

Defining Physical Clusters in Nucleation Theory from the N -Particle Distribution Function[†]P. Schaaf,[‡] B. Senger,[§] and H. Reiss^{*,||}

Institut Charles Sadron (CNRS-ULP), 6 Rue Boussingault, 67083 Strasbourg Cedex, France, Ecole Européenne de Chimie, Polymères et Matériaux de Strasbourg, 1 Rue Blaise Pascal, BP 296F, 67008 Strasbourg Cedex, France, and Institut Universitaire de France, Strasbourg Cedex, France, Institut National de la Santé et de la Recherche Médicale, Unité 424, Fédération de Recherche Odontologique, ULP, 11 Rue Humann, 67085 Strasbourg Cedex, France, and Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90095-1569

Received: February 4, 1997; In Final Form: May 16, 1997[⊗]

In this paper we propose a refined definition of a cluster to be used in a theory for the rate of homogeneous nucleation. It contains n particles in a volume v (n/v cluster). Starting from the N -particle distribution function, we define the free energy of an n/v cluster interacting with its vapor. The expression obtained for the free energy is the same as that obtained previously using a different approach. However, the method of derivation proposed in this paper has the advantage of clarifying the nature of any approximation involved in obtaining this expression. We also discuss methods for evaluating this free energy using Monte Carlo simulation.

1. Introduction and Definition of the n/v Cluster

The rigorous definition of a *physical* cluster as part of a macroscopic phase occasions considerable difficulty. Such clusters may be used to implement molecular theories of nucleation,^{1–4} microemulsions,⁵ micelles,⁶ vesicles,⁷ etc. In general, the clusters must be defined so that they closely represent the entities actually involved in the physical process under consideration. In this paper we focus on clusters that can serve as embryos for the formation of drops in a super-saturated vapor, *i.e.*, in the *nucleation* of liquid drops in such a vapor.

An excellent early attempt to place this subject on a sound basis is due to Stillinger.¹ The Stillinger cluster is defined by a distance criterion. A snapshot of the system is taken, and a sphere of radius b is drawn around each center of a particle (we assume here that the particles are spherical). The whole system can then be subdivided into subsets of particles. Each subset is formed of all the particles of the system whose centers can be joined by an unbroken sequence (or chain) of overlapping spheres (of radii b). Particles whose spheres do not overlap with any of the spheres of the other particles constitute a cluster composed of *one* molecule. This definition of a cluster has, for example, been used in computer simulations in order to follow the evaporation process of argon clusters.⁸ However, although the Stillinger cluster certainly satisfies the requirement of rigor and can be used to develop useful theorems concerning clusters, it seems not well-adapted to nucleation theory because it may take many configurations into account which never lead to a critical cluster and ultimately to a droplet.

The actual process of nucleation evolves through the occurrence of density fluctuations, and it is these fluctuations that must be modeled by clusters. A given fluctuation could be characterized by a multitude of features, *e.g.* (crudely speaking), by molecular content, energy content, shape, etc., and each such

cluster may develop into a macroscopic drop at a characteristic rate. The average rate of drop formation, *i.e.*, the nucleation rate, must then involve the sum of these characteristic rates. Except by simulation,⁹ itself almost impossible, it is in practice not possible to characterize and sum these rates. As a result it has usually been necessary to define an *ensemble averaged* cluster and then compute the *average* rate at which it develops into a drop. One is then confronted with an inversion of the order of averaging whose error is difficult to assess.

In the so-called “classical” theory of nucleation¹⁰ the average cluster is modeled as a liquid drop, usually at equilibrium, and is then characterized by molecular content alone. This highly *ad hoc* definition has been subjected to many refinements whose fundamental validities remain obscure since, for the most part, they have consisted of molecular ideas grafted onto a phenomenological model. The situation is further complicated by a heavy reliance upon an “equilibrium” distribution of clusters¹⁰ to be used in a dynamic theory based on the principle of detailed balance, whose applicability may vary from case to case.

Assuming the relevance of detailed balance and, correspondingly, of the equilibrium distribution of clusters, a molecular approach to nucleation based on an “averaged” cluster becomes feasible. One such approach is based on density functional theory and is due to Oxtoby and co-workers,^{11,12} and especially to Talanquer and Oxtoby.⁴ This theory offers a means for calculating the properties of the density fluctuation that can play the role of the nucleus, *i.e.*, the density fluctuation that can be in *unstable* equilibrium with the mother phase. Other advantages of this theory are that, given the intermolecular potential, it can in principle be solved by analytical means rather than by means of simulation and that it is relatively easy to extend it beyond condensation to cavitation and boiling. However, it still involves ensemble averaging and the associated inversion of the order of averaging. Furthermore, in order to treat fluctuations in addition to the nucleus (fluctuations that must be treated if a fully independent theory of *rate* is to be developed), it is necessary to introduce a nonfundamental (but not unreasonable) ansatz. The problem with full ensemble averaging is that configurations may be averaged into the resulting cluster that do not participate in the actual dynamic process of nucleation.

Another molecular approach involves the so-called i/v cluster^{13,14} (i particles in a spherical volume v together with a

* To whom correspondence should be addressed.

[†] It is a pleasure to dedicate this paper to Professor Daniel Kivelson as a means of honoring his sixty-seventh birthday. We hope that our contribution will be equal to our respect for Professor Kivelson.

[‡] Institut Charles Sadron, Ecole Européenne de Chimie, and Institut Universitaire de France.

[§] Institut National de la Santé et de la Recherche Médicale.

^{||} University of California at Los Angeles.

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1997.

“shell molecule” on the surface of v and with v itself centered on the center of mass of the collective $i + 1$ particles). This approach constitutes, with the Stillinger cluster, one of the attempts to give a precise definition of a cluster. These clusters exhibit a free energy of formation surface in i, v space that contains a ridge. On the near side (smaller i) of the hill leading to the ridge, the surface, at fixed i , always slopes downward toward increasing v , but, beyond the ridge, it contains a valley whose axis is directed toward increasing i and v along a path that maintains a density i/v roughly similar to that of the bulk liquid. In the “flow” of clusters on this surface, those that enter the valley are identified as embryos for the formation of liquid drops.

In spite of the compelling picture provided by the theory of this cluster, further studies revealed several flaws. For example, using a molecular dynamics simulation (with the argon intermolecular potential),¹⁵ an i/v cluster (having a *noninteracting* shell molecule and i and v values that placed it on the *near* side of the ridge) was prepared and “thermalized”. Then, with a *vacuum* outside, the containing spherical shell was removed. With the cluster’s temperature maintained, its immediate response was to quickly evaporate a few particles, after which a more or less tightly bound core of particles persisted (even in the vacuum) for the long time during which the simulation was continued. Several techniques revealed that the density of the core was fairly uniform right up to its bounding surface, although the shape of the cluster experienced considerable fluctuation. Such a tightly bound core cluster is reminiscent of the droplike cluster of the classical theory, although both its density and surface properties are not the same. The primary message of this result is that the i/v cluster, having a *decoupled* shell molecule, could not be the one involved in the actual dynamic process of nucleation. Crudely speaking, such clusters could be described as having a liquidlike core surrounded by a gaseous envelope all within the spherical container. Such clusters are suitable for evaluating the equilibrium thermodynamic properties of the supersaturated vapor, but only the liquidlike cores are involved in the nonequilibrium condensation process. The gaseous envelop is a consequence of the equilibrium averaging process in which configurations, unrelated to the dynamic process, are averaged into the volume represented by the container. To some extent, the density functional approach which also includes equilibrium ensemble averaging must deal with the same problem. To what extent remains to be determined.

The i/v cluster may be assumed to have originated in the classic work of Lee *et al.*² who introduced a cluster consisting of i particles confined to the interior of a spherical volume v centered on the center of mass of the particles. Using Monte Carlo simulation, these authors were able to quantitatively specify the physical properties of the cluster, including calculations of its free energy and its radial distribution of density. However, the cluster was considered in isolation, and the authors did not give a precise definition that allowed one to specify which particles in a gaseous system were part of the cluster. They were thus unable to use it to determine, with precision, the thermodynamic properties of say an imperfect gas of which a set of clusters formed a part. In addition they provided no prescription for employing their cluster in the development of a molecular theory of nucleation. Indeed, in the conventional approach to nucleation, one is interested in deriving an *equilibrium* distribution of clusters, and, in this respect, their cluster fails since all of the configurations of particles in the cluster of smaller v would be contained in the cluster of larger v , so that the distribution is not unique. Nevertheless, it has many

computational advantages and, moreover, cleanly separates translational from internal degrees of freedom. Therefore, efforts have been made to improve the definition of the i/v cluster in a manner that would introduce the necessary element of uniqueness.

The addition of the shell molecule represented one of the first of these efforts. It was required that in all configurations of the i interior particles the strength of interaction between these particles and the shell molecule exceeded a certain lower limit. In principle the lower limit was to be chosen so that the interaction of the shell molecule with the interior particles always exceeded the interaction of the interior particles with the slightly imperfect vapor considered to lie outside of the cluster. Indeed it was assumed that the interaction with the outside particles was so small as to be neglected. Also, the interaction among clusters themselves could be ignored because of their small concentration. To a degree, but not completely, this solved the uniqueness problem, and the equilibrium distribution was evaluated using two different methods. In the first method¹³ the cluster partition functions were incorporated into the partition function for the entire vapor, and the distribution that maximized that partition function was determined. The uniqueness problem arises in the formulation of the partition function for the whole vapor where configurations of particles must be counted exhaustively but not redundantly. In the second method¹⁴ one uses fluctuation theory to calculate the probability of having *at least one* cluster and then shows that, for small enough cluster concentrations (fluctuation representing the cluster), the probability of observing at least one particular cluster is essentially identical with its concentration. In this way the problem of redundant counting is avoided, *i.e.*, the partition function does not have to be evaluated, but other subtleties arise (including a more hidden problem of uniqueness).

In order to place the derivation of the equilibrium cluster distribution on as sound a basis as possible (and also to see the effects of approximations in the clearest manner), it is desirable to adopt the conventional procedure of statistical mechanics and begin with the familiar N -particle distribution function.¹⁶ We now follow this procedure, but first we further augment the interaction criterion mentioned above.

The lifetime of a cluster depends, among other things, on the mean time between two consecutive evaporation processes in which the cluster loses a particle and on the mean time between two consecutive capture processes. These are strongly dependent on the interaction energy of a particle in the cluster with all of the other particles of the cluster. Thus, instead of using a distance criterion or only requiring that the shell molecule be subject to a lower limit of interaction with the remaining particles, we now require that *every* molecule in the cluster be subject to this same lower energy limit with respect to its interaction with the remaining particles. We thus use the following definition to decide to which cluster a given molecule in the gas belongs: A snapshot is taken of the gas consisting of N particles. A subset of n particles constitutes a configuration which belongs to a cluster if (i) the sum of the interaction energies $w(r)$ of any of the n particles with the remaining $(n - 1)$ is smaller than a given energy α (lower limit on the *strength* of interaction since interaction energy is a negative quantity) and (ii) the sum of the interaction energies $w(r)$ of any of the $(N - n)$ particles outside of the cluster with the n particles of the cluster is larger than α .

We will call this condition embodied in i and ii the $C(\alpha)$ criterion. The interaction energy $w(r)$ is not the real interaction potential between two atoms, with a center-to-center distance

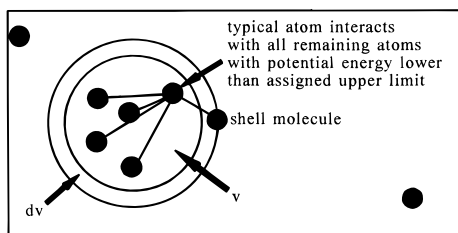


Figure 1. Typical configuration of an n/v cluster, with $n = 6$. The volume v is defined by the shell molecule within the volume dv .

of r , but corresponds to a modified pair potential. It is defined by $w(r) = u(r)$ if $r > r^*$, $w(r) = -u_0$ otherwise, where $u(r)$ is the true pair potential with a minimum equal to $-u_0$ located at $r = r^*$. It has the effect of counting particles that are very close to one another as part of the cluster. Then, particles, which, because of the strong repulsive potential at close distances, would not satisfy the $C(\alpha)$ condition if the actual pair potential was used at such small separation, can satisfy the condition under the modified potential. Once we have identified the particles belonging to a same cluster, we can determine the center of mass of the n particles and construct a sphere centered on that center of mass and having a radius equal to the largest distance between the center of mass and the center of a cluster particle. All of the particles belonging to this cluster are then in a volume v , which is called an n/v cluster (Figure 1). In fact these n particles at their respective positions constitute a given configuration of the n/v cluster. The n/v cluster is thus defined as the assembly of all configurations that conserve the center of mass and satisfy the $C(\alpha)$ criterion. It is characterized by n particles in the volume v , one of the particles being located in the shell of the sphere. In this definition of the cluster, the shell molecule is counted as part of an n cluster, whereas in the definition used in the refs 13 and 14 it was part of an $(n - 1)$ cluster.

In the following, our theory will be confined to monoatomic fluids since it does not address the internal degrees of freedom of possible polyatomic molecules. Therefore the term "atom" will be used to describe the particles we have in mind. Nevertheless, the term "shell molecule", systematically used in the former papers by Reiss and co-workers, is retained although it has here the meaning of "shell atom".

Identifying a group of n atoms, all of them satisfying the $C(\alpha)$ criterion, leads to the definition of a volume v as explained above. However, while drawing the sphere of volume v , it may happen that one or several atoms will be included in it, although they do not satisfy the criterion. These atoms are assumed not to be part of the n/v cluster. This implies in particular that v does not correspond to the excluded volume but that to each configuration of an n/v cluster there belongs a given volume v' which actually excludes the atoms of the gas. However, if $|\alpha|$ is not too small compared to kT , most of the configurations of the clusters should be relatively compact and thus v' should usually be nearly equal to v . In all of the remaining analysis we will assume this approximation to be valid. The quantity v' (as well as the shape of v') that denotes the volume of a configuration of the cluster within the spherical volume v , if actually used in the theory, would constitute a much more detailed description of the cluster than that offered by the original n/v cluster. Stated in another way, the extent of the undesirable "inversion of the order of averaging", implicit in the n/v and many other cluster definitions, would be significantly reduced. However, the use of such a detailed definition would surely increase the complexity of the theory to an astronomical degree. In this connection, it should be observed that our

method of proceeding (below), beginning with the N -particle distribution function, is rigorously equal to the task of considering clusters in which all of the atoms in v satisfy $C(\alpha)$. This corresponds to averaging over all of the configurations corresponding to a set of v' in which the center of mass and shell molecule requirements defined a certain v , but in which there were no non- $C(\alpha)$ atoms in v . Once again, the inverted order of averaging, is increased but we profit from a concomitant increase in the simplicity of the theory. Also, as has been mentioned above, since the dynamic aspects of the nucleation rate theory (not addressed here) undoubtedly focus on compact clusters, the error involved in excluding non- $C(\alpha)$ atoms will again not be serious.

If one is interested in the original weaker energy requirement,^{13,14} the same derivation presented here can be used, but it will clearly be unnecessary to implement the derivation for that case, since it is a special case of the derivation that we now provide for the case of the stronger requirement. The theory of the nucleation rate remains one in which detailed balance is used so that the equilibrium distribution of clusters continues to occupy a position of central importance. Weaker values of α allow larger sets of clusters, but it is assumed that those involved in the dynamic process are subsets of these larger sets. The goal is to choose α strong enough so that the larger sets that include uninvolved clusters are eliminated. Clues concerning how to do this are available from the molecular dynamics simulation described above and some recent Monte Carlo work, but in this paper we do not elaborate this issue. Instead, we focus on deriving the equilibrium distribution of n/v clusters subject to the $C(\alpha)$ criterion and on the specification of the Monte Carlo procedure for evaluating its properties. We denote the equilibrium concentration of clusters containing n atoms and volumes in the range v to $v + dv$ by $C_n(v) dv$. The earlier methods^{13,14} have shown this distribution to be given by

$$C_n(v) dv = dv \exp[-\beta(\bar{A}_{n,v}^* - kT \ln(\gamma n^{3/2} V) + Pv - n\mu)] \quad (1)$$

with

$$\bar{A}_{n,v}^* = -kT \ln \left\{ \frac{\gamma^{n-1} n^{3/2}}{(n-1)!} \int_v \dots \int_v \exp[-\beta U_n(\mathbf{r}'_1, \dots, \mathbf{r}'_n)] \times \right. \\ \left. d\mathbf{r}'_1 \dots d\mathbf{r}'_{n-1} \right\} \quad (2)$$

In these equations k is the Boltzmann constant, T is the temperature ($\beta = 1/kT$), γ is the reciprocal of the cube of the thermal de Broglie wavelength for an atom, P is the pressure of the surrounding vapor contained in volume V , and μ is the chemical potential of an atom in the surrounding vapor. Furthermore, U_n is the potential energy of interaction of the n atoms, dependent on the coordinates of these atoms, coordinates that, represented in the cluster center of mass system, are $\mathbf{r}'_1 \dots \mathbf{r}'_n$, where the primes indicate center of mass coordinates. It is because the center of mass of the n atoms remains fixed that the integration is only performed over the positions of $n - 1$ particles. The $n^{3/2}$ before the integral sign in eq 2 is a factor in the Jacobian of the transformation from the laboratory to the center of mass system.¹⁷

2. Derivation of $C_n(v) dv$ Using the N -Particle Distribution Function

For an equilibrium system of N atoms in a volume V , the probability of finding an atom in $d\mathbf{r}_1$ at the position \mathbf{r}_1 , an atom in $d\mathbf{r}_2$ at \mathbf{r}_2 , ... an atom in $d\mathbf{r}_n$ at \mathbf{r}_n , regardless of the positions

of the remaining $N - n$ atoms, is given by

$$\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_1 \dots d\mathbf{r}_n = \frac{N!}{(N-n)!} \frac{d\mathbf{r}_1 \dots d\mathbf{r}_n \int_V d\mathbf{r}_{n+1} \dots \int_V d\mathbf{r}_N \exp[-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)]}{Z(N, V)} \quad (3)$$

where $Z(N, V)$ is the configuration integral of the system, *i.e.*, the numerator of eq 3 with the integration carried over all N atoms and $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the potential energy of the N atoms. Assuming pairwise additivity, $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{2} \sum_{i \neq j} u(r_{ij})$, where $u(r)$ is the molecular pair potential. Later, we will find it convenient to set $u(r)$ equal to the 12-6 Lennard-Jones pair potential [$u(r^*) = -u_0$ and $u(r_0) = 0$].

We now introduce the n/v cluster. We can write the probability of finding a given n particle configuration [as in eq 3], but with the additional condition $C(\alpha)$, as

$$R^{(n)}(\mathbf{r}_1 \dots \mathbf{r}_n; \alpha) d\mathbf{r}_1 \dots d\mathbf{r}_n = \frac{N!}{(N-n)!} \frac{d\mathbf{r}_1 \dots d\mathbf{r}_n}{Z(N, V)} \prod_{i=1}^n \Theta \left[\sum_{\substack{j=1 \\ j \neq i}}^n w(r_{ij}) - \alpha \right] \times \int_{V-v} d\mathbf{r}_{n+1} \dots \int_{V-v} d\mathbf{r}_N \prod_{k=n+1}^N \Theta \left[-\sum_{i=1}^n w(r_{ik}) + \alpha \right] \times \exp[-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{r}_{n+1}, \dots, \mathbf{r}_N)] \quad (4)$$

where Θ is the unit step function defined by

$$\begin{aligned} \Theta(x) &= 1 & \text{for } x \leq 0 \\ \Theta(x) &= 0 & \text{for } x > 0 \end{aligned}$$

and where the modified potential $w(r)$ is used. Note that, by limiting the integrals in eq 4 to $V - v$, we are assuming that no atoms beyond the n that satisfy $C(\alpha)$ are in v .

Transforming the coordinates of the n atoms to the center of mass system (now defined by primes), we can write the expression for the probability of having a given configuration of an n particle cluster with its center of mass in $d\mathbf{R}$ at \mathbf{R} (in the laboratory frame) and with the condition $C(\alpha)$ satisfied. This is

$$R^{(n)}(\mathbf{r}'_1 \dots \mathbf{r}'_{n-1}, \mathbf{R}; \alpha) d\mathbf{R} d\mathbf{r}'_1 \dots d\mathbf{r}'_{n-1} = \frac{N!}{(N-n)!} \frac{d\mathbf{R} d\mathbf{r}'_1 \dots d\mathbf{r}'_{n-1}}{Z(N, V)} n^3 \prod_{i=1}^n \Theta \left[\sum_{\substack{j=1 \\ j \neq i}}^n w(r_{ij}) - \alpha \right] \times \int_{V-v} d\mathbf{r}_{n+1} \dots \int_{V-v} d\mathbf{r}_N \prod_{k=n+1}^N \Theta \left[-\sum_{i=1}^n w(r_{ik}) + \alpha \right] \times \exp[-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{r}_{n+1}, \dots, \mathbf{r}_N)] \quad (5)$$

The probability of finding one n/v cluster, *i.e.*, such that one of the n atoms is in the volume $d\nu = 4\pi r^2 dr$ at a distance r from the center of mass, \mathbf{R} in $d\mathbf{R}$, while the remaining $n - 1$ atoms are in $v = 4\pi r^3/3$ and the n atoms satisfy the criterion $C(\alpha)$, is then

$$d\mathbf{R} \int_{d\nu} d\mathbf{r}'_1 \int_{d\nu} d\mathbf{r}'_2 \dots \int_{d\nu} d\mathbf{r}'_{n-1} R^{(n)}(\mathbf{r}'_1 \dots \mathbf{r}'_{n-1}, \mathbf{R}; \alpha) = \frac{N!}{(N-n)!} \frac{n^3}{Z(N, V)} \frac{d\mathbf{R}}{(n-1)!} \int_{d\nu} d\mathbf{r}'_1 \int_{d\nu} d\mathbf{r}'_2 \dots \int_{d\nu} d\mathbf{r}'_{n-1} \times \prod_{i=1}^n \Theta \left[\sum_{\substack{j=1 \\ j \neq i}}^n w(r_{ij}) - \alpha \right] \int_{V-v} d\mathbf{r}_{n+1} \dots \int_{V-v} d\mathbf{r}_N \times \prod_{k=n+1}^N \Theta \left[-\sum_{i=1}^n w(r_{ik}) + \alpha \right] \exp[-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{r}_{n+1}, \dots, \mathbf{r}_N)] \quad (6)$$

where we have used the fact that, because of symmetry, the integrals over v are independent of \mathbf{r}'_1 .

We note that (because the coordinates of the $N - n$ atoms are in the laboratory frame) this equation is only valid if \mathbf{R} is not within a distance of several r (the radius of the cluster) from the bounding walls of V , a condition which for all intents and purposes is satisfied in the thermodynamic limit such that $V \rightarrow \infty$.

Finally, the probability of finding at least one n/v cluster is obtained by integrating \mathbf{R} in eq 6 over the entire volume V of the system. In the integrand in eq 6 we have the factors

$$\prod_{i=1}^n \Theta \left[\sum_{\substack{j=1 \\ j \neq i}}^n w(r_{ij}) - \alpha \right] \prod_{k=n+1}^N \Theta \left[-\sum_{\substack{i=1 \\ i \neq k}}^n w(r_{ik}) + \alpha \right] \times \exp \left[-\frac{\beta}{2} \sum_{i=1}^n \sum_{\substack{j=1 \\ j \neq i}}^n u(r_{ij}) \right] \exp \left[-\beta \sum_{i=1}^n \sum_{j=n+1}^N u(r_{ij}) \right] \times \exp \left[-\frac{\beta}{2} \sum_{i=n+1}^N \sum_{\substack{j=n+1 \\ j \neq i}}^N u(r_{ij}) \right] \quad (7)$$

For a single atom of the gas which is not part of the cluster, it should be clear that its interaction energy with the cluster is larger (*i.e.*, less negative) than α . If this were not the case, this atom would be part of the cluster, which would then be an $(n + 1)/v'$ cluster. In fact, several atoms may surround the cluster, each of them with an interaction energy weaker than $|\alpha|$ by definition. Then, however, the sum of their interaction energies might be different from zero. We denote this energy by U_0 :

$$U_0 = \sum_{i=1}^n \sum_{j=n+1}^N u(r_{ij}) \quad (8a)$$

The energy U_0 varies from one configuration of the whole system to another. If α is chosen such that $|\alpha|$ is not too large (*e.g.*, of the order of $0.1 kT$), the term U_0 can be assumed to be small, and thus, in first approximation, $\exp(-\beta U_0) \approx 1$. For larger values of $|\alpha|$ one can also calculate an approximate value of U_0 : Assume that, for an n/v cluster, the n atoms are randomly distributed over the volume v of radius R_c . $u_1(r)$ denotes the interaction energy between this average cluster and an atom at a distance $r > R_c$ from the center of the cluster. One then has

$$U_0 \approx \rho \int_{r_m}^{\infty} 4\pi r^2 u_1(r) dr \quad (8b)$$

where $\rho = N/V = P/kT$ is the number density of the gas and r_m the distance from the center of the cluster defined by $u_1(r_m) = \alpha$. From this discussion it appears that there is a range of values of α for which all of the approximations made in this analysis are optimized. This range can only be derived from simulation and could even vary from one system to another. The discussion of this point is, however, beyond the scope of this paper.

This analysis shows that the volume excluded by the average cluster is larger than v , and thus, one should replace v by the volume $v_m = (4/3)\pi r_m^3$ in the term Pv . On the other hand, we have seen previously that for a given configuration of an n/v cluster the real excluded volume is not v but v' , which can be smaller than v . In fact, for each configuration v' should be replaced by a volume v'_m in which each atom interacts with the cluster with an energy smaller than α (stronger interaction). This volume must lie between v' and v_m and should therefore be close to v . This latter value of the excluded volume should thus be fairly correct due to compensating errors.

A closely related argument is to consider $U_0 = 0$. Crudely speaking, this assumption would correspond to increasing the excluded volume v to v'_m as far as the $N - n$ atoms outside of v are concerned, since these atoms must be kept further from v in order to reduce the interaction. Actually, since the Lennard-Jones has an asymptotic tail rather than a sharp cutoff, the only way to reduce the interaction to a true zero would be to keep the outside atoms infinitely far from v . In practice, of course they would only have to be kept at a finite distance in order to achieve a high degree of approximation to zero interaction. Thus, $\exp(-\beta U_0) \approx 1$ would be true, but in eqs 4–6 the limits $V - v$ in the integrals should then be replaced by $V - v'_m$ where $v'_m > v$. The value of v'_m , however (even if approximate), would have to be established by some physical reasoning.

In an initial approximation, one might set $v'_m - v = 0$ on the grounds that a large fraction of vapor phase nucleation phenomena and measurements involve supersaturated vapors that are, at the most, slightly imperfect gases in which the free energy of formation of the cluster (see below) will differ only by the quantity $P(v'_m - v)$, where P is the pressure of the vapor. Then, if $v'_m - v$ is of the order of the volume per atom in the nearly ideal gas (a not unreasonable assumption), $P(v'_m - v)$ will only be of the order of kT and will not constitute a large error.

Using the approximations described above, we obtain for the probability $p(n/v) dv$ of having at least one n/v cluster, with volume between v and $v + dv$, somewhere in V

$$p(n/v) dv = \frac{N!}{(N-n)!(n-1)!} \frac{n^3 V}{Z(N,V)} \exp(-\beta U_0) \int_{dv} d\mathbf{r}'_1 \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} \times \exp[-\beta U(\mathbf{r}'_1, \dots, \mathbf{r}'_{n-1})] \prod_{i=1}^n \Theta[\sum_{j=1, j \neq i}^n w(r_{ij}) - \alpha] \quad (9)$$

We denote the term $\exp[-\beta U(\mathbf{r}'_1, \dots, \mathbf{r}'_{n-1})] \prod_{i=1}^n \Theta[\sum_{j=1, j \neq i}^n w(r_{ij}) - \alpha]$ by $f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha)$. We then find

$$kT \ln[p(n/v) dv] = kT \ln \left[\frac{N!}{(N-n)!(n-1)!} \right] + kT \ln n^3 V + kT \ln [Z(N-n, V-v)] - kT \ln [Z(N, V)] + kT \ln \left[\frac{1}{(n-1)!} \int_{dv} d\mathbf{r}'_1 \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \right] - U_0 \quad (10)$$

Since the Helmholtz free energy of the system is given by

$$F(N, V) = -kT \ln \left[\frac{Z(N, V)}{N! \Lambda^{3N}} \right] \quad (11)$$

where Λ is the thermal de Broglie wavelength of a atom, we obtain

$$kT \ln[p(n/v) dv] = kT \ln \left[\frac{N!}{(N-n)!(n-1)!} \right] + kT \ln(n^3 V) - F(N-n, V-v) + kT \ln[(N-n)!] + kT \ln(\Lambda^{3(N-n)}) + F(N, V) - kT \ln(N!) - kT \ln(\Lambda^{3N}) + kT \times \ln \left[\frac{1}{(n-1)!} \int_{dv} d\mathbf{r}'_1 \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \right] - U_0 \quad (12)$$

Thus,

$$kT \ln[p(n/v) dv] = kT \ln(\Lambda^{-3} n^{3/2} V) + kT \ln \left[\frac{\Lambda^{-3(n-1)} n^{3/2}}{(n-1)!} \int_{dv} d\mathbf{r}'_1 \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} \times f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \right] + F(N, V) - F(N-n, V-v) - U_0 \quad (13)$$

The thermodynamic relation

$$F(N, V) - F(N-n, V-v) = \left(\frac{\partial F}{\partial N} \right)_{V,T} n + \left(\frac{\partial F}{\partial V} \right)_{N,T} v = -Pv + \mu n \quad (14)$$

where P represents the pressure of the system and μ , the chemical potential of the atoms in the gas, can be substituted into eq 13 to yield

$$p(n/v) dv = \Lambda^{-3} \exp \left\{ -\beta \left[-kT \ln(\Lambda^{-3} n^{3/2} V) + Pv - \mu n + U_0 - kT \ln \left(\frac{\Lambda^{-3(n-2)} n^{3/2}}{(n-1)!} \int_v d\mathbf{r}'_1 \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} \times f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \right) \right] \right\} \quad (15)$$

But

$$\ln \left(\frac{\Lambda^{-3(n-2)} n^{3/2}}{(n-1)!} \int_v d\mathbf{r}'_1 \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \right) = \ln(dv) + \ln \left(\frac{\Lambda^{-3(n-2)} n^{3/2}}{(n-1)!} \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \right) \quad (16)$$

where, as mentioned above, the integration in the last term in eq 16 is performed by keeping particle 1, the shell atom, at first fixed in the frame of the center of mass of the n atoms and then, after the remaining integrations have been performed, simply rotating the system (appealing to symmetry) to obtain $dv = 4\pi r^2 dr$. We finally obtain

$$p(n/v) dv = \frac{dv}{\Lambda^3} \exp \left\{ -\beta \left[-kT \ln(\Lambda^{-3} n^{3/2} V) + Pv - \mu n + U_0 - kT \ln \left(\frac{\Lambda^{-3(n-2)} n^{3/2}}{(n-1)!} \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \right) \right] \right\} \quad (17)$$

Substitution of eq 2 into eq 1 and recalling that $\gamma = \Lambda^{-3}$ as well as the above definition of $f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha)$ shows that $C_n(v) dv$ given by eq 1 and $p(n/v) dv$ in eq 17 are equal if U_0 is approximately zero. But, as indicated earlier, it was proved in ref 14 that $p(n/v) dv$ and $C_n(v) dv$ represent the same quantity, so that we have derived the equilibrium distribution of n/v clusters from the N -particle distribution function as we set out to do. The expression in the exponential of relation 17 represents the free energy of formation of an n/v cluster. The

first term of this expression represents the contribution of the movement of the center of mass of the cluster to the free energy. The second term represents the reversible work required to create, in the gas, with pressure P , a cavity of volume v . The third term represents the work required to extract n atoms from the gas. The last term corresponds to the free energy of the constrained assembly of n atoms in the volume v , one of the atoms being *fixed* at the shell of v , the center of mass of the n atoms remaining fixed at the center of the spherical container of volume v and all atoms satisfying the $C(\alpha)$ criterion.

3. Computational Procedure

We will now describe one possible method for evaluating $p(n/v) dv$. We closely follow the method used by Lee *et al.*² To this end, we have to compute the term in brackets in the exponential appearing in eq 17. We denote this term by $F'(n, v, T; \alpha)$:

$$F'(n, v, T; \alpha) = -kT \ln \left(\frac{\Lambda^{-3(n-2)} n^{3/2}}{(n-1)!} \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} \times \right. \\ \left. f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \right) \quad (18a)$$

and we also write

$$Z'(n, v; \alpha) = \int_v d\mathbf{r}'_2 \dots \int_v d\mathbf{r}'_{n-1} f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha) \quad (18b)$$

This last term represents a constrained configuration integral.

We start with a state of volume V_1 and temperature T_1 in which the system of n particles behaves as an ideal gas, the center of mass still remaining fixed and with a fixed shell molecule. Moreover, the fact that the system behaves as an ideal gas implies that all of the configurations have to be equiprobable and thus α must be zero; *i.e.*, $C(\alpha)$ has been removed. (Note that the use of the modified Lennard-Jones potential makes $\alpha = 0$ equivalent to $\alpha = \infty$.) We show in the Appendix that

$$\frac{n^{3/2}}{V_1^{n-2}} Z'(n, v; \alpha=0) = b(n) = \frac{2}{\pi} n^{3/2} 3^{n-2} \times \\ \int_0^\infty \left(\frac{\sin x - x \cos x}{x^3} \right)^{n-1} \frac{\sin x}{x} x^2 dx \quad (19)$$

for the constrained ideal gas, where $b(n)$ is a function of n only. $F'(n, V_1, T_1; \alpha=0)$ thus becomes

$$F'(n, V_1, T_1; \alpha=0) = -kT \ln \left[\frac{N_1^{-3(n-2)}}{(n-1)!} V_1^{n-2} b(n) \right] \quad (20)$$

This expression is almost identical to that found by Lee *et al.* except for the slight modifications introduced by the replacement of their function $a(n)$ by the function $b(n)$ and of their exponents $(n-1)$ by $(n-2)$. These modifications have their origin in the presence of the shell molecule. Λ_1 corresponds to the de Broglie wavelength at the temperature T_1 . Note in passing that the function $b(n)$ is related to the function $a(n)$ by the simple relation $b(n) = [(n-1)/n]a(n)$, $n \geq 2$, as can be demonstrated through integration by parts.

The temperature is then reduced from T_1 to the actual temperature T of the system while the volume is kept fixed at V_1 . The change in free energy ΔF_T associated with this transformation can be evaluated using the following thermodynamic relation:

$$\Delta \left(\frac{F'}{T} \right) = \int_{T_1}^T E d \left(\frac{1}{T'} \right) \quad (21)$$

with

$$E = \frac{\partial [F'(n, V_1, T'; \alpha=0)/T']}{\partial (1/T')} = \frac{3}{2} (n-2) kT' + \left\langle \sum_{i=1}^{n-1} \sum_{j=i+1}^n u(r_{ij}) \right\rangle \quad (22)$$

where $\langle \rangle$ represents the mean value in the canonical ensemble. The volume of the sphere is then reduced from V_1 to v , at constant temperature T . The corresponding change in free energy ΔF_v is given by

$$\Delta F_v = - \int_{V_1}^v p_c dv' \quad (23)$$

where p_c is a formal pressure of the cluster [$p_c = -(\partial F_v / \partial v)_{n, T}$]. Applying the scaling procedure of Born and Green¹⁸ to the system with fixed center of mass and a shell molecule, one finds

$$p_c = - \frac{\partial F'(n, v', T; \alpha=0)}{\partial v'} = (n-2) \frac{kT}{v'} - \\ \frac{1}{3v'} \left\langle \sum_{i=1}^{n-1} \sum_{j=i+1}^n r'_{ij} \frac{du(r'_{ij})}{dr'_{ij}} \right\rangle \quad (24)$$

A direct application of statistical mechanics would lead to

$$F' = -kT \ln \left(\sum_i \exp(-\beta U_i) \right) \quad (25)$$

where the summation runs in principle over all configurations of the system, each characterized by the potential energy U_i . In practice, however, the configurations contributing most to the sum in eq 25 occur rarely. Consequently, it is known that numerically eq 25 leads to a poor evaluation of the free energy. Therefore, the alternative method (eqs 21–24) called “thermodynamic integration” had been developed.²

Expressions 22 and 24 are computed on the basis of a large number ν_0 of configurations. Those retained in the evaluation of E and p_c satisfy the Metropolis criterion. According to this importance sampling, a given configuration may be taken into account several times, *i.e.*, has a high weight with respect to other configurations that are selected seldomly or even not at all. In any case, E and p_c are based on exactly ν_0 configurations. Furthermore, each of them is characterized by a given value of α , say α_i for the i th configuration, at fixed (n, v, T) , where α_i represents the interaction energy, calculated with the modified potential, of the most loosely bound atom of the cluster. If we are interested in the free energy of an n/v cluster, characterized in addition by the upper value α of the individual binding energies of its atoms, we write first the identity

$$-kT \ln \left[\sum_{i=1}^{\nu_0} \exp(-\beta U_i) H(\alpha - \alpha_i) \right] = \\ -kT \ln \left[\frac{\sum_{i=1}^{\nu_0} \exp(-\beta U_i) H(\alpha - \alpha_i)}{\sum_{i=1}^{\nu_0} \exp(-\beta U_i)} \right] - kT \ln \left[\sum_{i=1}^{\nu_0} \exp(-\beta U_i) \right] \quad (26)$$

where $H(x)$ is the usual Heaviside step function: $H(x \geq 0) = 1$, $H(x < 0) = 0$. ν_0 represents the total number of microscopic

configurations to which the system has access. Since $H(\alpha - \alpha_i) \equiv 1$ when $\alpha = 0$, the second term on the right hand side of eq 26 corresponds to the free energy $F'(n, \nu, T; \alpha=0)$. In practice, the Boltzmann weight disappears from the summations, since each of the ν_0 tried configurations is accepted or rejected by the Metropolis criterion following the value of this Boltzmann factor; hence, the free energy given by eq 26 reduces to

$$F'(n, \nu, T; \alpha) = F'(n, \nu, T; \alpha=0) - kT \ln[\nu(\alpha)/\nu_0] \quad (27)$$

where $\nu(\alpha) = \sum_{i=1}^{\nu_0} H(\alpha - \alpha_i)$. Since $\nu(\alpha) < \nu_0$, unless $\alpha = 0$, the second term on the right hand side of this equation is always negative. Hence, the free energy associated with $\alpha < 0$ is always larger than the free energy corresponding to all configurations. This corresponds simply to the fact that choosing $\alpha < 0$ is equivalent to a constraint imposed on the system.

Finally, we remark that the term containing $\nu(\alpha)/\nu_0$ reflects the frequency of the configurations with $\alpha_i \in [-\infty, \alpha]$. It may be assumed that certain values of α_i occur rarely: crudely, these are the very negative values of α_i at large volumes and the values of α_i near zero when the cluster is strongly compressed. These respective parts of the α spectrum, $\nu(\alpha)$, may then be poorly represented if compared to the α_i values occurring the most frequently. It is therefore important to take ν_0 large in order to enhance the estimation of the rare event frequencies. However, an error on these frequencies is much less severe than a misrepresentation of the potential energies in eq 25 since there the inaccuracy is exponentially magnified, whereas in eq 27 it is linear in the argument of the logarithm.

4. Conclusion

In this paper, we have refined the definition of an n/ν cluster as introduced earlier by Reiss and co-workers. We introduce, in particular, an energy criterion $C(\alpha)$ which allows us to assign each particle in the gas to a given cluster without any ambiguity. Starting from the n -particle distribution function in addition to our $C(\alpha)$ criterion, we establish the formula for the free energy corresponding to an n/ν cluster. This result had been obtained previously by another method. The derivation presented in this paper, however, has the advantage of clearly identifying and emphasizing the approximations introduced in obtaining the free energy. We also extend the Monte Carlo method of evaluation of the free energy, introduced by Lee *et al.* to our definition of the n/ν cluster. This paper thus constitutes a foundation for subsequent evaluations of the free energy of formation of clusters which directly enter the theory of homogeneous nucleation as outlined previously.¹⁹

Acknowledgment. The authors wish to thank the National Science Foundation and the Centre National de la Recherche Scientifique for their support.

Appendix

In this appendix we derive $Z'(n, \nu; \alpha=\infty)$ of eq 20 for an ideal gas composed of n molecules in a sphere of radius R with the constraint that the center of mass of the n molecules remains at the center of the sphere and one of the n particles is located at a fixed position in the shell of the sphere. We follow the procedure outlined by Lee *et al.*² We have to evaluate the integral

$$Z'(n, \nu; \alpha=\infty) = \int_{\nu} d\mathbf{r}'_2 \dots \int_{\nu} d\mathbf{r}'_{n-1} f(\mathbf{r}'_1, \dots, \mathbf{r}'_n; \alpha=\infty) \quad (A1)$$

where u in f is now set to zero and where the integration is

performed in the presence of a fixed particle (which we denote as particle 1) in $d\nu$, the volume of the shell, while the center of mass of the n particles is maintained at the center of the sphere. The $C(\alpha)$ criterion does not apply in this integration since α is infinitely large. In order to be able to integrate over all space, we introduce the step function

$$\begin{aligned} g(\mathbf{r}) &= 1 & \text{for } |\mathbf{r}| \leq R \\ g(\mathbf{r}) &= 0 & \text{for } |\mathbf{r}| > R \end{aligned} \quad (A2)$$

We can then write

$$Z'(n, \nu; \alpha=\infty) = \int d\mathbf{r}'_2 \dots \int d\mathbf{r}'_{n-1} g(\mathbf{r}'_2) \dots g(\mathbf{r}'_{n-1}) g(\mathbf{r}'_E) \quad (A3)$$

with $\mathbf{r}'_{\Sigma} = \mathbf{r}'_n = -\sum_{i=1}^{n-1} \mathbf{r}'_i$, and where the integration now extends over all space. We introduce the Fourier transform of $g(\mathbf{r})$, namely,

$$G(\mathbf{K}) = (2\pi)^{-3/2} \int g(\mathbf{r}) \exp(-i\mathbf{K} \cdot \mathbf{r}) d\mathbf{r} \quad (A4)$$

and the inverse transform

$$g(\mathbf{r}) = (2\pi)^{-3/2} \int G(\mathbf{K}) \exp(i\mathbf{K} \cdot \mathbf{r}) d\mathbf{K} \quad (A5)$$

Then

$$\begin{aligned} Z'(n, \nu; \alpha=\infty) &= \\ (2\pi)^{-(3/2)(n-1)} \int d\mathbf{r}'_2 \dots \int d\mathbf{r}'_{n-1} \int d\mathbf{K}_2 \dots \int d\mathbf{K}_{n-1} \int d\mathbf{K}_{\Sigma} \times \\ &G(\mathbf{K}_2) \dots G(\mathbf{K}_{n-1}) G(\mathbf{K}_{\Sigma}) \exp[i(\sum_{j=2}^{n-1} \mathbf{K}_j \cdot \mathbf{r}'_j + \mathbf{K}_{\Sigma} \cdot \mathbf{r}'_{\Sigma})] \end{aligned} \quad (A6)$$

But $\mathbf{r}'_{\Sigma} = -\sum_{i=1}^{n-1} \mathbf{r}'_i$ so that

$$\begin{aligned} Z'(n, \nu; \alpha=\infty) &= (2\pi)^{-(3/2)(n-1)} \int d\mathbf{K}_2 \dots \int d\mathbf{K}_{n-1} \int d\mathbf{K}_{\Sigma} \times \\ &\exp(-i\mathbf{K}_{\Sigma} \cdot \mathbf{r}'_1) \int d\mathbf{r}'_2 \exp[-i(\mathbf{K}_2 \cdot \mathbf{r}'_2 - \\ &\mathbf{K}_{\Sigma} \cdot \mathbf{r}'_2)] \dots \int d\mathbf{r}'_{n-1} \exp[-i(\mathbf{K}_{n-1} \cdot \mathbf{r}'_{n-1} - \\ &\mathbf{K}_{\Sigma} \cdot \mathbf{r}'_{n-1})] G(\mathbf{K}_2) \dots G(\mathbf{K}_{n-1}) G(\mathbf{K}_{\Sigma}) \end{aligned} \quad (A7)$$

But we know that

$$\int d\mathbf{r} \exp[i(\mathbf{K} \cdot \mathbf{r} - \mathbf{K}_{\Sigma} \cdot \mathbf{r})] = (2\pi)^3 \delta(\mathbf{K} - \mathbf{K}_{\Sigma}) \quad (A8)$$

where δ is the Dirac delta function. Thus, eq A7 becomes

$$\begin{aligned} Z'(n, \nu; \alpha=\infty) &= (2\pi)^{-(3/2)(n-1)} (2\pi)^{3(n-2)} \int d\mathbf{K}_2 \dots \times \\ &\int d\mathbf{K}_{n-1} \int d\mathbf{K}_{\Sigma} \exp(-i\mathbf{K}_{\Sigma} \cdot \mathbf{r}'_1) G(\mathbf{K}_2) \dots G(\mathbf{K}_{n-1}) G(\mathbf{K}_{\Sigma}) \times \\ &\delta(\mathbf{K}_2 - \mathbf{K}_{\Sigma}) \dots \delta(\mathbf{K}_{n-1} - \mathbf{K}_{\Sigma}) \end{aligned} \quad (A9)$$

This equation simplifies to

$$\begin{aligned} Z'(n, \nu; \alpha=\infty) &= (2\pi)^{(3/2)(n-2)} (2\pi)^{-3/2} \int_{\nu} d\mathbf{K}_{\Sigma} \times \\ &\exp(-i\mathbf{K}_{\Sigma} \cdot \mathbf{r}'_1) [G(\mathbf{K}_{\Sigma})]^{n-1} \end{aligned} \quad (A10)$$

The evaluation of $G(\mathbf{K})$ performed by Lee *et al.* remains valid, and we obtain

$$G(\mathbf{K}) = (2\pi)^{-3/2} (4\pi R^3) \frac{\sin(kR) - kR \cos(kR)}{(kR)^3} \quad (A11)$$

where $k = |\mathbf{K}|$. Equation A10 thus becomes

$$Z'(n, \nu; \alpha = \infty) = (2\pi)^{-3} (4\pi R^3)^{n-1} \frac{2\pi}{R^3} \int_0^\pi d\theta \sin \theta \int_0^\infty dx \times \exp(-ix \cos \theta) \left(\frac{\sin x - x \cos x}{x^3} \right)^{n-1} \quad (\text{A12})$$

This finally leads to

$$Z'(n, \nu; \alpha = \infty) = \frac{2}{\pi} (3^{n-2}) \left(\frac{4}{3} \pi R^3 \right)^{n-2} \int_0^\infty \left(\frac{\sin x - x \cos x}{x^3} \right)^{n-1} \frac{\sin x}{x} x^2 dx \quad (\text{A13})$$

References and Notes

- (1) Stillinger, F. R., Jr. *J. Chem. Phys.* **1963**, 38, 1486.
- (2) Lee, J. K.; Barker, J. A.; Abraham, F. F. *J. Chem. Phys.* **1973**, 58, 3166.
- (3) Reiss, H.; Tabazadeh, A.; Talbot, J. *J. Chem. Phys.* **1990**, 92, 1266.
- (4) Talanquer, V.; Oxtoby, D. W. *J. Chem. Phys.* **1994**, 100, 5190.
- (5) Israelachvili, J. *Intermolecular and Surface Forces*; Academic Press: San Diego, 1991; Chapter 17.
- (6) International Discussion Meeting of the Deutsche Bunsen-Gesellschaft, Göttingen, Sep 4–6, 1995, published in: *Ber. Bunsen-Ges. Phys. Chem.* **1996**, 100.
- (7) Safran, S. A. *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes*; Addison-Wesley Publishing Co.: Reading, MA, 1994; Chapter 8.
- (8) Dumont, R. S.; Jain, S.; Basile, A. G. *J. Chem. Phys.* **1995**, 102, 4227.
- (9) Swope, W. C.; Andersen, H. C. *Phys. Rev. B* **1990**, 41, 7042.
- (10) Oxtoby, D. W. *J. Phys. Condens. Matter* **1992**, 4, 7627.
- (11) Oxtoby, D. W.; Evans, R. *J. Chem. Phys.* **1988**, 89, 7521.
- (12) Zeng, X. C.; Oxtoby, D. W. *J. Chem. Phys.* **1991**, 94, 4472.
- (13) Ellerby, H. M.; Weakliem, C. L.; Reiss, H. *J. Chem. Phys.* **1991**, 95, 9209.
- (14) Ellerby, H. M.; Reiss, H. *J. Chem. Phys.* **1992**, 97, 5766.
- (15) Moss, R. To be published.
- (16) Hill, T. L. *Statistical Mechanics*; McGraw-Hill Book Co., Inc.: New York, 1956; Chapter 6.
- (17) Reiss, H. *Adv. Colloid Interface Sci.* **1977**, 7, 1.
- (18) Born, M.; Green, H. S. *Proc. R. Soc. A* **1947**, 191, 168.
- (19) Weakliem, C. L.; Reiss, H. *J. Chem. Phys.* **1994**, 101, 2398.