B and their two first volume derivatives have been assumed finite.

To get an expression for ϵ and its derivatives, consider the saddle point equation,

$$2s_s/\alpha=\frac{1}{(2\pi)^3}\int\int_0^{2\pi}\int\frac{d\omega}{s_s+a+\beta\Lambda(\omega)}.$$

This can be rewritten by the approximations used above

$$2(-\tilde{S}+\epsilon)/\alpha=\frac{1}{(2\pi)^3}\left\{\int_0^{\Omega}\frac{w^2dw}{\epsilon+\beta f w^2}+\int\int_{\Omega}^{2\pi}\int\frac{d\omega}{\beta F}\right\},$$

$$2(-\tilde{S}+\epsilon)/\alpha=\frac{1}{(2\pi)^3}\left\{\frac{-\epsilon^{\frac{1}{2}}J}{\beta f}+4\pi\int_0^{\Omega}\frac{w^2dw}{\beta f w^2}+\int\int_{\Omega}^{2\pi}\int\frac{d\omega}{\beta F}\right\}.\qquad(\text{I.5})$$

J is defined in (I.2); the upper limit of integration becomes infinite as $\epsilon\to 0$. Disregarding terms of order greater than $\epsilon^{\frac{1}{2}}$, we can write (I.5) as

$$\epsilon^{\frac{1}{2}}=\frac{f}{J}\left(\int\int_0^{2\pi}\int\frac{d\omega}{F}+\frac{2\beta\tilde{S}}{\alpha}\right).\qquad(\text{I.6})$$

Differentiating,

$$\frac{\partial\epsilon}{\partial v}=2\epsilon^{\frac{1}{2}}\left\{\frac{\partial}{\partial v}\left(\frac{f}{J}\right)\left(\int\int_0^{2\pi}\int\frac{d\omega}{F}+\frac{2\beta\tilde{S}}{\alpha}\right)+\frac{f}{J}\left(-\int\int_0^{2\pi}\int\frac{d\omega}{F^2}\frac{\partial F}{\partial v}-\frac{2\beta}{\alpha}\frac{\partial\Lambda_1}{\partial v}\right)\right\}.\qquad(\text{I.7})$$

This vanishes as $\epsilon\to 0$. A second differentiation will yield the following term, which will not vanish as $\epsilon\to 0$:

$$\operatorname*{Lim}_{\epsilon\to 0}\frac{\partial^2\epsilon}{\partial v^2}=2\left(\frac{f}{J}\right)^2\left(\int\int_0^{2\pi}\int\frac{d\omega}{F^2}\frac{\partial F}{\partial v}+\frac{2\beta}{\alpha}\frac{\partial\Lambda_1}{\partial v}\right)^2.\qquad(\text{I.8})$$

The vanishing of ϵ assures the continuity of the pressure at the transition points; the vanishing of $\partial\epsilon/\partial v$ as $\epsilon\to 0$ assures the continuity of $\partial p/\partial v$ by (I.3); the nonvanishing of $\partial^2\epsilon/\partial v^2$ shows that $\partial^2 p/\partial v^2$ is discontinuous (I.4).

APPENDIX II: CORRELATION FUNCTION

In this appendix, some special features of the function $H(r_{jk};s_s)$ defined by Eq. (6.14) are considered. This function satisfies an integral equation which can be obtained in the following way. Introduce

$$h_{jk}\equiv\frac{1}{N}\sum_{m=3}^{(N+1)/2}\frac{\cos[(2\pi/N)(k-j)(m-1)]}{s_s+a+\beta\Lambda_m}.\qquad(\text{II.1})$$

Then

$$H(r_{jk};s_s)=\operatorname*{Lim}_{N\to\infty}h_{jk}.$$

Multiply both sides of (II.1) by $\cos[(2\pi/N)(k-j)\times(m'-1)]$ and sum over k from 1 to N. One gets

$$\frac{1}{s_s+a+\beta\Lambda_{m'}}=2\sum_{k=1}^{N}h_{jk}\cos\left[\frac{2\pi}{N}(k-j)(m'-1)\right].\qquad(\text{II.2})$$

Substitute for $\Lambda_{m'}$ its definition,

$$\Lambda_{m'}\equiv a_{11}+\sum_{p=2}^{(N+1)/2}U_{1p}\cos\left[\frac{2\pi}{N}(p-1)(m'-1)\right].$$

Then (II.2) becomes, choosing $j=1$ for simplicity,

$$\tfrac{1}{2}=(s_s+a+\beta a_{11})\sum_{k=1}^{N}h_{1k}\cos\left[\frac{2\pi}{N}(k-1)(m-1)\right]+\beta\sum_{p=2}^{(N+1)/2}U_{1p}\sum_{k=1}^{N}h_{1k}\cos\left[\frac{2\pi}{N}(k-1)(m-1)\right]\times\cos\left[\frac{2\pi}{N}(p-1)(m-1)\right].\qquad(\text{II.3})$$

Multiply both sides of (II.3) by $\cos[(2\pi/N)(q-1)\times(m-1)]$ and sum over m from 3 to $N-1$. For $q\neq 1$, there results

$$h_{1q}=-\frac{1+2\cos[(2\pi/N)(q-1)]}{N(s_s+a+\beta a_{11})}-\frac{\beta}{s_s+a+\beta a_{11}}\sum_{l=1,\,l\neq q}^{N/2}h_{1l}U_{lq},\qquad(\text{II.4})$$

while for $q=1$,

$$h_{11}=\frac{1}{2}\frac{N-3}{N(s_s+a+\beta a_{11})}-\frac{\beta}{(s_s+a+\beta a_{11})}\sum_{l=1}^{N/2}h_{1l}U_{lq}. \quad \text{(II.5)}$$

In the limit $N\rightarrow\infty$, replacing the sums with an integral,

$$H(r_{jk};s_s)=\frac{\delta(r_{jk}/v^{\frac{1}{3}})}{2(s_s+a+\beta a_{11})}-\frac{\beta}{(s_s+a+\beta a_{11})}\times\frac{1}{v}\int\int\int' U(r_{kk'})H(r_{jk'};s_s)d\tau_{k'} \quad \text{(II.6)}$$

where

$$\delta(r_{jk}/v^{\frac{1}{3}})=\begin{cases}1 \text{ if } r_{jk}\leq v^{\frac{1}{3}}\\ 0 \text{ otherwise,}\end{cases}$$

and the prime on the integral signifies that the integration is over all space excluding a volume v centered at $\mathbf{r}_k$. Consider the case when $U(r)=0$ for $r>R_0$. The asymptotic value for $H(r_{jk};s_s)$ can be obtained in the following way. If $H(r_{jk'};s_s)$ in the integrand of (II.6) is expanded in a Taylor series about r_{jk} and integrated term by term,

$$H(r_{jk};s_s)=\frac{\delta(r_{jk}/v^{\frac{1}{3}})}{2(s_s+a+\beta a_{11})}-\frac{\beta}{(s_s+a+\beta a_{11})v}\times\sum_{n=0}^{\infty}\frac{[\Delta^n H(r_{jk})]}{(2n)!(2n+1)}\int\int\int' r_{kk'}{}^{2n}U(r_{kk'})d\tau_{k'}, \quad \text{(II.7)}$$

where Δ is the Laplacian operator. All the integrals can be expressed in terms of derivatives of $\lambda(\omega)$ at $\omega=0$ by

$$\left(\frac{d^{2n}\lambda(\omega)}{d\omega^{2n}}\right)_{\omega=0}=(-1)^n\frac{1}{(2n+1)v^{2n/3}}\times\frac{1}{v}\int\int\int' r_{kk'}{}^{2n}U(r_{kk'})d\tau_{k'}. \quad \text{(II.8)}$$

Introducing this in (II.7) and putting $p_{jk}=r_{jk}/v^{\frac{1}{3}}$,

$$H(p_{jk};s_s)=\frac{\delta(p_{jk})}{2(s_s+a+\beta a_{11})}-\frac{\beta}{(s_s+a+\beta a_{11})}\times\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n)!}\left(\frac{d^{2n}\lambda(\omega)}{d\omega^{2n}}\right)_0\Delta^n H(p_{jk};s_s). \quad \text{(II.9)}$$

For large p_{jk}, we expect $H(p_{jk})$ to depend on distance only, so that if we put $f(p)=pH(p_{jk})$, then

$$\Delta^n H(p_{jk})=\frac{1}{p}\frac{d^{2n}f(p_{jk})}{dp^{2n}}.$$

If further we assume $f(p)=e^{-\alpha p}$, then (II.9) becomes

$$(s_s+a+\beta a_{11})=-\beta\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n)!}\left(\frac{d^{2n}\lambda(\omega)}{d\omega^{2n}}\right)_0\alpha^{2n}$$
$$=-\beta\lambda(i\alpha). \quad \text{(II.10)}$$

Replacing $i\alpha$ by Z, we have for the form of the function $H(r_{jk};s_s)$ at large distances

$$H(r_{jk};s_s)=A\frac{\exp(-iZr_{jk}/v^{\frac{1}{3}})}{r_{jk}/v^{\frac{1}{3}}}, \quad \text{(II.11)}$$

where Z is determined from $s_s+a+\beta a_{11}+\beta\lambda(Z)=0$. In the gas region Eq. (II.10) has two equal and opposite roots, with Z imaginary, $Z=\pm iy$. We then have for large $r_{jk}/v^{\frac{1}{3}}$,

$$H(r_{jk};s_s)=A\frac{\exp(-yr_{jk}/v^{\frac{1}{3}})}{r_{jk}/v^{\frac{1}{3}}},$$

where A is a positive constant which can in principle be determined from Eq. (II.1). As the transition region is approached, these two roots approach the origin. In the transition region, $Z=0$, and $H(r_{jk};s_s)=A(r_{jk}/v^{\frac{1}{3}})^{-1}$. In the liquid region close to the transition region we have again $Z=\pm iy$, so that $H(r_{jk},s_s)$ has the same asymptotic form as in the gas region. We believe that the correlation function has oscillatory behavior at small distances and that it in general has the required characteristics.

The correlation function may be evaluated exactly in a one-dimensional system with nearest neighbor interaction only. The characteristic behavior to be expected of the one-dimensional system is found.

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