

Isothermal-isobaric ensemble for small systems

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(Received 1 March 2001; published 26 June 2001)

The application of the isothermal-isobaric (N - P - T) ensemble to small systems is considered. In the small system limit, which is currently gaining in scientific and technological significance, a volume scale must be introduced in order to obtain a partition function that is dimensionless. The volume scale, however, must be carefully chosen since it depends upon the nature of the boundary separating the system from the surroundings. If the incorrect volume scale is used, the resulting N - P - T ensemble partition function will not rigorously describe the small system of interest. Although volume scales become inconsequential in the thermodynamic limit, care must be exercised in formulating the ensembles used to study small systems.

DOI: 10.1103/PhysRevE.64.016128

PACS number(s): 05.20.-y, 05.90.+m, 05.20.Jj

I. INTRODUCTION

The isothermal-isobaric (N - P - T) ensemble, when applied to small systems in which the volume is a continuous variable, has recently been placed on a rigorous foundation [1,2]. Some of the arguments used in the reformulation, however, are still contested. Since these disagreements were brought to the attention of the authors after Refs. [1,2] were published, we revisit several issues concerning the application of the isothermal-isobaric ensemble to small systems.

Choosing and properly formulating the statistical mechanical ensemble most appropriate for describing various small systems is particularly important in this era of nanotechnology. Small systems are strongly influenced by the surrounding medium that serves as a temperature, pressure, or chemical potential reservoir. Beyond the effects of temperature, pressure, etc., the surrounding bath also influences the small system via interfacial effects.

The choice of which ensemble to use, at least for small systems, is largely motivated by how the system is separated from its surroundings. In the thermodynamic limit, the choice of ensemble is a matter of convenience. For a small system, the chosen ensemble should conform to the situation in which the system is found. The system of interest may have a fixed volume or its volume may fluctuate against an externally imposed pressure. In the case of a small system that is appropriately described by the N - P - T ensemble, the system will be immersed in some reservoir that imposes a fixed external pressure (in addition to a fixed external temperature). How the surroundings “communicate” with the system, i.e., how the external pressure is imposed on the system, is of prime importance in determining the final form of the N - P - T ensemble partition function. The external pressure may be imposed via a physical boundary, or “wall,” that is present between the system and surroundings. The boundary sets the system volume and allows the system to fluctuate against the imposed pressure. In contrast, a physical constraining wall may not be present, as would be the case for the clusters that form during vapor phase nucleation. For this example, the boundary between the system and surroundings is a mathematical construct, or constraint (i.e., no additional degrees of freedom may be assigned to the boundary), that enables one to define the volume of the cluster. The

volume of the cluster is then allowed to fluctuate against the external pressure imposed by the surrounding vapor phase. As we discuss in the next section, the nature of the boundary influences the final form of the N - P - T ensemble partition function for a small system. Since surface effects are negligible for macroscopic systems, the properties of the boundary are of no concern in the thermodynamic limit.

Determining the precise form of the N - P - T ensemble for small systems is not simply of academic interest. In this era of nanophysics, the application of the N - P - T ensemble to small systems may be desirable in various theoretical and experimental situations. For example, an important consideration in several nanotechnological processes is the phenomena of nucleation. Recent work in the area of molecular theory of vapor phase nucleation [3–5] focused on determining the properties of the clusters that formed in a supercooled vapor. An appropriately defined physical cluster enabled the vapor partition function to be evaluated exhaustively and nonredundantly. Although these authors were not explicitly interested in the constant pressure ensemble, the isothermal-isobaric ensemble partition function—the summing of volume states (volume fluctuations of a liquid droplet) under an imposed external pressure (the surrounding vapor phase)—follows naturally from their approach.

Another possible application of the N - P - T ensemble to an important small system concerns the imposition of a fixed pair of forces acting at the chain ends of a single polymer chain of N monomers, i.e., the constant force ensemble. The constant force ensemble is the polymer counterpart of the constant pressure ensemble of N -particle systems. Ensemble averages, in particular stress-strain curves, of small polymer chains differ when the ends are held with a constant force or are maintained at a fixed end-to-end distance, i.e., the constant length ensemble (the N -particle counterpart is the constant volume ensemble). Consequently, the constant force and constant length ensembles lead to distinct elasticity laws [6]. Advances in experimental techniques now allow for a single chain to be maintained at a fixed length or held with a constant force so that single chain mechanical or thermodynamic properties can be probed [7]. The ability to compare experimental results with theoretical predictions necessitates that the constant force, or constant pressure ensemble, for small systems be placed on a rigorous foundation.

Ensuring the proper formulation of the isothermal-isobaric ensemble will also impact current molecular simulation algorithms. Since most experimental observations are performed under conditions of constant pressure and temperature, the N - P - T ensemble has been widely used in Monte Carlo and molecular dynamics simulations. As interest in small systems increases, current simulation methods should be modified to ensure that the properties of small systems are rigorously obtained. The required changes of the Monte Carlo method in the isothermal-isobaric ensemble will be the subject of a forthcoming publication.

II. THE ISOTHERMAL-ISOBARIC ENSEMBLE

In the late 1950s, and again in the 1990s, questions were raised concerning the degree of rigor underlying the formulation of the isothermal-isobaric ensemble [8–11,1,2]. The constant pressure ensemble was first introduced by Guggenheim [12] who derived, largely based on analogy, the following partition function

$$\Delta = \sum_V Q(N, V, T) \exp\{-PV/kT\}, \quad (1)$$

where $Q(N, V, T)$ is the canonical ensemble partition function for a system of N molecules confined to a volume V and having a temperature T . In Eq. (1), P is the constant external pressure to which the system is subjected and k is Boltzmann's constant. The characteristic thermodynamic potential for the N - P - T ensemble is the Gibbs free energy G in which

$$G = -kT \ln \Delta. \quad (2)$$

Although Eq. (1) is formally correct, Guggenheim never specified the set of values of V over which the sum was to proceed. In the thermodynamic limit, this omission is inconsequential since almost any reasonable set of volumes will do [13]. The lack of specification of the volumes over which the sum extends is one of the unsatisfactory features of the N - P - T ensemble. The success of the N - P - T ensemble, despite the failure to specify the set of volumes, is closely connected to the properties of all partition functions in the thermodynamic limit. As the system becomes macroscopic in size, Δ can be represented by its maximum term, so in essence one is dealing only with the canonical ensemble [1,13]. Therefore, the role of the sum in Eq. (1) is reduced primarily to facilitate certain mathematical manipulations needed in the derivation of thermodynamic properties.

Since the volumes of most systems are regarded as continuous variables, some authors have attempted to remove the conceptual difficulty associated with the sum over an unspecified set of discrete volumes by expressing Δ as

$$\Delta = \frac{1}{\Gamma} \int_V Q(N, V, T) \exp\{-PV/kT\} dV. \quad (3)$$

The replacement of the sum in Eq. (1) by an integral enables the inclusion of all volumes, but at the expense of generating a partition function that has the dimensions of volume. Consequently, this partition function must be rendered dimensionless through division by some constant ‘‘quantum’’ of volume [13] denoted by Γ in Eq. (3). Note that the original, and formally correct, partition function in Eq. (1) is dimensionless. Therefore, Eq. (3), which approximates Eq. (1) via the replacement of the summation by an integral, must also be dimensionless. Partition functions, which by definition are pure numbers (i.e., sums over states), are related to thermodynamic potentials via a logarithm and so should not have dimensions. The constant Γ , however, cancels out when determining the ensemble average of a given variable and so need not be specified. Even so, Sack [10] showed in the thermodynamic limit that

$$\Gamma = \frac{kT}{P}. \quad (4)$$

Although the volume scale Γ is unimportant for analytical theories in the thermodynamic limit, concerns have been raised about whether the above form of Γ is valid for systems considered *not* in the thermodynamic limit [11,1,2]. For small systems, arguments have been put forth suggesting that Γ depends upon the system volume and therefore must be taken inside the integral in Eq. (3). The form of the proposed volume scale reduces to Eq. (4) in the thermodynamic limit, but is a function of volume when the system is small. In this era of nanophysics, in which small systems are attracting greater attention, the choice of the proper form of Γ is of particular interest.

As we discuss in the next section, the final form of the volume scale Γ is dependent upon the nature of the boundary that separates the system from the surroundings. The boundary serves to define the volume of the system and allows the system to fluctuate against the external pressure imposed by the surroundings. The properties and effect of the boundary, however, must be determined precisely since they influence the exact form of the volume scale in Eq. (3). For example, if a mass can be assigned to the boundary, or if the boundary interacts with the system and surroundings, then these additional degrees of freedom must be taken into account. We demonstrate in the next section that if the boundary is a physical object (i.e., has a mass and momentum), the volume scale is a constant and may remain outside of the integral in Eq. (3). If, on the other hand, the boundary is merely a mathematical construct to aid in the specification of the system volume (i.e., a constraint whose net effect is that no additional degrees of freedom have been introduced), Γ becomes dependent upon the system volume and must be placed inside the integral in Eq. (3). In the thermodynamic limit, ensemble averages obtained in both cases are identical. When the system is small, however, ensemble averages will differ.

As noted earlier, the boundary separating the system from the surroundings cannot be chosen arbitrarily, especially when dealing with systems not in the thermodynamic limit, and must conform to the actual physical situation in which the system is found. Not assigning additional degrees of freedom to the boundary is certainly appropriate for several small systems of interest, an example being the work on cluster formation and the molecular theory of vapor phase nucleation [3–5]. What physical situations correspond to the

boundary being a physical object are not readily apparent. One example includes the circumstance in which the system volume is defined by the position of a movable wall or piston. Although cases like this may arise, whether they are appropriate to the various small systems of interest (e.g., clusters in a vapor, polymer chains in solution, nanoparticles) remains to be seen.

III. THE ISOTHERMAL-ISOBARIC ENSEMBLE FOR A SMALL SYSTEM

The isothermal-isobaric ensemble partition function appropriate for small systems is derived in this section. The following derivation is similar to the one presented in Ref. [2], which in turn is related to the derivation of the small system grand ensemble by Soto-Campos *et al.* [14]. Soto-Campos *et al.* obtained an expression for the probability that given a subvolume of size v there will be *exactly* n molecules inside. A very important consideration of their derivation is the surface interactions between molecules inside and outside of v . One of the key characteristics of this work is that the size of the subvolume v remains constant while the number of particles inside v fluctuates. In this paper, we are interested in describing an ensemble in which an external pressure is imposed on the system. Since the system volume is now allowed to fluctuate, we need to determine the probability that a fixed number of particles n will be enclosed by a volume v (in the given derivation, the identity of the n particles is allowed to vary). In the following analysis, our attention is restricted to volumes of spherical shape. The results are the same for other volumes of fixed symmetrical shape (e.g., cube) but more complicated shapes need to be considered separately.

Let us begin with a macroscopic system of volume V containing N particles maintained at a temperature T . The system is in the thermodynamic limit such that, $N \rightarrow \infty$, $V \rightarrow \infty$ and $N/V = \text{const}$. Without loss of generality, assume the N particles are monatomic (an extension to systems with molecular orientation is straightforward). The canonical ensemble partition function Q for this system is given by

$$Q(N, V, T) = \frac{1}{N! \Lambda^{DN}} \int_V e^{-\beta U_N} d\tau_1 \cdots d\tau_N, \quad (5)$$

where Λ is the de Broglie wavelength, D is the system dimensionality, $\beta = 1/kT$, and $d\tau_i$ denotes the volume element for particle i . U_N is the total potential energy of the N particles. The limits on the integral indicate that the particles are to be integrated over the entire volume V .

Next, for a given configuration of the N particles in Eq. (5), consider a subsystem of n particles. The remaining $N - n$ particles will constitute the surrounding bath since $N \gg n$. In general, and without the requirement of pairwise additivity, one can separate U_N into three terms,

$$U_N = U_n + U_{N-n} + U_\sigma. \quad (6)$$

U_n is the mutual collective potential energy of the n particles (system), U_{N-n} is the collective potential energy of the $N - n$

particles (bath) and U_σ is the potential energy corresponding to the interaction between the n and $N - n$. In addition, the total volume V can be divided into two terms: the volume v occupied by the n particles and the volume $V - v$ enclosing the $N - n$ particles of the bath.

Since the volume occupied by the n particles is allowed to vary continuously, we need to specify the volume lying between v and $v + dv$ occupied by the n particles such that the remaining $N - n$ particles are outside of this volume. One can define a partition function, $Q_N^{n,v} dv$, that accounts for all the configurations of the N particles in which $N - n$ are outside of $v + dv$ and n are in $v + dv$. (In anticipation of later results, we let $Q_N^{n,v} dv$ represent a pure number, indicating that $Q_N^{n,v}$ is a density of states.) Thus, the probability, $P_n(v) dv$, that the n particles occupy a given volume between v and $v + dv$ is given by

$$P_n(v) dv = \frac{Q_N^{n,v} dv}{Q(N, V, T)}. \quad (7)$$

Since $P_n(v) dv$ must be normalized to unity, we find that

$$\int Q_N^{n,v} dv = Q(N, V, T). \quad (8)$$

Clearly $Q_N^{n,v} dv$ must be evaluated in such a way that the repeated counting of configurations is avoided when $Q_N^{n,v} dv$ is integrated over all values of the volume v .

In the above analysis the boundary separating the n particles from the bath is simply a mathematical construct (the boundary is not a physical object to which a mass or momentum can be assigned) to aid in the specification of the system volume v . Local fluctuations already occur spontaneously within the macroscopic system, and no local boundary is explicitly present within the system (except of course for the boundary that encloses the entire macroscopic system). In order to calculate the thermodynamic properties of the subsystem, however, we must introduce an effective potential that is zero for the configurations that we wish to allow and infinite otherwise. The net result, though, is that no external potential energy is introduced into the system. When we consider local volume fluctuations of a subsystem, we need to introduce a boundary that identifies the volume states of the subsystem. The boundary, or effective potential, prevents the surroundings from entering the volume v and the n particles from leaving the volume v . Since the boundary has no mass or momentum and was not present to begin with when the macroscopic system was formed, its effects must not appear in the final result.

At this point, a problem arises concerning the unique specification of the *exact* volume of the n particles [1,2]. To illustrate this problem, turn to Fig. 1 that demonstrates how two volumes of the same size (always chosen to be spherical) may enclose the same configuration of n particles and be surrounded by the same configuration of $N - n$ particles. As noted for Eqs. (7) and (8), each configuration of N particles must correspond to only *one specific volume state* of the n particles. Otherwise, the same configuration of N particles will be counted more than once in Eq. (8).

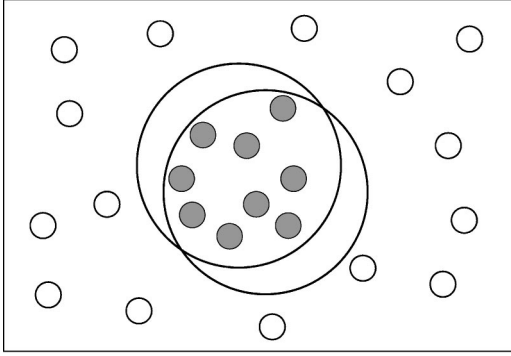


FIG. 1. One particular configuration of N particles enclosed within a total volume V demonstrating how two subvolumes (bold circles) of equal size may surround the same n particles (shaded circles) while keeping the positions of the all N particles fixed. The unshaded circles represent the surrounding $N-n$ particles that comprise the bath. Each particle center is surrounded by an effective diameter. (Adapted from Fig. 1 of Ref. [2].)

To uniquely determine the volume occupied by the n particles, one must first choose a particular point in V as the origin of the system (to avoid edge effects, this origin should be sufficiently far from the walls of the macroscopic container). Given a reference point, however, there are still several volumes centered at the origin that enclose the same configuration of n particles and are surrounded by the same configuration of $N-n$ particles (see Fig. 2). The volumes shown in Fig. 2 cannot be counted as distinct volume states of the n -particle system. Otherwise, configurations of the N -particle system will be counted redundantly in Eq. (8).

The problem of overcounting, or redundancy, is resolved by defining the volume v via a “shell” particle [1,2] (see Fig. 2), in which at least one of the n particles resides in the shell dv that encapsulates the system volume v . A new and distinct state of the N -particle system is necessarily created when the volume of the n -particle system is varied (whether or not the configuration of the surrounding $N-n$ particles changes), since the position of the shell particle changes as well. Consequently, the inclusion of configurations of the n particles common to larger values of v is explicitly avoided

in Eq. (8). Eliminating the redundant counting of configurations also leads to the specification of the volume scale Γ (as we discuss later, the shell particle is the volume scale).

The volume of the system is now uniquely defined via the shell particle. In other words, the boundary separating the system from the surroundings is now attached to the degrees of freedom of the system. The boundary becomes in effect part of the system, but only because it is *indistinguishable* from the shell particle. Since the boundary was introduced as a mathematical construct needed to specify the various volume states of the system, no additional degrees of freedom beyond those already present should be assigned to the boundary.

One may suggest, however, that an effective interaction is still introduced, unintentionally, between the boundary and the system (and surroundings). Since the n particles must remain inside the system volume and the surroundings must remain outside, an interaction arises between the boundary and the system (and also the surroundings). In effect, we have introduced additional degrees of freedom beyond those already present in the system and surroundings (and so the boundary becomes equivalent to another particle). Consequently, movement of the boundary, irrespective of changes of the positions of the n particles and the surroundings, generates a new and distinct configuration of the macroscopic system. The dotted spheres in Fig. 2 therefore correspond to distinguishable volume states and cannot be considered redundant configurations.

Nevertheless, all the boundary does is to select those configurations in which n molecules are confined to v . The same nonuniform distribution, n in v and $N-n$ in $V-v$, would still be observed in the N particle system in one of its fluctuated configurations. Thus, no degrees of freedom should be attributed to the boundary. As stated previously, the boundary is simply an effective potential that is either zero, for the configurations that we wish to allow, or infinite. The net result, though, is that no external potential energy is introduced into the system, and so the effects of the boundary must not appear in the final result.

Having found an unambiguous means of specifying the volume of the n -particle system, we define $Q_N^{n,v} dv$ as [2]

$$\begin{aligned} Q_N^{n,v} dv &= \frac{N!}{(n-1)!(N-n)!} \frac{1}{N! \Lambda^{DN}} \int_{dv} d\tau_1 \int_{v+dv} e^{-\beta(U_n + U_\sigma)} d\tau_2 \cdots d\tau_n \int_{V-(v+dv)} e^{-\beta U_{N-n}} d\tau_{n+1} \cdots d\tau_N \\ &= \frac{N!}{(n-1)!(N-n)!} \frac{dv}{N! \Lambda^{DN}} \int_{v+dv} e^{-\beta(U_n + U_\sigma)} d\tau_{12} \cdots d\tau_{1n} \int_{V-(v+dv)} e^{-\beta U_{N-n}} d\tau_{1(n+1)} \cdots d\tau_{1N}, \end{aligned} \quad (9)$$

where particle 1 is the shell particle whose position is to be integrated throughout dv and $d\tau_{12} \cdots d\tau_{1N}$ are the coordinates of the remaining $N-1$ particles relative to the position of particle 1 (a process during which particle 1 is considered to be at a fixed position in the spherical shell). Due to the

symmetrical shape of $v+dv$, particle 1 can be integrated separately throughout the shell, indicated by the inclusion of dv in the second expression of Eq. (9). The binomial coefficient accounts for the number of indistinguishable ways of arranging the N particles into $n-1$, $N-n$ and the shell par-

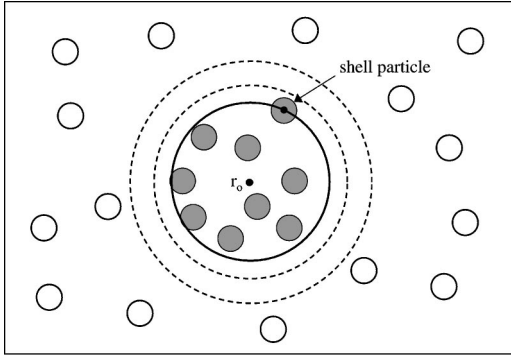


FIG. 2. One particular configuration of N particles enclosed within a total volume V demonstrating how to uniquely define *one specific volume state* of n particles (shaded circles). The unshaded circles represent the surrounding $N-n$ particles that comprise the bath. Each particle center is surrounded by an effective diameter. The first step in determining the volume occupied by the n particles is to choose a particular reference point in V as the origin, r_0 . Yet, several volumes (dashed circles) centered at r_0 still enclose the n particles and therefore include common configurations. The *exact* volume v (bold circle) of the n particles is defined by the presence of a *shell particle* (dark shaded particle) that is farthest from r_0 and resides in the shell dv encapsulating v . (Adapted from Fig. 1 of Ref. [2].)

ticle (due to its fixed location in the shell, the shell particle is now distinguishable from the remaining $n-1$ particles). The second $N!$ in the denominator accounts for the indistinguishability of all the N particles. The interactions U_σ between the n and $N-n$ particles have been included as part of the total potential energy of the n interior particles.

For notational convenience, we define a partition function $Q_{n,v}^* dv$ as

$$Q_{n,v}^* dv = \frac{dv}{(n-1)! \Lambda^{Dn}} \int_{v+dv} e^{-\beta(U_n + U_\sigma)} (d\tau)^{n-1}, \quad (10)$$

where $(d\tau)^{n-1} = d\tau_{12} \cdots d\tau_{1n}$. Equation (10) is simply the partition function of the n particles in $v+dv$ such that at least one particle is in the shell dv . In this expression the configuration of the $N-n$ particles outside of $v+dv$ is kept fixed, i.e., the exterior particles are maintained in a *frozen configuration*. The n particles are integrated throughout $v+dv$, still subject to U_σ , but the values of U_σ are limited by the fixed configuration of the $N-n$ particles in $V-(v+dv)$.

Substituting Eq. (10) into Eq. (9) yields

$$Q_N^{n,v} dv = \frac{dv}{(N-n)! \Lambda^{D(N-n)}} \int_{V-(v+dv)} Q_{n,v}^* e^{-\beta U_{N-n}} (d\tau)^{N-n}, \quad (11)$$

where $(d\tau)^{N-n} = d\tau_{1(n+1)} \cdots d\tau_{1N}$. The above expression can be rewritten as [2]

$$Q_N^{n,v} dv = Q(N-n, V-v, T) \langle Q_{n,v}^* \rangle_o dv, \quad (12)$$

where $v+dv$ has been replaced by v , $Q(N-n, V-v, T)$ is the partition function of $N-n$ particles in a volume $V-v$ and

$$\langle Q_{n,v}^* \rangle_o = \frac{\int_{V-v} Q_{n,v}^* e^{-\beta U_{N-n}} (d\tau)^{N-n}}{\int_{V-v} e^{-\beta U_{N-n}} (d\tau)^{N-n}}, \quad (13)$$

in which $\langle \cdots \rangle_o$ denotes ensemble averaging over the configurations of the $N-n$ particles in $V-v$. This allows $Q(N, V, T)$ to be rewritten as

$$Q(N, V, T) = \int_0^V Q(N-n, V-v, T) \langle Q_{n,v}^* \rangle_o dv. \quad (14)$$

The importance of the shell particle is demonstrated in the Appendix where the above integral is evaluated for an ideal gas.

Now, $P_n(v) dv$ can be rewritten as

$$P_n(v) dv = \frac{Q(N-n, V-v, T) \langle Q_{n,v}^* \rangle_o dv}{Q(N, V, T)}. \quad (15)$$

One can show that [15,2]

$$\frac{Q(N-n, V-v, T)}{Q(N, V, T)} = e^{\beta n \mu} e^{-\beta W(v)}, \quad (16)$$

where μ is the chemical potential of the surroundings and $W(v)$ is the work required to form an empty cavity of size v within the bath. Thus,

$$P_n(v) dv = e^{\beta n \mu} e^{-\beta W(v)} \langle Q_{n,v}^* \rangle_o dv. \quad (17)$$

Utilizing the normalization condition of the probability density, and noting that $\exp(\beta n \mu)$ is independent of v , we define the small system isothermal-isobaric ensemble partition function Δ as

$$\Delta = \int \langle Q_{n,v}^* \rangle_o e^{-\beta W(v)} dv, \quad (18)$$

in which $\Delta = \exp(-\beta n \mu)$. The above partition function is dimensionless, since $\langle Q_{n,v}^* \rangle_o dv$ is a pure number, and does not need to be divided by some volume scale. If the system approaches macroscopic size, in which $W(v) = Pv$ and interactions between the system and surroundings become negligible, then the isothermal-isobaric partition function reduces to

$$\Delta = \int Q_{n,v}^* e^{-\beta Pv} dv. \quad (19)$$

The importance of the shell particle in the above result is also discussed for an ideal gas in the Appendix.

A volume scale is implicit in Eqs. (18) and (19), having been absorbed inside the integral via the use of the shell particle, i.e., the shell particle *is* the volume scale. What has emerged is a volume scale that depends on v with a depen-

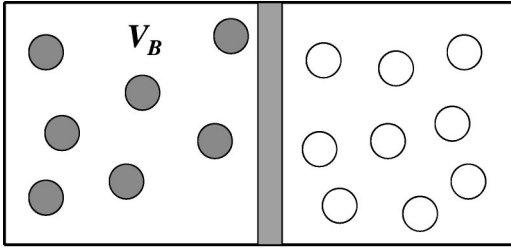


FIG. 3. One particular configuration of n particles (shaded circles) contained within a volume v_B . The volume v_B is bounded by fixed sides and also by a movable (and shaded) boundary of finite thickness. The unshaded circles represent the surrounding $N - n$ particles that comprise the bath. All of the N particles are enclosed within a total volume V .

dence that vanishes in the thermodynamic limit [1] (one can show that Sack's value of Γ , given by Eq. (4), is recovered in the thermodynamic limit [16]). Since the volume scale (or shell particle) serves to eliminate possible states of the system, the determination of Γ follows naturally from the consideration of redundancy, and not from the requirement that a partition function must be dimensionless (although this requirement must ultimately be satisfied as well). Only after considering the elimination of redundant volume states is the need for a shell particle, or volume scale, introduced. Consequently, the partition function, which is given by an integral over volumes specified by the shell particle, is now dimensionless. For a more detailed discussion of the above arguments, we refer the reader to the cited references [1,2].

We conclude this section by moving to a somewhat different system (but one that is still immersed in a bath that supplies an external pressure P). We now consider a situation in which the boundary of v is a physical object that can be assigned a mass and, if desirable, an internal molecular structure. The boundary is now distinguishable from the n particles and the surroundings and may be allowed to interact with the n molecules in v via a potential that does more than simply limit these molecules to v . This case is illustrated in Fig. 3 in which the system volume is no longer spherical.

Now that the boundary acts as a real wall separating the system from its surroundings, the degrees of freedom of the boundary must be taken into account. The canonical ensemble partition function of the n -particle system may be expressed as $Q_{n,B,v} dv_B$ where B indicates the boundary and dv_B is the volume element within which the center of mass of the boundary is located. The boundary is now treated as a particle, different from the remaining n particles. The boundary will give rise to a momentum partition function (where Λ_B is the de Broglie wavelength of the boundary) that can be extracted from $Q_{n,B,v}$ so that we can write

$$Q_{n,B,v} dv_B = Q'_{n,B,v} \frac{dv_B}{\Lambda_B^3}, \quad (20)$$

where $Q'_{n,B,v}$ is that part of $Q_{n,B,v}$ that remains when the momentum partition function of the boundary is extracted from $Q_{n,B,v}$. One of the n particles is no longer required to be a shell particle since the boundary, which has its own

degrees of freedom, uniquely defines the system volume. (Note that the boundary, being equivalent to another particle, becomes in effect the shell particle.) In this case, redundancy is not a problem. When the boundary has a different location, the physical state of the system must be different.

If the system is sufficiently large so that interactions between the surroundings, the system and the boundary can be ignored, the isothermal-isobaric partition function reduces to

$$\Delta = \frac{1}{\Lambda_B^3} \int_{v_B} Q'_{n,B,v} e^{-\beta P v} dv_B. \quad (21)$$

Although redundancy is no longer an issue, we note that a volume scale still appears in Eq. (21); the volume scale is now seen to be the cube of the de Broglie wavelength of the boundary. Since the volume scale is a constant, it can be taken outside of the integral, and therefore will not affect the calculation of ensemble averages. In general, the properties of the boundary that enter into $Q'_{n,B,v}$ will affect the ensemble averages (if the system is not in thermodynamic limit), so that the boundary cannot be chosen arbitrarily and must conform to the actual physical situation in which the system is found.

IV. CONCLUSION

The form of the volume scale that appears in the isothermal-isobaric ensemble partition function for small systems is dependent upon the properties of the boundary that separates the system from the surroundings. When no degrees of freedom may be assigned to the boundary, the volume scale becomes equivalent to the shell particle (and must therefore remain inside the integral over the appropriate volume states of the system). When the boundary is a physical object with a given mass or momentum, the volume scale is a constant, independent of the system volume. The exact specification of the volume scale is inconsequential in the thermodynamic limit, where the volume scale has an entirely negligible effect on the thermodynamic properties of macroscopic systems computed with the aid of the N - P - T ensemble. We emphasize that in the present era in which nano-sized systems are of practical importance, volume scales cannot be ignored, and appropriate N - P - T ensembles must be developed with a care that includes the actual nature of the system and its surroundings.

In closing this paper, we note that there is an interesting parallel between the current formulation of the N - P - T ensemble partition function for small systems and the so-called ‘‘replacement free energy’’ controversy that lasted for almost 30 years in connection with the phenomenological classical theory of nucleation [17,18,4]. The ‘‘replacement free energy’’ controversy deals with the correct treatment of the separation of the internal and translational degrees of freedom of the clusters that participate in nucleation. In the current paper, the introduction of the shell particle followed directly from the elimination of redundant configurations as the volume of the system is varied continuously. Likewise, the replacement free energy factor follows directly from the elimination of redundant configurations of the cluster upon

translation of its bounding surface [4]. A recent controversy over the ‘‘mapping’’ of localized fluctuations onto a macro-system [19–22], related to the development of theories of nucleation, also shares a similar solution. Given the probability of appearance of a fluctuation in a small cell, how is that result to be ‘‘mapped’’ onto the macrosystem in order to specify the equilibrium number of such fluctuations in that system? The answer again involves the removal of redundant configurations to ensure that the mapping is rigorously performed [22].

ACKNOWLEDGMENTS

The author is grateful to Dr. G. Medvedev and Professor H. Reiss for useful discussions and acknowledges the Shreve Trust of the Purdue Research Foundation for support of this work.

APPENDIX: THE IDEAL GAS

For the ideal gas, $U_\sigma=0$, so that

$$\langle Q_{n,v}^* \rangle_o = Q_{n,v}^* = \frac{v^{n-1}}{(n-1)! \Lambda^{Dn}}, \quad (\text{A1})$$

and

$$Q(N-n, V-v, T) = \frac{(V-v)^{N-n}}{(N-n)! \Lambda^{D(N-n)}}. \quad (\text{A2})$$

Substituting the above expressions into Eq. (14), we find that [23]

$$\begin{aligned} Q(N, V, T) &= \int_0^V \frac{(V-v)^{N-n}}{(N-n)! \Lambda^{D(N-n)}} \frac{v^{n-1}}{(n-1)! \Lambda^{Dn}} dv \\ &= \frac{V^N}{N! \Lambda^{DN}}, \end{aligned} \quad (\text{A3})$$

which is equal to the canonical ensemble partition function of the ideal gas.

If the system volume were not defined via the shell particle, so that all of the n particles were allowed to sample the entire volume v , then the n -particle partition function, now denoted by $Q_{n,v}$, would be given by

$$Q_{n,v} = \frac{v^n}{n! \Lambda^{Dn}}. \quad (\text{A4})$$

The above expression, when substituted into Eq. (14), yields [23]

$$\begin{aligned} Q(N, V, T) &= \int_0^V \frac{(V-v)^{N-n}}{(N-n)! \Lambda^{D(N-n)}} \frac{v^n}{n! \Lambda^{Dn}} dv \\ &= \frac{V^{N+1}}{(N+1)! \Lambda^{DN}}, \end{aligned} \quad (\text{A5})$$

which, in addition to having units of volume, is not the correct result for the ideal gas.

The importance of the shell particle can also be seen if the N - P - T ensemble partition function is evaluated for the ideal gas. Since $U_\sigma=0$ and $W(v)=Pv$ for the ideal gas, Δ is given by Eq. (19) in which

$$\Delta = \int_0^V Q_{n,v}^* e^{-\beta P v} dv = \int_0^\infty \frac{v^{n-1}}{(n-1)! \Lambda^{Dn}} e^{-\beta P v} dv = \left(\frac{\Lambda^D}{\beta P} \right)^n. \quad (\text{A6})$$

Since the volume V is of macroscopic size, we have let $V \rightarrow \infty$ in the upper bound of the integral. Noting that [13]

$$\langle v \rangle = -kT \left(\frac{\partial \ln \Delta}{\partial P} \right)_{\beta, n}, \quad (\text{A7})$$

where $\langle v \rangle$ is the ensemble average of the system volume, we find using Eq. (A6) that

$$P \langle v \rangle = nkT. \quad (\text{A8})$$

If the shell particle were not used to define the system volume, the N - P - T partition function would instead be equal to

$$\Delta = \int_0^V Q_{n,v} e^{-\beta P v} dv = \int_0^\infty \frac{v^n}{n! \Lambda^{Dn}} e^{-\beta P v} dv = \frac{\Lambda^{Dn}}{(\beta P)^{n+1}}. \quad (\text{A9})$$

The equation of state that follows from this partition function is

$$P \langle v \rangle = (n+1)kT. \quad (\text{A10})$$

The use of $(n+1)$ or n is clearly inconsequential in the thermodynamic limit. Yet, the difference between Eqs. (A8) and (A10) is significant when the system is sufficiently small.

In general, the ensemble averages calculated within different ensembles will not be the same for small systems. In contrast, ensemble averages are independent of the particular ensemble chosen to evaluate them when the system is in the thermodynamic limit. One exception, however, is the ideal gas. Due to the absence of interparticle interactions, identical results should be obtained within all ensembles and for all system sizes. Hence, the small system N - P - T partition function of the ideal gas should yield Eq. (A8), and not Eq. (A10), as the correct equation of state for any value of n [compare Eq. (A8) to the equation of state obtained using the canonical ensemble which predicts that $\langle P \rangle v = nkT$].

- [1] G.J.M. Koper and H. Reiss, *J. Phys. Chem.* **100**, 422 (1996).
- [2] D.S. Corti and G. Soto-Campos, *J. Chem. Phys.* **108**, 7959 (1998).
- [3] P. Schaaf, B. Senger, and H. Reiss, *J. Phys. Chem. B* **101**, 8740 (1997).
- [4] H. Reiss, W.K. Kegel, and J.L. Katz, *J. Phys. Chem. A* **102**, 8548 (1998).
- [5] B. Senger, P. Schaaf, D.S. Corti, R. Bowles, J.-C. Voegel, and H. Reiss, *J. Chem. Phys.* **110**, 6421 (1999).
- [6] J.T. Titantah, C. Pierleoni, and J.-P. Ryckaert, *Phys. Rev. E* **60**, 7010 (1999).
- [7] S.B. Smith, L. Finzi, and C. Bustamante, *Science* **258**, 1122 (1992).
- [8] W.B. Brown, *Mol. Phys.* **1**, 68 (1959).
- [9] A. Munster, *Mol. Phys.* **2**, 1 (1959).
- [10] R.A. Sack, *Mol. Phys.* **2**, 8 (1959).
- [11] P. Attard, *J. Chem. Phys.* **103**, 9884 (1995).
- [12] E.A. Guggenheim, *J. Chem. Phys.* **7**, 103 (1939).
- [13] T.L. Hill, *Statistical Mechanics* (Dover, New York, 1987).
- [14] G. Soto-Campos, D.S. Corti, and H. Reiss, *J. Chem. Phys.* **108**, 2563 (1998).
- [15] H. Reiss and G.A. Merry, *J. Phys. Chem.* **85**, 3313 (1981).
- [16] D.S. Corti (unpublished).
- [17] J. Lothe and G.M.J. Pound, in *Nucleation*, edited by A.C. Zettlemoyer (Marcel Dekker, New York, 1969).
- [18] H. Reiss, J.L. Katz, and E.R. Cohen, *J. Chem. Phys.* **48**, 5553 (1968).
- [19] H. Reiss, *J. Mol. Struct.* **485-486**, 465 (1999).
- [20] R.K. Bowles, *J. Chem. Phys.* **112**, 1122 (2000).
- [21] H. Reiss and R.K. Bowles, *J. Chem. Phys.* **112**, 1390 (2000).
- [22] H. Reiss and R.K. Bowles, *J. Chem. Phys.* **113**, 8615 (2000).
- [23] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series, and Products* (Academic Press, New York, 1980).