

taminated as the result of room-temperature hydrolysis. The need for water vapor in both reactions explains why air embrittlement occurs primarily in the summer, the most humid time of the year. Changes in ductility, due to physical adsorption of carbon dioxide or hydrogen chloride, were not observed.

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Rigorous Basis of the Frenkel-Band Theory of Association Equilibrium

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By means of the general theory of the classical grand ensemble, the complete formal relations for pressure and number of molecules in an open system, as a function of activity, are derived without approximation within the scheme of the Frenkel-Band equilibrium cluster theory of association. The physical clusters, defined geometrically by overlap of spheres drawn about each molecule, are not regarded as statistically independent, but their mutual exclusion property gives rise to free energies of formation work for cavities necessary to contain those clusters. A connection is established between these free energies and a suitable generalization of the Mayer irreducible cluster sum. The appropriate modification of the theory to include external forces (such as the gravitational field) is displayed. A rigorous expansion of molecular distribution functions in terms of physical (rather than Ursell-Mayer) cluster integrals is also presented.

I. INTRODUCTION

ALMOST simultaneously, Frenkel^{1,2} and Band³ pointed out the value of regarding the imperfection and condensation of real gases as association equilibria of molecules into physical clusters of various sizes, caused by intermolecular attractions. In this picture, the gas phase consists of free molecules (monomers), and descending numbers of bound molecular pairs (dimers), bound triplets (trimers), etc. These clusters of molecules, in "chemical" equilibrium with one another, were originally treated as noninteracting, to that the pressure in the system was taken simply to be the sum of ideal gas partial pressures for clusters so each size, considered as independent species. The appearance of liquid as the system is isothermally compressed beyond the saturation point, was supposed to be due to sudden appearance of clusters of macroscopic size.

Band⁴ also examined a refinement of this viewpoint by introducing hard sphere collision diameters for the clusters to account approximately for the interference effect between cluster pairs.

More recently ter Haar,⁵ using Wergeland's⁶ idealized cluster partition function for noninteracting clusters in

the grand ensemble, has shown that the Frenkel-Band approach has the capacity to reproduce the distinctive feature of subcritical pressure isotherms: monotonically increasing pressure as density is increased from zero, followed by a constant-pressure density region.

In spite of its own intuitive appeal, and the relation it bears to the important field of nucleation phenomena,⁷ the Frenkel-Band technique nevertheless still appears to lack a systematic deduction from first principles.⁸ It is this article's aim to provide such a basis. The major result is the pair of simultaneous Eqs. (14) and (17) for the number of molecules N and pressure p in the vessel as a function of the absolute activity γ . These equations include a set of density- and temperature-dependent functions W_s , which account for the entire effect of finite cluster size (leading to their strict nonindependence). In view of the fact that these quantities can be interpreted in terms of cavity formation works, one is in a good position to propose reasonable approximations to the important quantities W_s , based on extrapolation of macroscopic thermodynamics to the molecular regime.

The general theory is developed in Sec. II first on

⁷ D. Turnbull, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. III, pp. 256-266.

⁸ Hill [T. L. Hill, *J. Chem. Phys.* **23**, 617 (1955)] has developed an exact physical cluster theory, but with a different definition of "cluster" depending not only on particle positions, as in this paper, but on their relative momenta as well. Hill acknowledges the possibility of our choice (the traditional Frenkel-Band definition) but does not ever employ it.

¹ J. Frenkel, *J. Chem. Phys.* **7**, 200 (1939).

² J. Frenkel, *J. Chem. Phys.* **7**, 538 (1939).

³ W. Band, *J. Chem. Phys.* **7**, 324 (1939).

⁴ W. Band, *J. Chem. Phys.* **7**, 927 (1939).

⁵ D. ter Haar, *Proc. Cambridge Phil. Soc.* **49**, 130 (1953).

⁶ H. Wergeland, *Avhandl. Norske Videnskaps-Akad. Oslo, I. Mat.-Naturv. Kl.* **1943**, No. 11.

the basis of intermolecular pair potentials of a special cutoff form. This choice represents no fundamental restriction, but serves only to clarify the presentation by omission of distracting detail. At the end of Sec. II, the slight generalization required by more realistic molecular pair interactions, as well as by external force fields (e.g., gravity), is briefly presented.

Section III demonstrates that the W_s may be expressed in terms of series of modified irreducible Mayer cluster integrals. Thus, in spite of the superficial independence of the Mayer and the Frenkel-Band cluster theories, we establish an intimate relation between these alternatives.

Since our method is exact, its formal results for the corrected version of the Frenkel-Band equation of state are not restricted to fluids, but can in principle be applied to the solid-fluid coexistence. That this particular approach utilizing the physical cluster concept then may be rather uninformative, is illustrated by the example of the rigid sphere system, also in Sec. III.

In Sec. IV, the probable behavior of the clusters of various sizes is discussed, both with and without the modifying influence of the cavity free energies. It is suggested that certain electronic computer calculations simulating cluster statistics would be a valuable guide in understanding the nature of this rigorous version of Frenkel-Band theory at elevated temperatures, and especially in the critical region. Also in Sec. IV, we quote the result of extending the physical cluster idea to expansion of molecular distribution functions.

The exact formulation of the theory obtained here still identifies the condensation of gas into liquid (or directly into solid) as sudden appearance of one or more large clusters at temperatures well below the critical. However, in view of the obvious fact that such large aggregates use up much of the available vessel volume, leaving considerably less for others, it is clear that only by taking cluster noninterpenetration into account can a proper theory of phase transitions be constructed. It would be considered a triumph for the physical cluster ideas of the Frenkel-Band theory ultimately to lead to prediction of all major features of a vapor-liquid condensation, including the strange

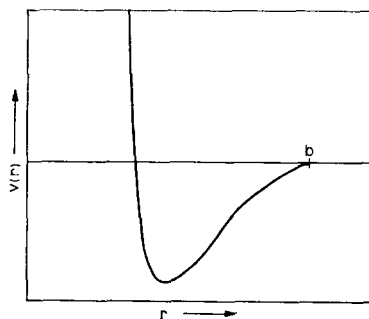


FIG. 1. The initially chosen cutoff pair potential $v(r)$, which vanishes identically beyond distance b .

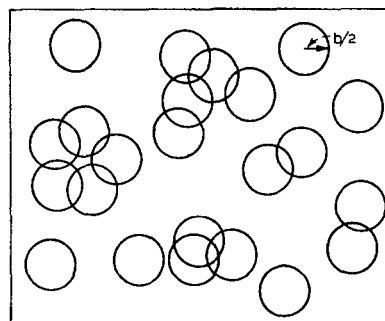


FIG. 2. Definition of physical clusters by overlap of concentric molecular spheres of radius $b/2$. The twenty-three particles shown are in a configuration corresponding to six clusters of just one molecule, two containing two molecules, one with three, and two with five.

critical region behavior; only on the foundation of the completed theory such as deduced in this article can this convincingly be accomplished.

II. THE GENERAL THEORY

We examine a classical assembly of molecules, at temperature T , whose members interact by a short-range pair potential energy, $v(r)$. For convenience, it will at first be assumed that $v(r)$ vanishes identically for all distances r greater than some cutoff distance b . The situation is illustrated in Fig. 1. It may be imagined that a sphere of radius $b/2$ has been drawn about each of the N molecular centers in the system.

The grand partition function, $\exp(-\beta\Omega)$, may be expressed as usual:

$$\exp(-\beta\Omega) = 1 + \sum_{N=1}^{\infty} (y^N/N!) \int_V \cdots \int \times \exp\left[-\beta \sum_{i < j=1}^N v(r_{ij})\right] d\mathbf{r}_1 \cdots d\mathbf{r}_N, \\ \beta = 1/kT, \quad y = (2\pi mkT/h^2)^{3/2} \exp(\mu/kT) \quad (1)$$

(the symbols m , k , T , μ , h have their usual meanings). The configuration integrals are confined to the interior of a container of volume V . In the absence of gravitational or other external forces, and with the neglect of surface free energy at the boundary of V (creating an error of vanishing magnitude relative to terms retained), $-\Omega$ may be identified as pV , where p is the system's pressure.

If one chooses to consider for a moment a term in the sum in Eq. (1) corresponding to some N , then a given configuration of the N particles will lead to a picture shown roughly in Fig. 2. The set of spheres drawn about each molecule will intersect one another to lead to a natural subdivision of the N into subsets. These subsets have no mutual overlap, but each pair of particles in the same subset either overlap themselves or are indirectly connected by an unbroken sequence

(or chain) of overlapping particles.⁹ If a given set of molecular center positions $\mathbf{r}_1 \cdots \mathbf{r}_N$ corresponds to n_1 clusters of just one molecule, \cdots , n_s clusters of s molecules, \cdots , where, of course,

$$N = \sum_{s=1}^{\infty} s n_s, \quad (2)$$

we note that there are

$$N! / \left[\prod_{s=1}^{\infty} n_s! (s!)^{n_s} \right]$$

essentially different ways of permuting the N molecules among subsets.

The grand partition function (1) can now be transformed into a sum over subdivisions of particles into subsets, of configuration space integrals which are restricted in their integrations to the requisite overlappings:

$$\exp(-\beta\Omega) = 1 + \sum_{\{n_s\}} \int_{\{n_s\}} \cdots \int \prod_{s=1}^{\infty} (1/n_s!) \prod_{\alpha=1}^{n_s} \times \left\{ (y^s/s!) \exp\left[-\beta \sum_{i<j=1}^s v(r_{i(\alpha)j(\alpha)})\right] \prod_{k=1}^s d\mathbf{r}_{k(\alpha)} \right\}. \quad (3)$$

On account of the variability of N in the grand ensemble, we are able to do away with the constraint (2), and sum in Eq. (3) over all sets of positive integers $\{n_s\}$. The appearance of $\{n_s\}$ below the multiple integral signs in (3) indicates the restriction of overlap to form the necessary clusters. The extra index α is required to distinguish the n_s different clusters of a given size s . $v(r_{i(\alpha)j(\alpha)})$ is the interaction between particles i and j in the same cluster: the α th one of size s .

Because $v(r)$ vanishes for $r > b$, no terms $v(r_{ij})$ can occur in the integrand of Eq. (3) which link a pair of particles in different clusters. If it were not for the very complicated configurational restriction on the positions and shapes of the clusters, which prevents the clusters from overlapping in a given term of the $\{n_s\}$ sum in (3), the multiple integrals would factor into independent cluster partition functions:

$$Q_s^{(0)} = (1/s!) \int_{(s)} \cdots \int \exp\left[-\beta \sum_{i<j=1}^s v(r_{ij})\right] d\mathbf{r}_1 \cdots d\mathbf{r}_s \quad (4)$$

(here, the s particles as indicated by (s) are constrained to form a single cluster). Under this factorization approximation, one readily recognizes that Eq. (3) would represent the expansion of the exponential of a sum; i.e.,

$$-\beta\Omega = \sum_{s=1}^{\infty} Q_s^{(0)} y^s. \quad (5)$$

Differentiation with respect to $\log y$ at constant β subsequently gives the average number of particles:

$$N(y) = \sum_{s=1}^{\infty} s Q_s^{(0)} y^s. \quad (6)$$

⁹ Excepting, of course, the trivial case of the single-particle cluster.

The very easily obtained approximate Eqs. (5) and (6) are the basis of the past Frenkel-Band theory which neglects "cluster interference," a convenient term for cluster configurational restrictions of non-overlap. It is the object of this investigation to avoid such simplification. For this reason we define the quantity

$$\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s) d\mathbf{r}_1 \cdots d\mathbf{r}_s$$

to be equal to the probability that the s particles of the same s cluster (serially numbered, and regarded as distinguishable) simultaneously occupy volume elements $d\mathbf{r}_1 \cdots d\mathbf{r}_s$. By observing the very strong analogy with the grand ensemble theory of molecular distribution functions,¹⁰ it is immediately possible to write out the appropriate grand ensemble expression for ρ_s :

$$\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s) = (y^s/s!) \exp\left[\beta\Omega - \beta \sum_{i<j=1}^s v(r_{ij})\right] \times \sum_{\{n_t\}} \int_{\{n_t\}} \cdots \int \prod_{t=1}^{\infty} (1/n_t!) \times \prod_{\alpha=1}^{n_{t-\delta_{st}}} \left\{ (y^t/t!) \exp\left[-\beta \sum_{i<j=1}^t v(r_{i(\alpha)j(\alpha)})\right] \prod_{k=1}^t d\mathbf{r}_{k(\alpha)} \right\}. \quad (7)$$

This form accounts for the possibility, for given $\{n_t\}$, that any of the n_s equivalent s clusters can occupy the volume elements $d\mathbf{r}_1 \cdots d\mathbf{r}_s$, though for a specific s cluster we allow the particles to occupy positions in only one way. The configurational restrictions are the same in (7) as in (3), but now one of the s clusters is held rigidly in place at $\mathbf{r}_1 \cdots \mathbf{r}_s$ and coordinate integration is only over those clusters remaining free to move (hence the Kronecker delta, δ_{st} , in the α -product upper limit for position-integrated s clusters).

Actually to perform the restricted multiple integrals in (7) is obviously no less impossible a task than for those in (3). It is, however, profitable at this stage to recognize that the complicated quantity on the right-hand side of (7) may be identified in a physically simple way. It will be noticed that the rigidly fixed s cluster appears to the entire remaining set of clusters as an impenetrable object since, by definition, mutual overlap of concentric spheres is excluded between them and the s cluster. Consequently, we may rigorously rewrite Eq. (7) in the much more compact way:

$$\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s) = (y^s/s!) \times \exp\left\{-\beta \left[\sum_{i<j=1}^s v(r_{ij}) + \Omega_s(\mathbf{r}_1 \cdots \mathbf{r}_s) - \Omega \right]\right\}; \quad (8)$$

the quantity $\exp[-\beta\Omega_s(\mathbf{r}_1 \cdots \mathbf{r}_s)]$ is precisely a grand partition function of the form (3) [or more simply Eq. (1)], except that all particle centers are excluded from the volume all of whose points are no further

¹⁰ T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), pp. 233-235.

than b from at least one of $\mathbf{r}_1 \cdots \mathbf{r}_s$. This volume, which we denote by τ_s , is a cavity from which all other particle centers must completely be absent so that the rigidly fixed s cluster may be put in place without its possibly overlapping more particles. τ_s would naturally change size and shape if $\mathbf{r}_1 \cdots \mathbf{r}_s$ were varied within the limits set by the s cluster connectivity definition.

If one introduces, for chosen $\mathbf{r}_1 \cdots \mathbf{r}_s$, a single-particle potential $u(\mathbf{r})$ which vanishes everywhere in V excepting inside τ_s , where it is positively infinite, then the explicitly written analog of Eq. (1) leading to $\Omega_s(\mathbf{r}_1 \cdots \mathbf{r}_s)$ is

$$\exp[-\beta\Omega_s(\mathbf{r}_1 \cdots \mathbf{r}_s)] = 1 + \sum_{N=1}^{\infty} (y^N/N!) \times \int_V \cdots \int_V \exp\left\{-\beta\left[\sum_{i=s+1}^{N+s} u(\mathbf{r}_i) + \sum_{i < j = s+1}^{N+s} v(r_{ij})\right]\right\} \times d\mathbf{r}_{s+1} \cdots d\mathbf{r}_{s+N}, \quad (9)$$

because each factor $\exp[-\beta u(\mathbf{r}_i)]$ vanishes inside τ_s , but is unity outside.

For any open system at equilibrium, the grand partition function may be identified thermodynamically in terms of displacement parameters of external fields acting on the system, and conjugate forces of reaction.^{11,12} Indeed, for the homogeneous system represented in Eq. (1), we have already noted in effect that the displacement parameter and conjugate thermodynamic force respectively are V and p . Now, however, there must be an additional parameter corresponding to placement of the repelling cavity within the system at the required position. This placement can be accomplished in a variety of ways: (a) The cavity containing the repelling potential $u(\mathbf{r})$ may be pushed into the system from outside V to the necessary final position. (b) The auxiliary function $u(\mathbf{r})$ may be "turned on" in place by increasing the potential energy within the region of the final desired cavity continuously from zero to plus infinity, thereby slowly squeezing out particles. (c) The cavity may be expanded in place from a point to its final finite size by a suitable generalization of the "scaled particle" trick.^{13,14}

Regardless of the method of introducing the fixed repelling cavity into the initially homogeneous fluid, the amount of reversible isothermal work required is the same, and we denote it by $W_s(\mathbf{r}_1 \cdots \mathbf{r}_s)$. The general thermodynamic identification of grand partition func-

tions thereupon rigorously states:

$$\Omega_s(\mathbf{r}_1 \cdots \mathbf{r}_s) - \Omega = W_s(\mathbf{r}_1 \cdots \mathbf{r}_s). \quad (10)$$

Accordingly, Eq. (8) is

$$\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s) = (y^s/s!) \times \exp\left\{-\beta\left[\sum_{i < j = 1}^s v(r_{ij}) + W_s(\mathbf{r}_1 \cdots \mathbf{r}_s)\right]\right\}. \quad (11)$$

The relation (11) shows clearly that the cavity work (it is a free energy, of course) has the effect of modifying the configurational probability distribution for the s -particle cluster. If the over-all system were a sufficiently dilute gas, the fixed s cluster would never encounter other clusters, and so W_s would vanish to leave ρ_s in (11) to contain a Boltzmann factor for only the internal potential energy of interaction in the s cluster. Obviously, therefore, $W_s(\mathbf{r}_1 \cdots \mathbf{r}_s)$ represents the effect of the finite-density medium in which the fixed cluster is immersed; this medium consists of segregated clusters which interfere geometrically with one another and with the fixed s cluster. For potential energies $v(r)$ which vanish outside $r=b$, W_s arises *only* from this geometrically determined configurational entropy, and since introduction of an impenetrable cavity restricts available configuration space, W_s must be positive for all $y > 0$.

Owing to the probability character of $\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s)$, this function may be integrated over all positions inside V to give $N_s(y)$, the average number of clusters of s :

$$N_s(y) = \int_{(s)} \cdots \int \rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s) d\mathbf{r}_1 \cdots d\mathbf{r}_s. \quad (12)$$

Then the total average number of particles, $N(y)$, must be

$$N(y) = \sum_{s=1}^{\infty} s N_s(y). \quad (13)$$

We choose to rewrite (13) as

$$N(y) = \sum_{s=1}^{\infty} s Q_s(y) y^s \quad (14)$$

to preserve the analogy with the independent cluster approximation (6). In view of Eq. (11), this requires that we define

$$Q_s(y) = (1/s!) \int_{(s)} \cdots \int \exp\left\{-\beta\left[\sum_{i < j = 1}^s v(r_{ij}) + W_s(\mathbf{r}_1 \cdots \mathbf{r}_s)\right]\right\} d\mathbf{r}_1 \cdots d\mathbf{r}_s, \quad (15)$$

for properly interfering clusters. Since the W_s , and therefore the Q_s , are functions of y , the form (14) for $N(y)$ is no longer a simple power series in y as one obtains in the elementary Frenkel-Band approach.

¹¹ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The MacMillan Company, New York, 1956), p. 234.

¹² F. H. Stillinger, Jr., and F. P. Buff, *J. Chem. Phys.* **37**, 1 (1962).

¹³ F. H. Stillinger, Jr., Part III of an unpublished dissertation submitted to the Graduate School of Yale University (1958) for the degree of Doctor of Philosophy.

¹⁴ H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).

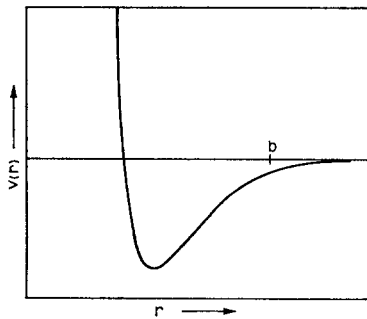


FIG. 3. The more realistic case of an intermolecular pair interaction possessing an attractive tail beyond the distance b .

Equation (6) amounts to replacing each Q_s in (14) by

$$Q_s^{(0)} = \lim_{y \rightarrow 0} Q_s^*(y). \tag{16}$$

The grand partition function (and therefore also the pressure) may be obtained by integrating (14) with respect to y . The result may be expressed in a way which is superficially similar to Eq. (5):

$$-\beta\Omega = \sum_{s=1}^{\infty} Q_s^*(y) y^s; \tag{17}$$

like $Q_s(y)$, $Q_s^*(y)$ is activity-dependent on account of proper attention to cluster interference:

$$Q_s^*(y) = (1/s!) \int_{(s)} \cdots \int \exp\{-\beta[\sum_{i < j=1}^s v(r_{ij}) + W_s^*(\mathbf{r}_1 \cdots \mathbf{r}_s, y)]\} d\mathbf{r}_1 \cdots d\mathbf{r}_s, \tag{18}$$

$$\exp[-\beta W_s^*(\mathbf{r}_1 \cdots \mathbf{r}_s, y)] = (s/y^s) \int_0^y (y')^{s-1} \exp[-\beta W_s(\mathbf{r}_1 \cdots \mathbf{r}_s, y')] dy'. \tag{18}$$

Equations (14) and (17) are the desired results. They possess the outward appearance of (6) and (5), respectively, but it is clear that one requires two different partition functions Q_s and Q_s^* , as "coefficients" in the exact Ω (or pressure) and N series, neither of which generally equals $Q_s^{(0)}$. Once again, though, it is easily verified that

$$Q_s^{(0)} = \lim_{y \rightarrow 0} Q_s^*(y). \tag{19}$$

So far, the results (14) and (17) have been restricted to pair potentials $v(r)$ which vanish for $r > b$, and to systems subject to no external forces. The form of our results however allows these conditions to be easily relaxed. Now let Fig. 3 represent the more realistic pair potential possessing an appropriate tail outside b , as does the traditional Lennard-Jones interaction, for example. One can still, as before, define physical clusters by overlap of the spheres of diameter b . However, the generalization of Eq. (3) now must include in its integrands the nonvanishing pair interaction between molecules not in the same cluster. Likewise, the

definition (7) must also incorporate the same modification, but Eq. (11), expressing $\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s)$ in terms of a cavity free energy $W_s(\mathbf{r}_1 \cdots \mathbf{r}_s)$ may still be deduced in its previous form. However, it is now necessary to understand that the "cavity," whose introduction reversibly and isothermally requires work W_s , acts not just as a particle-repelling object, but outside the region τ_s of complete repulsion, there must be a slight attraction for particles in the freely moving clusters. Each W_s is in principle completely specified by the corresponding $u(\mathbf{r}_i)$ which is again $+\infty$ inside τ_s , but

$$u(\mathbf{r}_i) = \sum_{j=1}^s v(r_{ij}) \tag{20}$$

outside, rather than zero.

The general conservative external force field may be included in the fundamental grand partition function, Eq. (1), as a single-particle potential energy $U(\mathbf{r}_i)$ acting separately on each molecule in the system. The most important example for nonelectrolytes is the gravitational field, for which one takes

$$U(\mathbf{r}_i) = mgz_i. \tag{21}$$

g is the gravitational constant, and z_i is the altitude of the i th particle relative to an arbitrarily chosen coordinate origin. For any $U(\mathbf{r}_i)$, Eq. (1) becomes^{12,15}

$$\exp(-\beta\Omega) = 1 + \sum_{N=1}^{\infty} (y^N/N!) \int_V \cdots \int \exp\{-\beta[\sum_{i=1}^N U(\mathbf{r}_i) + \sum_{i < j=1}^N v(r_{ij})]\} d\mathbf{r}_1 \cdots d\mathbf{r}_N. \tag{22}$$

In defining Eq. (7) for ρ_s also we need to add U 's for each particle appearing in the exponent. The fundamental results (14) and (17) are unchanged, but the defining relations for $Q_s(y)$ and $Q_s^*(y)$ must include the necessary U 's:

$$Q_s(y) = (1/s!) \int_{(s)} \cdots \int \exp\{-\beta[\sum_{i=1}^s U(\mathbf{r}_i) + \sum_{i < j=1}^s v(r_{ij}) + W_s(\mathbf{r}_1 \cdots \mathbf{r}_s, y)]\} d\mathbf{r}_1 \cdots d\mathbf{r}_s, \tag{23}$$

$$Q_s^*(y) = (1/s!) \int_{(s)} \cdots \int \exp\{-\beta[\sum_{i=1}^s U(\mathbf{r}_i) + \sum_{i < j=1}^s v(r_{ij}) + W_s^*(\mathbf{r}_1 \cdots \mathbf{r}_s, y)]\} d\mathbf{r}_1 \cdots d\mathbf{r}_s. \tag{23}$$

The conclusion to be reached therefore is that the grand potential Ω and average number of particles N are rigorously given by expressions (14) and (17), even when external conservative fields are present, and when the range of $v(r)$ exceeds b , so long as each W_s is the proper cavity free energy for repelling region

¹⁵ If one wishes to include an explicit interaction of molecules with the wall of the containing vessel as part of $U(\mathbf{r}_i)$, this single-particle potential will be essentially $+\infty$ outside V , and the integration in Eq. (22) may be extended over all space.

τ_s surrounded by the attractive field of Eq. (20), and if $Q_s(y)$ and $Q_s^*(y)$ are defined by (23).

In view of the fact that our general formalism applies to the gravitational field case, it is fitting to display the thermodynamic identification of Ω , where g is regarded as the new displacement parameter in addition to the old V . If once again surface terms are disregarded, one computes¹²

$$-\Omega = pV - m \int_0^g N(y, g') z_c(y, g') dg'. \quad (24)$$

p is the pressure at activity y in the homogeneous system when $g=0$, and z_c is the position of the center of mass, which generally decreases as g increases.

III. CAVITY FREE ENERGIES

We turn next to techniques for calculating, or at least approximating, the cavity free energies W_s . The identification (10) is especially useful in this connection, for it tells us that W_s is the difference between the grand potentials for assemblies with, and without, an extra "molecule" at a fixed position within the system.¹⁶ Because of the power and elegance of Mayer's expansion techniques for the grand ensemble,¹⁷ we elect to exhibit an irreducible Mayer cluster expansion for W_s .

Explicitly, the approach consists in developing the integrands of both grand partition functions into sums of products of the usual f bonds:

$$f(ij) = \exp[-\beta v(r_{ij})] - 1, \quad (25)$$

but in the Ω_s case it is necessary to include as well extraordinary bonds of the type:

$$f(\text{cluster}, i) = \exp[-\beta u(\mathbf{r}_i)] - 1 \quad (26)$$

to account for interactions between unconstrained particles and the fixed cluster. The required manipulations, involving topological identification of terms, is now a standard technique,¹² and need not be reproduced at length here. The result may be written:

$$\begin{aligned} \beta W_s(\mathbf{r}_1 \cdots \mathbf{r}_s) = & - \sum_{k=1}^{\infty} (1/k!) \int \cdots \int \\ & \times S_k(\mathbf{r}_1 \cdots \mathbf{r}_s | \mathbf{r}_{s+1} \cdots \mathbf{r}_{s+k}) \\ & \times \rho(\mathbf{r}_{s+1}, y) \cdots \rho(\mathbf{r}_{s+k}, y) d\mathbf{r}_{s+1} \cdots d\mathbf{r}_{s+k}. \end{aligned} \quad (27)$$

The integrations span all space. $\rho(\mathbf{r}, y)$ is the particle density at position \mathbf{r} in the absence of the fixed s cluster (except near the vessel walls $\rho(\mathbf{r}, y)$ would be constant if no external field is present). $S_k(\mathbf{r}_1 \cdots \mathbf{r}_s | \mathbf{r}_{s+1} \cdots \mathbf{r}_{s+k})$ is the generalized irreducible cluster sum of f bonds of

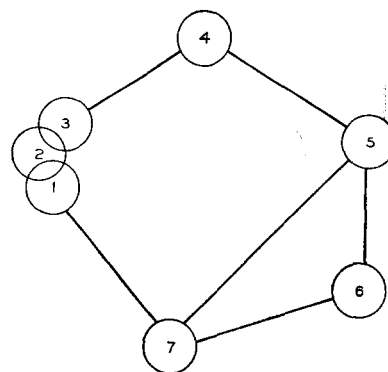


FIG. 4. Illustration of an irreducible (at least doubly connected) cluster occurring in $S_4(\mathbf{r}_1 \cdots \mathbf{r}_3 | \mathbf{r}_4 \cdots \mathbf{r}_7)$, for a three-particle cluster, and four other particles. The term equals $f(\text{cluster}, 4)f(45)f(56)f(67)f(57)f(\text{cluster}, 7)$.

both types (25) and (26); it connects the s cluster (still to be regarded for convenience as a single polyatomic molecule) to k other particles by bonds of type (26), and these k particles are connected among themselves by f 's of type (25), such that the graph of the resulting term is at least doubly connected.¹⁸ The graph of a typical f bond product for $s=3, k=4$ is shown in Fig. 4.

If the number of particles s in the cluster of interest were very large, and the cluster reasonably compact, one is assured that the primary contribution to W_s is the hydrostatic pressure p of the undisturbed fluid, times the cluster volume τ_s . Indeed, if the cluster almost always had a smooth spherical surface, one would argue that surface tension work would be the dominant remainder. Under this circumstance, the Reiss-Frisch-Helfand-Lebowitz theory of spherical cavity formation work in real fluids would apply.¹⁹ More generally though, it is necessary to be concerned with finite-size clusters with often quite rough and convoluted surfaces. To obtain a procedure for calculating W_s , still using to good advantage the macroscopic limit, we may subtract term by term from (27), in the $\rho(\mathbf{r}, y)$ constant case, τ_s times the well-known pressure virial series:²⁰

$$\begin{aligned} \beta p = & \rho - \sum_{k=1}^{\infty} [k\rho^{k+1}/(k+1)!] \\ & \times \int \cdots \int S_k(\mathbf{r}_1, \mathbf{r}_2 \cdots \mathbf{r}_{k+1}) d\mathbf{r}_2 \cdots d\mathbf{r}_{k+1}. \end{aligned} \quad (28)$$

If $f_0(\text{cluster}, i)$ is defined to be the same as (26), but with the original cutoff-potential form of $u(\mathbf{r}_i)$ ($+\infty$

¹⁶ The grand potential Ω_s in Eq. (10) it will be noticed refers only to the set of particles excluding those that form the fixed s cluster, though the former are affected by the presence of the latter.

¹⁷ Reference 10, Chap. 5.

¹⁸ For the terminology basic to these cluster specifications, the reader is referred to: J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), Chap. 13.

¹⁹ H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.* **32**, 119 (1960).

²⁰ Reference 18, p. 291.

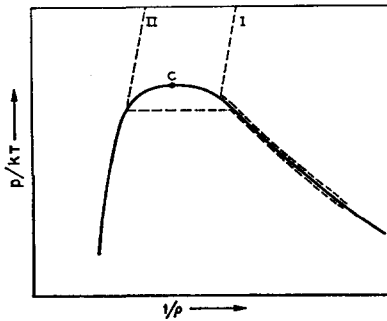


FIG. 5. The dotted curves I and II are the loci of densities, for different temperatures, at which ξ in Eq. (32) transforms from a quantity of order one (to the right of the locus), to a quantity of order V (to the left of the locus). The two curves correspond to different choices for b , with $b(\text{II}) < b(\text{I})$. Neither curve necessarily passes through the critical point C . The locus behavior below the critical temperature is drawn under the assumption that the liquid phase is present on the average as one or a few droplets of macroscopic size. The solid curve is the boundary of the two-phase region.

in τ_s , 0 outside), so f_0 is -1 in τ_s and 0 outside, then:
 $\beta W_s(\mathbf{r}_1 \cdots \mathbf{r}_s) = \beta p \tau_s$

$$\begin{aligned}
 & + \rho \int [f_0(\text{cluster}, \mathbf{r}_{s+1}) - f(\text{cluster}, \mathbf{r}_{s+1})] d\mathbf{r}_{s+1} \\
 & - \sum_{k=2}^{\infty} (\rho^k/k!) \int [S_k(\mathbf{r}_1 \cdots \mathbf{r}_s | \mathbf{r}_{s+1} \cdots \mathbf{r}_{s+k}) \\
 & + (k-1)f_0(\text{cluster}, \mathbf{r}_{s+1}) S_{k-1}(\mathbf{r}_{s+1}, \mathbf{r}_{s+2} \cdots \mathbf{r}_{s+k})] \\
 & \quad \times d\mathbf{r}_{s+1} \cdots d\mathbf{r}_{s+k}. \quad (29)
 \end{aligned}$$

The integrand of the second term on the right-hand side of Eq. (29) is nonvanishing only because the actual $v(r)$'s differ slightly from zero for $r > b$; it is never large, and is confined to the immediate exterior neighborhood of τ_s . Similarly, for large clusters, the succeeding integrals have integrands confined to the surface region of τ_s , so the individual terms in the series (29) will tend to be smaller than those in (27) which do not have this surface confinement. The series in (29) is therefore a Mayer cluster expansion of cavity surface free energy.

Although one now has in principle a systematic procedure for calculating to arbitrary precision²¹ the W_s , a significant improvement of existing Frenkel-Band calculations should result simply from use of the approximation for all s :

$$W_s = p \tau_s, \quad (30)$$

corresponding to neglect of all but the leading term in

²¹ Convergence naturally must be assumed for the Mayer cluster expansions involved. It is possible that whereas the pressure virial expansion may diverge before one reaches densities in the condensation region, the subtractive procedure leading to expansion (29) might have sufficiently reduced the magnitude of the individual terms, that convergence in the liquid density range obtains. We cannot at present clarify this point.

the complete expression (29). The limited literature which accounts for cluster interference,⁴ uses Eq. (30), but with the further approximations of spherical cluster shape, and only a correction to ideal gas pressure (for the set of physical clusters acting as independent molecules) amounting to hard sphere collisions for isolated pairs of physical clusters. Using Eq. (30) in an unqualified way, on the other hand, leads to pressure appearing in both members of the fundamental result (17), and hence requires construction of a self-consistent solution.

We close this section on the nature of the W_s 's by examining the case of the rigid sphere fluid. Here, if one takes b to be equal to the distance of closest approach for a pair of rigid spheres, then of course $v(r)$ does rigorously vanish for $r > b$. Furthermore, no clusters of more than one particle can ever form, so Eqs. (14) and (17) terminate after just one term. In the absence of external forces, they are

$$\begin{aligned}
 \rho(y) &= y \exp[-\beta W_1(y)], \\
 \beta p(y) &= y \exp[-\beta W_1^*(y)], \quad (31)
 \end{aligned}$$

where now W_1 and W_1^* are independent of any position coordinates. One finds immediately from (27) that W_1 is itself the irreducible cluster integral sum for rigid spheres. Although it has in the past been assumed that cluster interference effects should not alter the qualitative nature of the liquid-vapor coexistence, this hard sphere example shows that they can be of paramount importance in certain contexts. For if the suspected first-order fluid-solid phase transitions in the two- and three-dimensional rigid sphere systems really exist,²² then it is only through the singularities of $W_1(y)$ [and $W_1^*(y)$] that Eqs. (31) can reflect these phase changes. In view of the generally limited possibility of obtaining precise and detailed knowledge of the behavior of the W_s in this high-density range, the Frenkel-Band approach alone does not appear to be a promising tool to aid in understanding fluid-solid transitions.

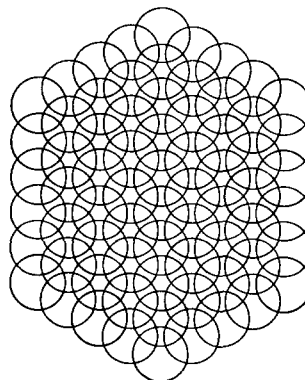


FIG. 6. Low-temperature "microcrystalline" arrangement of particles in the physical cluster.

²² B. J. Alder and T. E. Wainwright, Phys. Rev. **127**, 359 (1962).

IV. DISCUSSION AND SUGGESTIONS

Because the expressions (14) and (17) for average number of particles and the grand potential are both formally exact, they must obviously be independent of the value of b , if proper account is taken of the redefinition of the W_s 's when the range of the intermolecular potential exceeds b . As b tends to smaller and smaller values, the average number of physical clusters of a given size decreases. On the other hand, even in the dilute homogeneous gas case, if b is chosen to be several times the cube root of the density, virtually all particles will be contained in the same cluster, extending from one side of the vessel to the other.

In practice, one avoids very small or very large b . A value is chosen large enough so that molecules held together by attractive forces into a small droplet (with particle neighbor distances comparable to those in the liquid) are relegated to the same physical cluster, but pairs separated by more than, say, three times the distance of the minimum in $v(r)$, are not to overlap. The resulting compromise thus simultaneously tries to minimize the amount of the tail of $v(r)$ outside b so as not to complicate the W_s 's unduly, and yet not to have b so large that at moderate temperatures the s cluster partition functions cannot reasonably be approximated by liquid bulk and surface properties.²³ Well below the critical temperature, the existence of a suitable compromise b seems to imply that physical clusters of more than just a few molecules really are spherical droplets of liquid, and the density at which droplets (clusters) of macroscopic size become probable then should be the condensation point for the vapor.

On a per-particle basis, the average size ξ of the physical clusters is

$$\begin{aligned}\xi(y) &= \left[\sum_{s=1}^{\infty} s \cdot s N_s(y) \right] / N(y) \\ &= \left[\sum_{s=1}^{\infty} s^2 N_s(y) \right] / \left[\sum_{s=1}^{\infty} s N_s(y) \right].\end{aligned}\quad (32)$$

The above condensation condition is equivalent to stating that $\xi(y)$ becomes of order V for y greater than its value, y_0 , at condensation, whereas in the vapor phase ($y < y_0$), $\xi(y)$ is of order one, and essentially independent of V .²⁴

Figure 5 shows the loci, in the $p, 1/\rho$ plane for a homogeneous fluid, of these points at which ξ becomes of order V for different temperatures. Curves for two

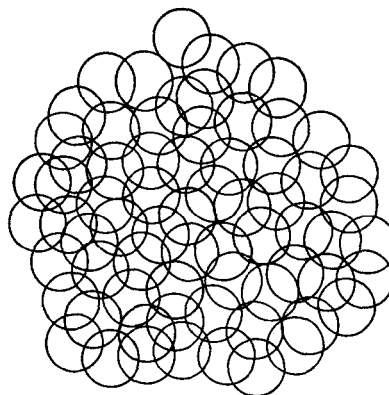


FIG. 7. Intermediate temperature "liquid droplet" form of physical clusters.

different b values have been drawn. Since the locus for a given b generally cannot be expected to pass through the critical point, there will exist isotherms for temperatures just below the critical temperature T_c with the property that they intersect the locus *outside* the coexistence region. Well below T_c , though, the locus will presumably travel down the vapor phase boundary of the coexistence region (since liquid should be present as one or a small number of droplets sufficiently dense to be interpreted each as distinct physical clusters of macroscopic size). Therefore, in attempting to use the Frenkel-Band approach to describe the critical region of fluids, one either must abandon the ξ locus as equivalent to the condensation point (especially since the locus exists for all temperatures greater than T_c), or b must be selected so that the locus passes strictly through the critical point, and the condition obviously must be applied only below a T_c calculated, for example, by the condition that $p(T_c, \rho)$ have a horizontal inflection point.

The question of critical behavior raises a set of interesting questions concerning the behavior of the physical clusters of various sizes for different temperatures. Neglecting the W_s , Reed²⁵ has calculated approximate partition functions for physical clusters of from 2 to 6, as well as 8, particles which were constrained to certain regular arrangements, where particles interacted only harmonically. Even if the W_s can be disregarded, this microcrystalline picture is probably appropriate only at very low temperatures. For a reasonably large number of particles in the cluster (perhaps 50 or more), one anticipates rather well-defined temperature ranges of distinct behavior illustrated by Figs. 6, 7, and 8.

The first of these is in accord with Reed's assumptions—the temperature is so low that its disordering effect is unable to overcome the attractive potential between particles, and a small crystal lattice should result. As T increases, the cluster should "melt," to

²³ J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946), pp. 366–374.

²⁴ The quantity ξ is a particular percolation process measure. Its point of transition from order-one to order- V behavior is known as the "critical percolation value" (of activity or density). For a comprehensive discussion of percolation problems, see: H. L. Frisch and J. M. Hammersley, *J. Soc. Ind. Appl. Math.* (to be published); also, relevant literature references appear in: H. L. Frisch, E. Sonnenblick, V. A. Vyssotsky, and J. M. Hammersley, *Phys. Rev.* **124**, 1021 (1961).

²⁵ S. G. Reed, Jr., *J. Chem. Phys.* **20**, 208 (1952).

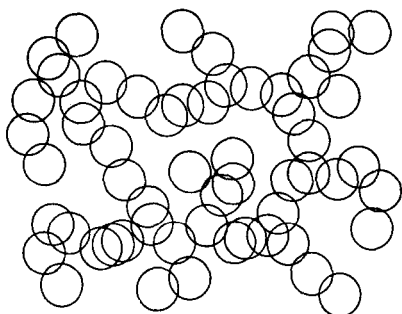


FIG. 8. High-temperature spongelike structure in physical clusters.

form a compact and roughly spherical droplet with an average coordination number still comparable to that of the ordered array, but with much more over-all configurational disorder. Finally, at high temperature the attractive forces between particles would be virtually completely overcome by thermal agitation, and only the requirement of overlapping b spheres should hold the cluster together. As shown in Fig. 8, the cluster then should have no reason to remain at all compact, and could assume the aspect of an open network or sponge. It is not yet known which of these latter two structures more appropriately describes the clusters in the vicinity of T_c .

As the number of particles in a cluster increases it is natural to suppose that the sharpness of transitions between these forms increases. In the limit of infinite cluster size, these transitions should have precisely the character of true phase transitions, and would be observed as singularities in:

$$\lim_{s \rightarrow \infty} (1/s) \log Q_s^{(0)}.$$

It would be valuable to have available electronically computed Monte Carlo²⁶ or molecular-dynamic²⁷ estimates of these free energies to see for a given $v(r)$, even neglecting the cavity free energies, at which temperature these transitions occur, how they sharpen as cluster size increases, and what is the average value of τ_s in each of the three forms.

The observed phase transition for the actual system, which we have analyzed into a collection of clusters,

²⁶ N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).

²⁷ B. J. Alder and T. E. Wainwright, "Molecular Dynamics by Electronic Computers," in *Transport Processes in Statistical Mechanics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958).

must therefore be the result of a delicate interplay between the individual cluster transitions, and cluster interference effects. The latter, through the W_s , not only modify the cluster size distribution, but also the transition temperatures for the clusters. The rapid electronic computing techniques should also make possible accurate estimation of $Q_s(y)$ in Eq. (15), including W_s , by immersing the connected physical cluster in a bath of particles identical with those forming the cluster; the bath particles would have to be free to "cluster" among themselves exactly as the real fluid of interest. The results of such calculations might substantially improve our understanding of the mysterious critical region.

As a final matter, we acknowledge that parallelism between this Frenkel-Band procedure and the Mayer cluster expansion, suggests that since the latter gives important insight into the behavior of molecular distribution functions $\rho^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n)$,¹⁰ it might be eventually enlightening to apply the former to evaluation of these important quantities. Although we shall give no details here, but reserve this general problem for later more detailed analysis, the results can easily be stated and recognized as very similar to those above. One finds:

$$\begin{aligned} & \rho^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n) \\ &= \sum_{k=0}^{\infty} (y^{n+k}/k!) \int_{(k \text{ conn. to } n)} \exp\{-\beta[\sum_{i=1}^{n+k} U(\mathbf{r}_i) \\ &+ \sum_{i < j=1}^{n+k} v(r_{ij}) + W_{n+k}(\mathbf{r}_1 \cdots \mathbf{r}_{n+k}, y)]\} d\mathbf{r}_{n+1} \cdots d\mathbf{r}_{n+k}. \end{aligned} \quad (33)$$

The terms of the sum represent connection of a certain number k of particles to the fixed set $1 \cdots n$ by means of overlapping of the familiar b spheres. The set of k need not be connected in this way among themselves, but only to at least one of $1 \cdots n$, either directly, or through a connected chain of other members of the set of k . The integration over the positions $\mathbf{r}_{n+1} \cdots \mathbf{r}_{n+k}$ of these k particles must include all configurations satisfying this connectivity condition. The quantity W_{n+k} is the total free energy of cavity formation for the entire set of $n+k$ particles, even though they may not form a singly connected grouping. W_{n+k} is *not* equal to the sum of cavity free energies for the separate connected subsets of the $n+k$ particles, but contains complicated interference effects between neighboring cavities. Once again, invariance of results to the value of b is assumed *ab initio*.