On the direct evaluation of the equilibrium distribution of clusters by simulation

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An expression is derived that relates the average population of a particular type of cluster in a metastable vapor phase of volume V_{tot} to the probability, estimated by simulation, of finding this cluster in a system of volume V taken inside V_{tot}, where $V \ll V_{tot}$. Correct treatment of the translational free energy of the cluster is crucial for this purpose. We show that the problem reduces to one of devising the proper boundary condition for the simulation. We then verify the result obtained previously for a low vapor density limit [J. Chem. Phys. **108**, 3416 (1998)]. The difficulty implicit in our recent calculation [J. Chem. Phys. **110**, 5249 (1999)], in which the approach in the former was generalized to higher vapor densities, is shown to be resolved by a method already suggested in that paper. © *1999 American Institute of Physics.* [S0021-9606(99)50944-6]

I. INTRODUCTION

Recently, we presented a new approach to cluster simulation suitable for studying vapor to liquid nucleation.[1,2] The approach is free of any ad hoc cluster criteria, which have often been introduced in such simulations. However, Reiss[3] and Reiss and Bowles[4] have subsequently raised a question about the particular way the translational free energy of a cluster is handled in our approach. This has motivated us to supplement the formulation in Refs. 1 and 2 to clarify the issue, since it is crucial for an accurate prediction of the equilibrium cluster size distribution by simulation.

The outline of the paper is as follows. In Sec. II A, we present a brief overview of our approach. In Sec. II B, we start from a somewhat different point of view from that of Reiss.[3] In particular, we show that the problem of the correct treatment of cluster translation reduces to one of devising the proper boundary conditions for a simulation. The results obtained previously[1,2] will be discussed and justified from this point of view in Sec. II C for the low vapor density limit and Sec. II D for higher densities. In Sec. III, we examine the one dimensional ideal gas dimer model introduced by Reiss and Bowles.[4] The result of this section also supports the validity of our method in Sec. II C. Section IV discusses issues regarding the choice of the system volume. The paper then concludes with a brief summary.

II. THEORY

Our basic idea in Refs. 1 and 2 was to explore the stochastic evolution of a system properly chosen in the metastable vapor phase by means of a grand canonical Monte Carlo simulation aided by the umbrella sampling technique.[5] The physical clusters, i.e., density fluctuations that occur during nucleation, emerge naturally as macrostates involved in a coarse-grained description of this stochastic process that is attained by introducing proper order parameters. Once the relevant clusters are identified, they can be analyzed further to acquire more detailed information on the process of nucleation. Our method is not limited to vapor phase nucleation and was recently applied to bubble formation,[6] for example.

A. Choice of the system

Since nucleation refers to the formation of a critical nucleus, which can be regarded as a certain fluctuation well localized in space, it is convenient to choose the system as a small volume V taken inside the entire vapor phase of volume V_{tot}. Under the condition where nucleation is a relevant mechanism for phase transition, it is possible to take the system volume V to satisfy the following two conditions.[7] (1) V is large enough that events occurring inside it can be regarded as statistically independent from the surroundings. (2) V is small enough that the probability of finding more than one uncorrelated density fluctuation important for nucleation in V at any instant is negligible.

The first condition permits one to describe the nucleation process in the entire vapor by focusing on a small part. The second condition implies that if a proper coarse-grained observation is made of the system throughout the entire process of nucleation, each macrostate that emerges from such an observation can be regarded as containing a single cluster, which is then characterized by the appropriate order parameters. In the case of vapor to liquid nucleation in a single component system, the number of molecules N and the interaction potential U_N of the system serve as proper order parameters.[1,2]

According to the second condition, fluctuations that occur within the range of correlation are regarded as a single fluctuation rather than several separate ones. Under the conditions where nucleation is a relevant mechanism for the phase transition, such a composite fluctuation is still sufficiently localized. It follows that one can still choose the system large enough compared to the physical dimension of this

fluctuation to satisfy the first condition without violating the second. That these two conditions can be satisfied simultaneously over a wide range of system volumes is an intrinsic property of the system and hence no arbitrariness is introduced by a particular choice of the system volume. On the other hand, such a choice of the system becomes progressively more difficult as the system approaches the spinodal or the critical region. In such cases, however, nucleation is no longer a relevant mechanism for the phase transition and the concept of cluster is unlikely to be useful.

B. Cluster size distribution

The approach outlined above allows us to evaluate directly by simulation the probability p_c of finding a cluster in V. Since one is frequently interested in evaluating the average number n_c of clusters in V_{tot}, it becomes necessary to relate p_c obtained from a simulation that focuses on V to n_c in the whole vapor of volume V_{tot}, where $V \ll V_{tot}$. If we divide V_{tot} into cells of equal volume V, the first condition of choosing V seems to suggest at first sight that n_c is given by the product of the number of the cells V_{tot}/V times the probability p_c of finding a cluster in the system of volume V,

$$n_c(N, U_N) = \frac{V_{tot}}{V} p_c(N, U_N). \tag{1}$$

Whether or not Eq. (1) is valid depends of course on the particular simulation method used to determine p_c. Strictly speaking, p_c in Eq. (1) should be referred to as the probability density, which could be made explicit by multiplying both sides of Eq. (1) by dU, the infinitesimal interval for the potential energy. In the following, we shall not concern ourselves with such details since they bear no consequences for the main issues we wish to address.

For the sake of clarity, we introduce the following notation. Let $p^\otimes$, $p^\odot$, and $p^\square$ denote the probabilities of finding the system V at (N, U_N) in a simulation carried out in a rigid container, by fixing a particular molecule at the center of the container, and under periodic boundary conditions, respectively. For example, Reiss[3] focused his attention on $p^\otimes$ and argued that Eq. (1) is incorrect if $p^\otimes$ is used for p_c. To rectify the error, he derived an expression for the correction factor by considering a continuous translation of the system container V in V_{tot} while avoiding redundant enumeration of configurations.[3] He then attempted to relate $p^\otimes$ to $p^\odot$ in order to analyze the approach in Ref. 1 which involves $p^\odot$.

We believe that Reiss's method[3] is impractical since the correction factor involves parameters that can be estimated, if at all, only approximately by simulation. The use of $p^\otimes$ is also inadvisable since the quantity as defined above reflects artificial surface effects arising from the interaction between the cluster and the container wall of V. In the following, we present an alternative approach to the problem. Instead of focusing on a particular simulation method and trying to estimate the correction factor appropriate for that method, our aim is to devise a simulation method for which Eq. (1) is valid.

First, we must understand what p_c in Eq. (1) represents. Note that a given cluster can migrate throughout the vapor phase. Because the physical dimension of the cluster is neg-

ligible compared to V_{tot} (V_{tot} can be made arbitrarily large), the surface effect arising from the interaction between the cluster and the container wall of V_{tot} can be ignored, and one concludes that the cluster can be found anywhere in V_{tot} with equal probability. Let us focus on one such cluster and mark one of its molecules. The probability density of finding this tagged molecule at a given position in V_{tot} is uniform throughout V_{tot} and is given by $1/V_{tot}$. Thus, the probability that an observer who focuses solely on the system of volume V finds this tagged molecule somewhere in V is V/V_{tot}. When there are exactly n_c such clusters, and hence n_c tagged molecules, the probability of finding exactly one such cluster is given by

$$p_c = n_c \frac{V}{V_{tot}} \left(1 - \frac{V}{V_{tot}} \right)^{n_c - 1}, \tag{2}$$

where we have assumed that clusters do not interact with each other. In this probability p_c, a situation where more than one tagged molecule is found in V is excluded, since according to our specification of macrostates, the system is then regarded as containing one large cluster rather than separate smaller ones. Taking the thermodynamic limit of $V/V_{tot} \to 0$ at a fixed value of n_c/V_{tot}, Eq. (2) becomes

$$p_c = n_c \frac{V}{V_{tot}} \exp \left(- \frac{V}{V_{tot}} n_c \right) = \frac{V}{V_{tot}} n_c, \tag{3}$$

where we made use of the fact that $n_c V/V_{tot} \ll 1$, i.e., cluster formation is rare, in a vapor phase in which nucleation is the relevant mechanism for phase transition.

In reality, the number n_c of the clusters in question fluctuates, which amounts to replacing n_c in Eq. (3) by its average. By allowing the cluster to assume all the microstates that are consistent with the prescribed values of the order parameters N and U_N at each fixed position of the tagged molecule, we obtain from Eq. (3),

$$p_c(N, U_N) = \frac{V}{V_{tot}} n_c(N, U_N), \tag{4}$$

where p_c and n_c in Eq. (4) now have the same meaning as the corresponding quantities in Eq. (1), indicating that both equations are equivalent. How N and U_N is calculated for a given density fluctuation becomes clear in what follows.

Thus, the p_c that satisfies Eq. (1) is the probability of finding a cluster that is characterized by (N, U_N) with its position, arbitrarily defined as that of the tagged molecule, being found anywhere in V with uniform probability. The problem of correctly handling the translational free energy of a cluster then reduces to one of devising a simulation technique that assigns such uniform probability to the cluster when its tagged molecule is confined to V. Once this is accomplished, p_c obtained from the simulation can be used in Eq. (1).

The derivation of Eq. (4) indicates that Eq. (1) holds whether or not we divide V_{tot} into cells of equal volume. In this tagged molecule picture, the division by V in Eq. (1) can be regarded as "deactivating" the translation of the cluster in V, while multiplication by V_{tot} amounts to releasing that cluster to V_{tot} so that it can be found anywhere in the vapor phase V_{tot} with uniform probability.

The removal of redundancy in Reiss's approach[3] corresponds to the deactivation of the translational degrees of freedom from $p^{\otimes}$. In his method that focuses on $p^{\otimes}$, however, this cannot be achieved by the simple division by V since the cluster is confined entirely in the rigid container and hence the probability of finding the tagged molecule is not uniform in V due to the artificial surface effects arising from the interaction between the container wall and the molecules inside. The surface effects also affect the properties of the cluster in a nontrivial manner, rendering an accurate prediction of p_c from $p^{\otimes}$ formidable, if not impossible. This inaccuracy of the method is in fact the basis of his criticism of our approach.[3] However, it should be clear that the difficulty arises entirely from the particular manner the translational free energy is handled in his approach. In the following, we show how this difficulty can be avoided by rather simple procedures.

C. Low density limit

When nucleation takes place at a very low vapor density, molecules form very compact clusters. Fluctuations with long wavelengths are then expected to be unimportant in nucleation and one can suppress such fluctuations in a simulation by choosing V sufficiently small that $n_v V \ll 1$, where n_v is the number density of molecules in the vapor. When a simulation is carried out in such a small volume, N and U_N correlate strongly and we can characterize the cluster by N alone.[1]

Under such circumstances, the vapor phase can be regarded as an ideal gas mixture of clusters of various sizes, and translation of the cluster is essentially a free translation. It is then most straightforward to evaluate $p^{\odot}$ first and relate it to p_c. In particular, p_c can be obtained from $p^{\odot}$ by analytically integrating with respect to the coordinates of the molecule thus fixed over V while purposefully ignoring the interaction between the system wall and the cluster, leading to

$$p_c(N) = \frac{1}{C} V p^{\odot}(N), \quad (5)$$

where C is the normalization constant for p_c. Note that configurations in which a part of the cluster lies outside the system (Fig. 1 in Ref. 3) are correctly taken into account upon this analytical integration. The normalization constant in Eq. (5) was obtained in Ref. 1 and the resulting expression for p_c is given by[1]

$$p_c(0) = \frac{p^{\odot}(1)}{p^{\odot}(1) + zV\sigma},$$

$$p_c(N) = \frac{zV p^{\odot}(N)}{p^{\odot}(1) + zV\sigma} \quad (N = 1, \ldots, N_{cut}), \quad (6)$$

where z is the fugacity of the vapor and reduces to n_v in an ideal gas. We note that z in the present paper corresponds to $z\Omega$ in Ref. 1, where Ω arises from the orientational coordinates of a molecule. We also defined

$$\sigma \equiv \sum_{N=1}^{N_{cut}} p^{\odot}(N). \quad (7)$$

The somewhat complicated expression in the denominator of Eq. (6) arises from the upper bound N_{cut} on the number of molecules allowed in the system, a condition necessary to confine the system to a metastable state, and also from the fact that $p^{\odot}$, by construction, is not defined at $N = 0$. The necessity of the term $p_c(N=0)$ becomes clear if we recall that the system contains no molecules for most of the time because of the condition $n_v V \ll 1$.

One can avoid surface effects arising from the interactions between the cluster and the system wall in evaluating $p^{\odot}$ by choosing the volume V large enough to accommodate the cluster. This was in fact the approach in Ref. 1. Thus, we have shown that the method of Ref. 1 becomes exact in the low density limit.

An alternative to fixing the position of a molecule is to fix the center of mass of the system. However, there is a one to one correspondence between the coordinate system $(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ and $(\mathbf{R}, \mathbf{r}_1 - \mathbf{R}, \ldots, \mathbf{r}_N - \mathbf{R})$, where $\mathbf{r}_i$ is the position of the ith molecule in the cluster and $\mathbf{R}$ is the center of mass of the cluster so that $\mathbf{r}_i$ satisfies $\Sigma_i(\mathbf{r}_i - \mathbf{R}) = 0$. Strictly speaking, one must also transform the limit of integrations along with the coordinate system. However, in the low density limit where clusters are compact, physical properties of a cluster are insensitive to the actual choice of the boundary condition and one can choose the system as a spherical region centered around the origin irrespective of the particular choice of the coordinate system. Thus, the choice of the coordinate system is entirely a matter of convenience in performing the configurational integral rather than a fundamental one. We found that simulation is considerably simpler to implement if a molecule is fixed, since the position of the center of mass changes discontinuously upon trial creation or annihilation of a molecule in a grand canonical Monte Carlo simulation.

Recently, Reiss[3] and Reiss and Bowles[4] claimed that the analytical integration performed in arriving at Eq. (6) introduces redundancy in evaluating the configurational integral. However, what they actually showed is that the analytical integration is invalid if $p^{\otimes}$ is used. Clearly, their criticism does not apply to our method which uses $p^{\odot}$.

Reiss and Bowles[4] further argued that one should not use $p^{\odot}$ with the tagged molecule at the center of the system. Their reasoning, however, is erroneous as we now discuss. They questioned the possibility of labeling the molecules and proposed to define the location of the cluster by the position of a spherical container large enough to encapsulate the cluster and centered around a molecule chosen arbitrarily in the cluster. Then, the translation of a cluster was identified as the translation of the container. To argue for "positional redundancy," they considered a translation in which the center of the container jumps from one molecule to the other with all of the molecules fixed in space. Clearly, this virtual translation of the container does not lead to a new configuration, and hence results in a redundant enumeration of configurations. According to Reiss and Bowles,[4] if all N molecules in the cluster remained in the lens-shaped region formed by the container before the translation and that after the translation, this redundancy is properly removed by the factor of $N!$ present in the classical partition function. However, they

claim that if some of the molecules are not contained in the lens-shaped region, the situation cannot be remedied by the $N!$ factor and that the so-called ''positional redundancy'' arises.

The redundancy Reiss and Bowles asserted, however, is an artifact of the virtual translation that should not be considered in the first place. In fact, there is nothing in our approach or in the classical partition function that would require or validate such a virtual translation. They argue for this procedure on the grounds that molecules cannot be labeled because identical particles are inherently indistinguishable and that the container is the only feature that allows one to locate the cluster.

Their criticism, however, is based entirely on a misconception regarding the notion of indistinguishability of identical particles. Thus, it is helpful to clarify the precise meaning of this notion as embodied in quantum mechanics and how it manifests itself in classical statistical mechanics.

First, we recall that in quantum mechanics, the notion of indistinguishability of identical particles is realized through a postulate that a state ket of the system be either symmetric or antisymmetric with respect to the exchange of any pair of the identical particles depending on the statistics these particles obey.[8] Second, when the quantum mechanical partition function is evaluated using the symmetrized or the antisymmetrized state kets and the classical limit is taken, one observes that the $N!$ factor is the only signature left behind by these state kets that implement the actual indistinguishability of identical particles.[9,10] As a result, the classical partition function involves explicitly the coordinates of labeled particles without any symmetrization of these coordinates. It follows that in evaluating this partition function, one can simply label the identical particles in an arbitrary fashion and then correct for any effect arising from their actual indistinguishability by the $N!$ factor.

Reiss and Bowles[4] assert that ''positional redundancy'' exists by considering the virtual translation of the container when the labels on the molecules are erased. The above argument clearly indicates, however, that it is neither necessary nor valid to consider such a procedure and that the correct procedure is to label the molecules and consider a translation that actually moves these labeled molecules.

Thus, it is completely acceptable to identify the position of the cluster as the position of a molecule chosen arbitrarily in this cluster, say molecule 1, as is done in our approach. Then, the translation of the cluster necessarily accompanies the change in the position of this molecule and there is no need to consider the virtual translation of the container; thus there is no ''positional redundancy.''

We reiterate here that in quantum mechanics, the notion of indistinguishability of identical particles is implemented by means of the symmetrization postulate, *not* by ''erasing the labels'' of the molecules and that, in the classical limit, the only consequence of this symmetry requirement imposed on the state kets is the appearance of the $N!$ factor. One cannot even write down the Hamiltonian or the partition function without labeling the particles first.

Reiss and Bowles[4] clearly indicated that our method is exact if the molecules can be labeled and that nothing is wrong with our method except for ''positional redundancy.'' We have shown here that identical molecules can indeed be labeled and that ''positional redundancy'' does not arise in our approach; hence their criticism does not apply.

Reiss[3] and Reiss and Bowles[4] further criticized the results obtained in this section, claiming that it is inapplicable for higher vapor densities and it becomes approximately correct only in the low density limit where the cluster is compact. It should be emphasized here that the method described in this section is intended for this compact cluster limit in the first place and the case of higher vapor densities is handled separately in Sec. II D. Clearly their criticism is misguided, and arises from a misinterpretation of the proposed method and its intended range of applicability.

D. Higher densities

If the density is higher, the condition $n_v V \ll 1$ cannot be satisfied by a volume V that is large enough compared to the physical dimension of the cluster. In addition, interaction between a cluster and the surrounding vapor cannot be ignored and the translation of the cluster is no longer a free translation, rendering the above described procedure inapplicable. Nonetheless, since the modes of fluctuation accessible to the cluster are determined by the relatively short range correlations between the cluster and its surroundings, physical properties of the cluster, including the way this cluster explores its translational degrees of freedom in the vapor phase, are correctly reproduced if V is large enough to include the surrounding vapor as well as the cluster, and if the surface effect is eliminated. A straightforward way to achieve this is to impose periodic boundary conditions. Thus,

$$p_c(N, U_N) = p^\square(N, U_N). \tag{8}$$

In fact, the tagged molecule can be found in V with uniform probability in this case.

In this method, the cluster explores its translational degrees of freedom without our conscious effort to activate it. Hence the criticism by Reiss and Bowles is again not relevant.

Just how large V must be to ensure Eq. (8) still remains to be seen. Despite such uncertainty, the use of $p^\square$ seems more appropriate than the alternative approach of approximating p_c by $p^\otimes$ evaluated in a sufficiently large volume V, since the surface effect in $p^\otimes$ decreases only as $V^{-1/3}$ when compared to the volume term. Again, configurations in which part of the cluster lies outside the system as suggested by Fig. 1 in Ref. 3 are correctly taken into account under periodic boundary conditions.

In the usual implementation of periodic boundary conditions, the interaction potential is truncated at some cutoff distance and the interaction beyond this distance is treated in a mean field fashion[11] by assuming that the density beyond the cutoff distance is the same as the overall density of the system rather than that of the surrounding vapor, which may lead to a small but artificial volume dependence of $p^\square$. However, if the system is large enough, the difference in the densities becomes negligible. Also, since the dominant intermolecular interaction comes from molecules within the cutoff, the error introduced by the above mentioned mean field approximation is expected to be small.

The use of periodic boundary conditions is ubiquitous in the literature. It was also already suggested in Ref. 2. Since our primary goal in Ref. 2 was to identify the appropriate order parameters in describing vapor to liquid nucleation, however, we adopted a less accurate method of confining the cluster in a rigid container of relatively small volume and evaluated $p^{\otimes}$. As mentioned earlier, it is unsatisfactory to use $p^{\otimes}$ for p_c in Eq. (1), especially when V is small. Our choice in Ref. 2 was dictated solely by the required computational effort, and there is no fundamental reason not to use periodic boundary conditions with a sufficiently large system volume.

It is worthwhile to investigate systematically the volume dependence of the predicted value of p_c. In the case of vapor to liquid nucleation of the truncated and shifted Lennard-Jones potential (obtained by truncating the potential at 2.5 times the Lennard-Jones diameter and shifting the potential upward so that it is zero at this cutoff), ten Wolde and Frenkel suggested that a system with 864 molecules is sufficient to eliminate the volume dependence.[12] The required size in the case of crystallization from a melt, however, is considerably larger.[13,14]

We reiterate here that a large enough V can be chosen without violating the second condition of choosing V as discussed earlier. In this respect, we recall that N and U_N remain the appropriate order parameters irrespective of the system size, as we demonstrated in Ref. 2. In particular, U_N continues to characterize the spatial extent of the cluster when a larger system volume is chosen.

III. ONE DIMENSIONAL IDEAL GAS

Reiss and Bowles[4] examined a one dimensional ideal gas dimer model and claimed that their results disprove the validity of the results described in Sec. II C. In this section, we point out an inconsistency in their analysis and confirm that our method does yield the correct expression for the partition function of the dimer, and hence the correct equilibrium cluster size distribution.

The model consists of a dimer of ideal gas molecules confined in a line of length L. From the outset, it must be remembered that the method described in Sec. II C is intended for a compact cluster and that it should not be applied to the cases where clusters are not compact. This excludes the case where molecules are truly noninteracting. Nonetheless, the model warrants a closer look since it clearly exposes the flaw in their argument while supporting our method.

To analyze our approach described in Sec. II C, Reiss and Bowles chose a cell of length $2h$ and confined the molecules to this cell. They obtained the partition function Q in two ways. In one method, they first considered the configurations of the two molecules with the center of mass fixed at the center of the cell, and then moved the center of mass within the line segment L. Parenthetically, we note that they also considered translation of the cell while fixing the location of the center of mass. They found that such translation should not be considered since the whole set of configurations produced in this manner is redundant. This is expected since the translation of the cluster is already accounted for by that of the center of mass. In the other method, they first

considered arbitrary configurations of the two molecules in the cell for a fixed location of this cell, and then considered the translation of this cell while avoiding the redundant enumeration of the configuration of the molecules. The resulting expression of Q is given in their Eq. (16), which reads

$$Q = \frac{2hL}{\Lambda^2}, \tag{9}$$

where Λ is the thermal wavelength. Equation (9) also follows from their Eqs. (17)–(19).

To make a comparison between their result and the prediction of our method, Reiss and Bowles then examined our method using a cell of length $2h$. However, this choice of cell introduces inconsistency in their comparison of the two methods. We postpone discussing the problem in their analysis and first proceed to obtain an expression for Q using our method with this choice of cell.

The method described in Sec. II C prescribes the following procedure for evaluating the partition function of the dimer. By allowing molecule 2 to be anywhere in the interval $[-h,h]$, while fixing molecule 1 at the origin taken at the center of the cell, we have the following contribution to the partition function

$$\frac{1}{2!\Lambda^2} \int_{x_1=0} dx_2 = \frac{h}{\Lambda^2}, \tag{10}$$

where x_i denotes the position of the ith molecule and the integration is taken under the condition that $x_1=0$. The next step is to analytically integrate Eq. (10) with respect to x_1, which results in

$$\frac{2h^2}{\Lambda^2}. \tag{11}$$

To calculate the partition function Q of the dimer when it is confined in the line of length L, we multiply Eq. (11) by $L/2h$, which can be regarded as the number of cells of length $2h$ spanning the whole L. Alternatively, the division by $2h$ deactivates the translation of the cluster when it is confined to the segment $[-h,h]$. Multiplication by L releases the cluster into the line of length L. In doing so, we ignored the surface effect since L can be taken to satisfy $h \ll L$. In any event, we finally obtain

$$Q = \frac{hL}{\Lambda^2}, \tag{12}$$

which differs from Eq. (9).

Based on the discrepancy between Eqs. (9) and (12), Reiss and Bowles claimed that our method, which yields Eq. (12) was in error. However, the cluster involved in their method, which leads to Eq. (9), and the one they considered to examine our method are different, although both methods employ the cell of length $2h$. In fact, they used a constraint $|x_1-x_2| \leq 2h$ for the former, while the constraint they used in the latter is $|x_1-x_2| \leq h$. It is an overlook of this difference that has led Reiss and Bowles to the erroneous assertion regarding the validity of our method. If they had used the constraint $|x_1-x_2| \leq h$ consistently throughout, they would have obtained the result identical to Eq. (12), since it amounts to replacing $2h$ in Eq. (9) by h.

To demonstrate the validity of Eq. (12), we note that the cluster involved in arriving at Eq. (12) can be regarded as two molecules constrained to be within distance h of each other and confined in a line of length L. The partition function for the dimer is given by

$$Q = \frac{1}{2!\Lambda^2} \int_0^L dx_1 \int_0^L dx_2 \Theta(h - |x_1 - x_2|), \qquad (13)$$

where Θ is the step function. Employing the center of mass system,

$$X = \tfrac{1}{2}(x_1 + x_2),$$
$$Y = x_2 - X = \tfrac{1}{2}(x_2 - x_1), \qquad (14)$$

for which the Jacobian is $\tfrac{1}{2}$, we get

$$Q = \frac{1}{2!\Lambda^2} 2 \int_0^L dX \int_{-h/2}^{h/2} dY = \frac{hL}{\Lambda^2}, \qquad (15)$$

which is identical to Eq. (12). Thus, we see that the method described in Sec. II C indeed yields the correct result for the partition function of the dimer.

Finally, we note that the resulting partition function Q depends on the cell length h. This reflects the fact that we have applied the method of Sec. II C outside its intended range of applicability, as we pointed out at the beginning of this section. In other words, h has dual purpose in the present model in that it specifies the maximum separation of the two molecules as well as the cell length. If there is an interaction potential that favors configurations with $|x_1 - x_2| \ll h$, then there will be no h dependence.

IV. CHOICE OF THE SYSTEM VOLUME

Reiss and Bowles[4] claimed that ''there is no way to escape the use of a model, short of a full and direct molecular dynamics simulation of the macroscopic nucleating system.'' It should be noted that this is nothing more than a semantic discussion of the word ''model.'' Nucleation is a dynamical process and trying to describe it using equilibrium clusters and transition rates among them might itself be considered as the use of a model. Even in a full and direct molecular dynamics simulation, one would still have to specify how the process of nucleation is detected. Otherwise, nothing can be said about the rate of nucleation from such simulations. Here again, one might argue that the reference to the detection method itself implies the use of a model. Such semantics regarding the word ''model,'' however, bears no relevance to our goal of understanding nucleation. As we have already indicated in earlier publications,[1,2,6] the point we have been emphasizing is that our method does not involve any ad hoc cluster criteria regarding the microscopic details of the cluster, such as the intermolecular distance.

Reiss also argued that the two conditions we imposed on V are very specific requirements and that choosing a particular system volume necessarily introduces an arbitrariness and cluster definition.[3] In what follows, we show that this is not the case. The point we make is that a wide range of choice exists for V so that the physical reality of a nucleation process predicted using a certain V is independent of the actual choice of V.

In the low density limit, we characterized a cluster by N alone. In this case, there is a small volume dependence in the predicted cluster size distribution, since fluctuations with longer wavelength become more easily accessible to the system as the system becomes larger. This aspect was indicated in Ref. 1 as the volume dependence of the ''focus of the coarse-grained description.'' In the low density limit, this volume dependence can be made completely negligible since one can always choose V so that $n_v V \ll 1$ without violating the two conditions on V indicated in Sec. II A.

For a vapor phase with a higher vapor density, the loss of focus, i.e., the volume dependence, becomes significant and one must use both N and U_N as order parameters to resolve various microstates into macrostates beyond those possible when N alone is used. Note that a longer wavelength fluctuation corresponds to a less negative value of U_N, while the fluctuation becomes spatially localized as U_N becomes more negative. See Fig. 1 in Ref. 2, for example. In other words, U_N characterizes the spatial extent of the cluster.

This role of U_N is expected. Note that the spatial extent of the cluster is reflected in the value of the entropy and that a system with specified values of the order parameters can be regarded as being in a constrained equilibrium. Despite the fact that nucleation is inherently a dynamical process, such equilibrium states are nonetheless relevant in describing the process.[2] Thus, entropy is a function of internal energy, V, and N in a single component fluid. For given values of V and N, the internal energy then determines the entropy, i.e., the spatial extent of the cluster. If the system can exchange energy rapidly with the heat bath (the carrier gas in the case of vapor to liquid nucleation), the kinetic part of the internal energy can be replaced by its average, leaving U_N as the only variable to be considered explicitly.[2]

Thus, quite independent of the vapor density, we can find a wide range of system volumes over which the predicted behavior of a cluster upon nucleation is insensitive to the particular choice of V, though the actual values of N and U_N we use to characterize the cluster may change, motivating an alternative set of order parameters

$$N_c \equiv N - n_v V, \quad U_c \equiv U_N - u_v V, \qquad (16)$$

where u_v is a constant denoting the average potential energy per unit volume in the vapor phase. Note that the ''size'' of the cluster N_c is in general not an integer or even necessarily positive in this convention.

It is possible that still more order parameters in addition to those conceived here are required to achieve insensitivity to the system volume V. However, we note that those additional order parameters must also satisfy the conditions described in Ref. 2 and that the basic notions of our approach remain valid.

The insensitivity of the predicted behavior of a cluster upon nucleation as indicated above has a direct physical interpretation. In our approach, the volume can be regarded as determining the field of vision of the ''microscope'' by which we look at the cluster, as our derivation of Eq. (4) indicates. This insensitivity then follows simply from the fact that the phenomenon of nucleation is, to a very high degree

of accuracy, independent of how we observe it. This being the case, various observers equipped with different microscopes would agree on what is happening in the system, and hence one can describe nucleation as an objective process independent of particular factors, such as the choice of the system volume.

We note that the type of insensitivity discussed here is at the very foundation of statistical physics. In general, it is the insensitivity of physical quantities to microscopic details of the observational situation that allows us to regard these quantities as objective rather than subjective.[15] Thus, the sole act of choosing a particular V does not by itself introduce any ad hoc cluster criteria or arbitrariness which affect the natural stochastic evolution of the system. Rather it is a necessary step in setting up the observational situation (the detection method) that allows us to study the process of nucleation. To quantify the results of this observation made in V, we have to introduce order parameters. In our method, this was done at a quite general level following the principles of statistical mechanics, leaving completely to the system itself to explore various macrostates and all the microstates consistent with a given specification of each such macrostate. We have also shown by investigating the molecular dynamics trajectories of the system that the order parameters N and U_N we employed are in fact suitable for addressing the dynamics of nucleation.[2]

Reiss and Bowles[4] criticized our approach, claiming that we have tried to disregard the container. That this is not the case should be obvious from the above discussion as well as our earlier publications.[1,2,6] Again, their criticism arises from their misinterpretation of our method. Choosing a proper system volume is a vital part of the process in setting up the observational situation. Despite this, our approach does not involve any arbitrariness. This is a direct consequence of the fact that nucleation proceeds through the formation of a spatially localized and intense density fluctuation and that it can, therefore, be described as an objective process by any observer who focuses on a region larger than the physical dimension of such fluctuations.

The above discussion suggests that the clusters involved in our method should best be regarded as constitutive elements of the observational situation to which the phenomenon of nucleation is subjected. Hence they are markedly different from the ones involved in the conventional approaches which tend to regard a cluster as a definite entity without any reference to how it is observed in a system undergoing nucleation. To emphasize this nontrivial aspect, we venture to assign the term ''observational cluster'' to the clusters identified in our method and discard the term ''tiling method'' put forward by Reiss,[3] which we think is inadequate as a faithful description of our method; in fact, Eq. (4) was derived without any reference to ''tiling.''

Finally, we note that when nucleation is no longer a relevant mechanism, our attempt to describe nucleation as an objective process would have to fail, i.e., one can no longer find a range of insensitivity for V. This is the case when the system approaches the spinodal or the critical region.

V. SUMMARY

In summary, we have shown that the problem of the correct treatment of the translational free energy of a cluster reduces to that of devising proper boundary conditions in a simulation. In particular, we have demonstrated that the expression for the equilibrium cluster size distribution in Ref. 1 becomes exact in the low density limit. The difficulty implicit in Ref. 2, which involves $p^{\otimes}$, is shown to be resolved by imposing periodic boundary conditions with sufficiently large V, as already suggested in that paper. We stress that the inaccuracy of the method as indicated by Reiss[3] arises entirely from the particular manner he handled the translational free energy and it is by no means inherent to our approach, which was designed to avoid precisely this type of difficulty.

We have also disproved the recent criticism by Reiss and Bowles[4] by pointing out mistakes in their reasoning. In particular, we have shown that ''positional redundancy'' does not arise in our construction of the equilibrium cluster size distribution. Their claim that our method described in Sec. II C is inapplicable except for the low density limit is shown to be irrelevant as a criticism of the method since it is devised to handle precisely this limit. We have demonstrated, in the case of the one dimensional ideal gas dimer model proposed by Reiss and Bowles,[4] that our method described in Sec. II C yields the correct partition function, thus supporting further the validity of our method.

Finally, we have shown that our approach involves no cluster criteria or any arbitrariness that may affect the natural evolution of the system.

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