

Understanding the Limitations of the Virial in the Simulation of Nanosystems: A Puzzle That Stimulated the Search for Understanding[†]

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This paper is yet another study dealing with subtle variations that may be necessary in both methods of simulation and analytical computation of statistical thermodynamic phenomena in nanosystems, especially fluid nanosystems. In the present paper, we deal with the use of the virial in the simulation of the pressure of a nanosystem. Not surprisingly, we find that the use of the virial in this endeavor requires a careful definition of the boundary of the system that includes the potential specifying the interaction of the molecules with that boundary. Without these precautions, when the system is small enough (nanovolumes and less than 100 molecules), the conventional means of using the virial in a Monte Carlo simulation does not yield the experimental thermodynamic pressure, i.e., the pressure measured on the outside of the boundary. The institution of these precautions is generally a nontrivial task. However, there is one case in which the difficulty is minimal. This is the theoretically important case in which the molecules interact with the boundary or “wall” of a container enclosing the system as hard molecules interacting with a hard wall. In the present paper, this problem is studied in depth. However, here it can be mentioned that in this case the problem arises because the virial refers to the volume available to the center of masses of the molecules which differs from the “thermodynamic” volume that encloses the molecules. The error generated by this difference is entirely negligible for a macroscopic system but can be extremely large for a nanosystem. On the basis of this understanding we are able to resolve a puzzle associated with an earlier study of a model (not relying on an intermolecular potential) devised for the calculation of the thermodynamic behavior of a small number of molecules enclosed in a small container.

1. Simulation of Statistical Thermodynamics in Nanosystems

The current focus on nanoscience and nanotechnology has placed a heavy burden on computation and simulation, since many of the small systems of interest are not subject to direct measurement. At the same time, the more standard methods of simulation, appropriate to systems in the thermodynamic limit, can become inappropriate in subtle ways at the nanolevel. In solids, and at the quantal level in electron theory or lattice dynamics, the situation is usually better understood. A quantum dot,¹ for example, exhibits electronic energy levels that are in some ways reminiscent of “particles in a box”, and these levels collapse into a series of continuum bands if the dot is made large enough. If the dot is made smaller, it behaves more like a large molecule and its electrons can occupy states that have a molecular orbital-like character. The origin of surface states in such a system is also understood, at least in a qualitative sense. As a result, most of the disagreements that arise in connection with the physics of solid nanosystems are usually associated with the details of approximation and not with the fundamental rigor of that approach.

Unfortunately, the situation is not so straightforward with fluid nanosystems, examples of which may be clusters involved in nucleation, very thin films, flexible polymers, or fluids confined to nanopores in a process of capillary condensation. Usually, these systems behave classically and the proper application of

classical statistical thermodynamics, at the fundamental level, may be at issue. Consequently, there has been considerable disagreement over the need, with nanosystems, to modify those approaches that have been successful at the macroscopic level. Examples of this have involved (i) the proper formulation of the isobaric–isothermal ensemble² or the Gibbs ensemble³ when they are applied to nanosystems, (ii) the correct method for simulating the configuration integral of a nanocluster confined to a nanocontainer,⁴ (iii) the proper means for incorporating fluctuations into a simulation of a nanosystem,⁵ and (iv) the preservation of the role of fluctuations in the computational application of density functional theory (DFT) to nanosystems.⁶ Most of these problems arise with systems that are indeed very small, involving nanovolumes and very few (e.g., less than 100) molecules, and only *begin* to make an appearance at these very small sizes. Therefore, it is not surprising that many workers have opted to use computational and simulative methods that have succeeded in larger systems, and have been resistant to the idea that there is a need to modify these methods as we move downward in the nanoworld. Most of the controversy seems to be associated with this point of view and has been intensified because of the somewhat subtle nature of the issues involved.

Recently, partly by accident, we discovered still another problem. The discovery was made during a study of what has been called the “extended modified liquid drop model (EMLD)” introduced in a recent paper.⁵ The EMLD grew out of the “modified liquid drop model” (MLD),⁷ and is best described

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by addressing the MLD first. However, the reader should bear in mind that neither the EMLD or the MLD is the focus of this paper. Instead, the focus is the limitations implicit in the use of the virial theorem in the simulation of the pressure of a nanosystem. Our discussion, below, of the models (EMLD and MLD) is primarily a means of highlighting and demonstrating the virial problem by using a real example, although we do take the opportunity to show how the new understanding of its application has stimulated us to solve a vexing puzzle that was left unsolved in ref 5 even though the difficulty was not a misapplication of the virial theorem. Since that puzzle involved a large spherical molecule (drop) and smaller molecules enclosed in a container with hard walls, our explanation of the virial problem is couched in the language of hard molecules and walls. However, the problem is general and persists in the case of soft or deformable molecules where the appropriate interaction potential between a molecule and the wall of the containing volume must be taken into account. We do not treat such molecules since the models in our example ignore any “soft” potential interaction with the walls.

Before proceeding to the main part of this paper, it should be remarked that the problem of walls and potentials has not gone entirely unnoticed in the past. Rowlinson⁸ and McQuarrie and Rowlinson⁹ have discussed this issue in the somewhat different context of virial expansions in inhomogeneous systems and have opted to sidestep the wall question by working in the grand ensemble where their principal interest was in the chemical potential and pressure of the fluids absorbed in the pores of matrices such as zeolites. Furthermore, Oppenheim and Mazur¹⁰ have obtained the finite size corrections to the virial expansion and derived generalized density expansions of distribution functions applicable to systems of any size. However, problems such as those discussed below were not specifically addressed.

The relevance of our work lies in two features. One feature involves the provision of a correct means of simulating the pressure in a nanosystem. A second feature is the possible breadth of application of the EMLD model. If this model can be shown to be applicable to a large variety of substances, even those for which no reliable intermolecular potential exists, it may be possible to evolve theories of nucleation or capillary condensation even in the absence of a reliable intermolecular potential.

Among the “real” systems where the problem discussed in this paper might be relevant, the best examples involve nanoporous materials. The sizes of the pores in these systems can be in the nanometer range and phenomena such as capillary condensation have been intensively analyzed in recent years.

Before proceeding to the next section, it is useful to indicate that the virial problem is not an artifact of any model or even of the “puzzle” to which we have alluded above. It is obvious in the basis of the virial theorem itself and could have been discerned had this paper or our previous paper, never been written.

2. The MLD

Figure 1 visualizes the MLD, and will be helpful in its description. The system illustrated in Figure consists of a spherical container of volume V , containing N molecules at temperature T . The walls are assumed to be impermeable and hard. Under appropriate conditions, a liquid drop can form inside the container. The drop itself is assumed to contain n molecules, the maximum of n being $N - 1$, and it is surrounded by an ideal gas, constituted by the remaining $s = N - n$ molecules,

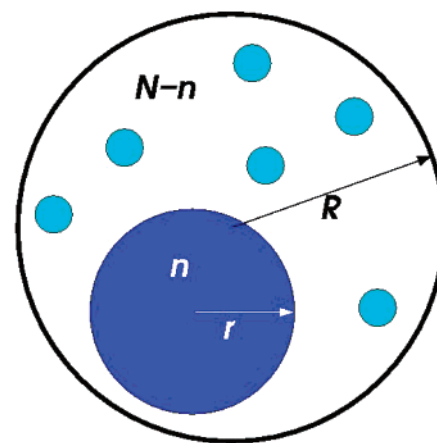


Figure 1. Schematic representation of the MLD model.

in equilibrium with the drop. The drop is modeled according to the “capillarity approximation” such that it is incompressible, possesses a sharp interface with the vapor, and a surface tension equal to that of the bulk planar interface. Furthermore, its density is uniform and equal to the bulk density of the liquid involved. The pressure of the gas is therefore assumed to be specified by the Kelvin relation¹¹

$$p_1 \cong p_1^{\text{eq}} e^{2\sigma v_l / rkT} \quad (1)$$

in which p_1 is the vapor pressure of the drop, p_1^{eq} is the vapor pressure of the bulk liquid, σ is the surface tension of the bulk liquid, v_l is volume per molecule in the bulk liquid, r is the radius of the drop, k is the Boltzmann constant, and T is the temperature. In this connection, it should be noted that, for a given N and T , a stable drop can be held within the container only for values of V smaller than a certain critical value.^{5,7,12} Above this value, only gas is stable within the container.^{5,7,12} The transition from drop to gas is essentially first order, although it must be realized that a true first-order transition cannot occur in a nanosystem ... only the signature of such a transition, incipient in the form of a sharp but continuous change of state, could occur.

Now, since the gas is in equilibrium with the drop, its pressure is also p_1 and, since it is assumed to be ideal, this pressure must be specified by

$$p_1 = \frac{(N - n)kT}{V - nv_l} \quad (2)$$

The radius of the drop is given by $r = (3nv_l/4\pi)^{1/3}$, while the radius of the container is $R = (3V/4\pi)^{1/3}$. For given V and T , eqs 1 and 2 can be solved simultaneously for n and p_1 . Thus, the pressure–volume isotherm of the system can be obtained. There are in fact two solutions of eqs 1 and 2, one stable and the other unstable, and the stable isotherm can be identified.^{5,7}

If the drop is not allowed to translate through V , the pressure on the walls of the container will be p_1 . However, if translation is possible, the drop can collide with the walls, thus contributing to the total pressure in the container. It is assumed, in the MLD, that the drop behaves as a single ideal gas molecule and therefore exerts an additional pressure given by

$$p_{\text{drop}} = \frac{kT}{\frac{4\pi}{3}(R - r)^3} \Theta(n) \quad (3)$$

where $\Theta(n)$ is the unit step function, and accounts for the fact

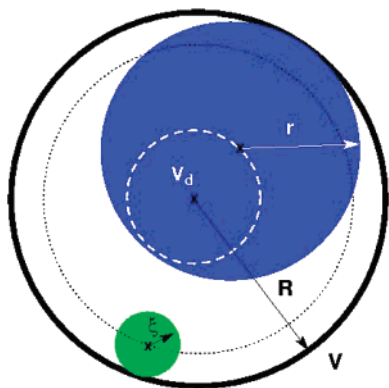


Figure 2. Spherical drop of radius r and a molecule of radius ξ inside a spherical container of radius R and volume V . V_d is the volume available for the center of the drop.

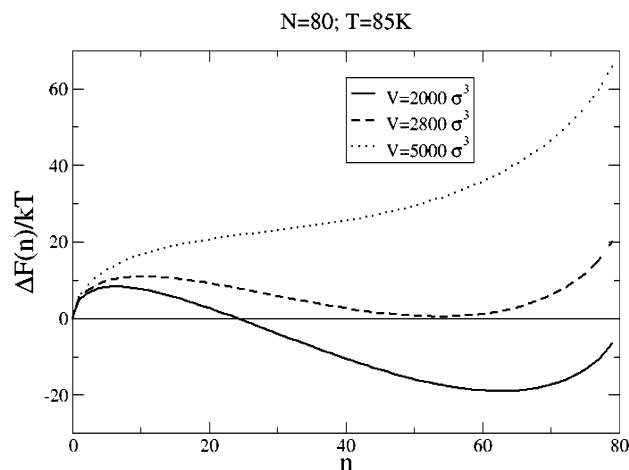


Figure 3. Free energy as a function of the size of the drop in the MLD model for $N = 80$ molecules of argon at $T = 85$ K, and three different values of the volume V of the container.

that this translational addition to the total pressure has to be considered only when the drop or cluster is present in the system. Note that $4\pi(R - r)^3/3 = V_d$ is the volume through which the center of the drop can translate (see Figure 2). It is different from V the volume of the container.

In the MLD, the total pressure is defined to be

$$P(T, V) = p_1(T, V) + p_{\text{drop}}(T, V) \quad (4)$$

Furthermore, neglecting $p_{\text{drop}}(T, V)$, the Helmholtz free energy of the system can be easily computed yielding⁵

$$\Delta F(n) \equiv F(n) - F(0) = -nkT \ln \frac{p_1}{p_1^{\text{eq}}} + \sigma A_{\text{drop}} + n(kT - v_1 p_1^{\text{eq}}) + NkT \ln \frac{p_1}{p_0} \quad (5)$$

in which A_{drop} is the surface area of the drop, and $p_0 = NkT/V$ is the pressure of the system in the pure vapor phase. $\Delta F(n)$ is actually $W(n)$, the reversible work of formation, starting from the pure gas phase, of a (nontranslating) drop of size n . Figure 3, taken from ref 5, shows plots of $\Delta F(n)/kT$ vs n for argon at $T = 85$ K and $N = 80$. The plots correspond to three different values of V . The salient features of these plots are the extrema (maximum and minimum) or the absence of extrema at a large enough value of V . The minimum corresponds to the stable drop of size n_{st} specified by the Kelvin relation, and the absence of extrema indicates that a stable drop cannot be retained within a container having the associated volume. These features and

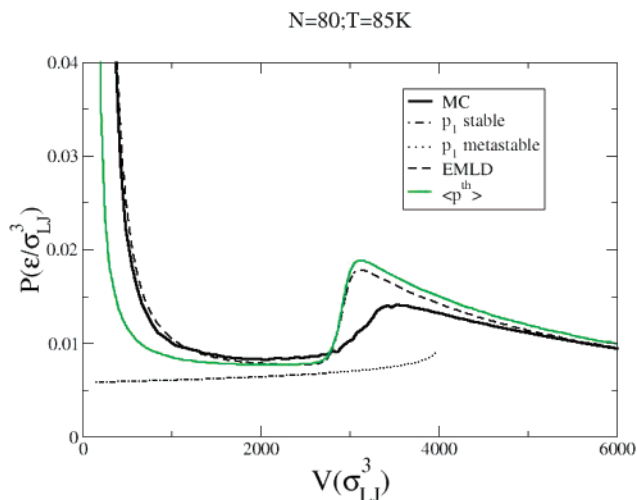


Figure 4. P - v isotherms for $N = 80$ molecules of Lennard-Jones argon at $T = 85$ K. The heavy line represents the results of the MC simulations; the dashed line is the prediction of the model using the simulated $\sigma = 13.6$ dyn/cm value of the surface tension; the dotted line and the dot-dash line are the thermodynamic predictions of the pressure for the metastable and stable states, respectively. The gray line is the “thermodynamic” pressure given by eq 9, averaged over fluctuations.

several others are discussed in ref 5. The discussion, thus far, has been limited to the MLD. In the next section we move to the EMLD.

3. The EMLD

The EMLD is derived from the MLD by taking fluctuations into account.⁵ Thus, consider a drop of size n_{st} at the minimum of one of the curves in Figure 3. With N , V , and T held constant, there is nothing to prevent the drop from fluctuating with a definite probability over the landscape represented by the particular curve in Figure 3. Such a fluctuation represents a fluctuation in n , the size of the drop, and the probability of realizing a certain size n is given by

$$f(n) = \frac{e^{-\Delta F(n)/kT}}{\sum_{j=0}^N e^{-\Delta F(j)/kT}} \quad (6)$$

Clearly, such fluctuations are only important in a very small system. Nevertheless, the thermodynamically consistent pressure-volume isotherm should be obtained by averaging $P(T, V)$ of eq 4 over the free energy landscape, using $f(n)$ as a weighting function. This averaging constitutes the extension of the MLD to the EMLD. When this is done⁵ for argon ($N = 80$, $T = 85$ K), the dashed curve in Figure 4 is obtained. Here, pressure is measured in units of ϵ/σ_L^3 and volume in units of σ_L^3 , where σ_L (not to be confused with surface tension) is the length scale in the argon Lennard-Jones potential and ϵ is the depth of the potential well. The dot-dash curve in the figure is simply $p_1(T, V)$ obtained from eq 1. As such it fails to contain the effects of both fluctuation and translation, whereas the dashed curve, based on the EMLD, does incorporate these effects. The solid curve in Figure 4 is the result of a Monte Carlo (MC) simulation, using the argon Lennard-Jones potential. In the simulation, the pressure exerted by the 80 molecules inside the container is evaluated in the standard way by means of the virial,¹³ without using any criteria to identify or define the drop, and without using the measured thermophysical properties of argon.

The remarkable agreement between the EMLD and MC results should be noted. Disagreement only occurs in the neighborhood of the first-order transition, i.e., near the volume where the drop is forced to abruptly evaporate. Actually, the disagreement occurs near the transition because of the large fluctuations that occur in that neighborhood, many of which are not accounted for by the EMLD, as described. In fact, it is possible to show that fluctuations in which there is more than one drop in the container are mainly responsible for the disparity near the transition. If, for example, the EMLD is expanded to allow two drops, the disparity is sharply reduced.⁵

Notice that the dot-dash $p_1(T,V)$ curve in Figure 4 is continued into a dotted curve. The isotherm can be shown to become metastable along this portion of the curve so that the transition is initiated at the point where dot-dash and dotted curves are joined. Furthermore, note that the dot-dash $p_1(T,V)$ curve does not rise precipitously as V is reduced whereas the dashed EMLD curve does rise. The rise is due to $p_{\text{drop}}(T,V)$, which is not represented in the dot-dash curve for $p_1(T,V)$. At small volumes, the system consists almost entirely of a drop and almost no gas molecules, confined to a volume hardly larger than the drop. Thus, the pressure becomes very large and consists almost entirely of $p_{\text{drop}}(T,V)$.

All of the features discussed above are elaborated upon in ref 5. Indeed the remarkable agreement between MC simulation and EMLD seems to hold for other N,V,T conditions and, in another paper,¹⁴ it is shown that it also extends to the ideal binary system, argon–krypton. Furthermore, under certain conditions, it leads to better agreement with simulation than density functional theory (DFT).¹⁵ This broad agreement suggests the possibility that the EMLD can be used reliably for systems consisting of molecules more complicated than the rare gases without having to have a reliable intermolecular potential. In this case, it would be an extremely valuable tool.

Despite all this, there are some puzzling features in the MLD and in the EMLD, and these stimulated the study of an issue that forms the main theme of the present paper, namely, the use of the virial in the simulation of nanosystems. We turn to this issue in the following sections.

4. The Virial and the Thermodynamic Pressure

Returning to the MLD, and considering the pressure–volume isotherm specified by eq 4, we can write $P(T,V)$ explicitly for the case of a system containing a total of N molecules (n of them forming a drop) by substituting eqs 2 and 3 into eq 4. Since, for the present demonstration, we will constrain n to be fixed, we will not require the $N - n$ gas molecules to be in equilibrium with the drop. The result is

$$P(T,V,n) = \frac{(N-n)kT}{V - nv_1} + \frac{kT}{\frac{4\pi}{3}(R-r)^3} \quad (7)$$

where $\Theta(n)$ has been set to unity since a drop is definitely present. At this point, one can notice that although the total volume of the system is actually V , the denominator of the second term on the right of this equation is the lesser volume V_d through which the center of the drop can move. Consequently, the second term in eq 7 is the pressure due to an ideal gas molecule confined to this lesser volume. In a sense, this second term corrects the pressure of the drop by accounting for the volume unavailable to it due to its finite size. However, from the thermodynamic point of view, the only meaningful volume is that of the container V , so that it seems as if the second

term on the right of eq 7 should be modified to reflect the actual pressure (the “thermodynamic pressure”) exerted by the drop on the walls of the container of volume V (instead of the pressure exerted on the surface of the volume V_d through which the center of the drop can move). This modification is easy since the *total stress (force)* exerted by the drop must be the same on the surface of the container as it is on the surface of the lesser volume. Thus, if $P_{\text{drop}}^{\text{th}}(T,V)$ is the thermodynamic pressure on the surface of V , it must be given by

$$P_{\text{drop}}^{\text{th}}(T,V) = \frac{(R-r)^2}{R^2} p_{\text{drop}}(T,V) \quad (8)$$

where $(R-r)^2/R^2$ is the ratio of the area of the surface of V_d , the lesser volume (the volume available for the center of mass of the drop), to that of V . Thus, to represent the pressure due to the drop in eq 7 as the thermodynamic pressure, the second term on the right should be multiplied by $(R-r)^2/R^2$.

Note that, in principle there should be a similar correction $(R-\xi)^2/R^2$ for the pressure p_1 exerted by the remaining $N - n$ gas molecules. Because of their finite size (see Figure 2), the center of mass of the vapor molecules cannot reach the walls of the container V , but it is also confined to a smaller volume $V_M = 4\pi(R-\xi)^3/3$. This correction was absent in both MLD and EMLD, since in both models these molecules were assumed to behave as ideal, but in general the finite size of the individual molecules should be also taken into account.

According to that, the total thermodynamic pressure will then be

$$P^{\text{th}}(T,V,n) = \frac{(N-n)kT}{V_M - nv_1} \left(\frac{(R-\xi)^2}{R^2} \right) + \frac{kT}{\frac{4\pi}{3}(R-r)^3} \left(\frac{(R-r)^2}{R^2} \right) \quad (9)$$

This result can actually be verified by working with the partition function of the system, i.e., by working with the free energy of the system rather than directly with the stress. The partition function is

$$Q(N,V,T) = \frac{(V_M - nv_1)^{N-n} \left(\frac{4\pi}{3}(R-r)^3 \right) q_m^{N-n} q_d}{(N-n)! \lambda_m^{N-n} \lambda_d} = \frac{\left(\frac{4\pi}{3} \left(\left[\frac{3V}{4\pi} \right]^{1/3} - \xi \right)^3 - nv_1 \right)^{N-n} \left(\frac{4\pi}{3} \left(\left[\frac{3V}{4\pi} \right]^{1/3} - \left[\frac{3nv_1}{4\pi} \right]^{1/3} \right)^3 \right) q_m^{N-n} q_d}{(N-n)! \lambda_m^{N-n} \lambda_d} \quad (10)$$

This form of Q is easily explained. In the numerator of the form following the first equality sign, $(V_M - nv_1)^{N-n}$ is the factor in the configuration integral referring to the $N - n$ “finite size” ideal gas molecules, since the quantity in parentheses is the volume available to one such molecule, independent of the position of the drop; nv_1 is the volume of the drop; and $(4\pi/3)(R-r)^3 = V_d$ is the volume available to the drop and is thus the factor corresponding to it. q_m and q_d are the internal partition functions of a gas molecule and the drop, noninteracting aside from the drop exclusion volume, respectively. $(N-n)!$ is the usual correction for the indistinguishability of the gas molecules and λ_m and λ_d are the thermal de Broglie wavelengths of a gas molecule and the drop, respectively. The form following the second equals sign is the same as that following the first, except

that R and r have been expressed in terms of V . The *full* V dependence of Q is explicit in the second form.

How is $P(T, V, n)$ to be determined from Q in eq 10? The conventional rule in the canonical ensemble is

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T, N, n} \quad (11)$$

However, by itself, this rule needs some clarification here. The reason lies in the fact that, because of its small size, the present system may possess other significant independent geometric variables beyond V . These are associated with the surface of the container and could be the surface area and curvature.¹⁶ Assuming, for the time being, that curvature can be neglected, the differential of the Helmholtz free energy of the system may be expressed as

$$dF(T, V, A, n, N - n) = -S dT - P_i dV + \gamma dA + \mu_m d(N - n) + \mu_d dn \quad (12)$$

Here, we are not necessarily requiring the container to be spherical, and S is the entropy, P_i is the pressure, A is the surface area of the container, μ_m is the chemical potential of a molecule in the gas, and μ_d is the chemical potential of a molecule in the drop. Finally, although it might appear, from its position as the coefficient of dA , that γ is the mechanical surface tension, it is not, because the surface of the container is not the so-called surface of tension.¹⁶ Below, we will have more to say about the meaning of γ .

From eq 12, it is clear that

$$P_i = - \left(\frac{\partial F}{\partial V} \right)_{T, N, n, A} \quad (13)$$

and that

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T, N, n, V} \quad (14)$$

Now, when the volume of the container is varied under the constraint that it remains spherical, A will not be an independently variable quantity and we can write

$$\left(\frac{\partial F}{\partial V} \right)_{T, N, n} = \left(\frac{\partial F}{\partial V} \right)_{T, N, n, A} + \left(\frac{\partial F}{\partial A} \right)_{T, N, n, V} \left(\frac{\partial A}{\partial V} \right)_{\text{spherical}} = -P_i(T, V, n) + \left(\frac{2}{R} \right) \gamma = -P^{\text{th}}(T, V, n) \quad (15)$$

where eqs 12–14 have been used. $P^{\text{th}}(T, V, n)$ is the (thermodynamic) pressure exerted by the system on the walls of the container. This follows from the fact that, under the constraint of sphericity, $(\partial F / \partial V)_{T, N, n}$ in eq 15 is the coefficient of dV in eq 12; there is no longer an independent dA . Equation 15 may be regarded as a Laplace relation¹¹

$$P_i(T, V, n) - P^{\text{th}}(T, V, n) = \frac{2\gamma}{R} \quad (16)$$

Thus, $P_i(T, V, n)$ plays the role of some “internal” pressure. However, in the Appendix, we show that, in the case of a spherical container, $\gamma = 0$, so that in fact $P_i(T, V, n)$ and $P^{\text{th}}(T, V, n)$ are equal.

It is straightforward to show that the usual relation

$$F = -kT \ln Q \quad (17)$$

holds, so that eq 16 can be rewritten as

$$P^{\text{th}}(T, V, n) = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T, N, n, A} - \frac{2\gamma}{R} \quad (18)$$

We note that the partial derivative is impossible if the container retains a spherical shape, since A will have to change with V . Thus, the derivative must be interpreted as referring to a change of volume that begins in a spherical container and ends in one distorted from the spherical shape. With $\gamma = 0$, however, eqs 15 and 17, combined, yield

$$P^{\text{th}}(T, V, n) = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T, N, n} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T, N, n, A} \quad (11')$$

which recovers eq 11. Indeed, it is obvious that for ideal *point* molecules γ would be zero. However, as already mentioned, it is shown in the Appendix that $\gamma = 0$, also, for a hard molecule and the hard incompressible drop “molecule” in a *spherical container*. Thus, for the MLD or EMLD system, eq 11 can be used to evaluate the thermodynamic pressure.

As the reader can easily prove for himself/herself, substitution of eq 10 into eq 11 and the use of the chain rule yields

$$P^{\text{th}}(T, V, n) = kT \frac{\partial \ln Q}{\partial V_M} \frac{\partial V_M}{\partial V} + kT \frac{\partial \ln Q}{\partial V_d} \frac{\partial V_d}{\partial V} = \frac{(N - n)kT}{V_M - nv_1} \frac{\partial V_M}{\partial V} + \frac{kT}{V_d} \frac{\partial V_d}{\partial V}, \quad (19)$$

which is exactly eq 9 when the relations $\partial V_M / \partial V = (R - \xi)^2 / R^2$ and $\partial V_d / \partial V = (R - r)^2 / R^2$ are also used. Therefore, the corrections to the virial pressure derived at the beginning of this section from mechanical arguments can also be obtained directly from the partition function.

This corroborates that the correct thermodynamic pressure must be calculated by including the force per unit area exerted by the individual molecules and the hard drop on the surface of the container of radius R rather than on the surface of the smaller spherical volumes of radius $R - \xi$ and $R - r$, respectively.

It is important to mention that the correction has been easy to derive for the case of hard molecules or a hard drop like those considered in the MLD, or for a binary (or multicomponent) mixture of hard molecules of different sizes. In effect, the inclusion of the potential between the hard particles and the hard wall is simply accounted for by restricting the centers of mass of the particles to volumes smaller than the thermodynamic volume (which we might refer to as virial volumes). For the case of nonhard molecules the molecular centers of mass can, in principle, reach the wall of the thermodynamic volume, and the situation is not so simple. Thus, if the interaction between the molecules and the walls of the container is not hard, the evaluation of the correction becomes more involved. However, the physical arguments supporting the need for a correction to the pressure derived from the standard application of the virial theorem, call it the “virial pressure”, remain. Again, the correction arises because the virial does *not* produce the actual thermodynamic pressure on the walls of the nancontainer, but rather a slightly different “spurious” pressure, corresponding to the pressures exerted, respectively by the hard incompressible drop on the surface of the volume V_d of radius $R - r$ available to the center of mass of the drop and by the hard individual molecules on the surface of the volume V_M of radius $R - \xi$ available to their centers of mass. This “incorrect” result is only significant in the case of systems that are very small, i.e., for systems at the nanolevel. For a macroscopic system, the effect is entirely negligible. This is probably the

reason that incorrect applications of the virial to small systems have not been noticed.

The puzzle alluded to above can now be described. In the derivation of the pressure using the MLD or the ELMD, i.e., eq 7, the drop is considered as an incompressible hard “molecule” and hence it is the volume available to its center of mass V_d that appears in the expression for the pressure. Accordingly, this pressure reflects the pressure of the drop on the surface of the smaller volume of radius $R - r$, and we have just shown that this is *not* the thermodynamic pressure. In fact, if the drop would behave as an ideal hard incompressible “molecule” its proper thermodynamic pressure would be given by eq 8. Yet, as Figure 4 and other comparisons show, for small volumes—where practically all the molecules are expected to be condensed into the drop—it is the pressure kT/V_d and not the thermodynamic pressure, $P_{\text{drop}}^{\text{th}} = kT(R - r)^2/(V_d R^2)$, that yields the excellent agreement with the pressure obtained from the MC simulation! How can we explain this result?

In ref 5, this puzzling situation was already noted, but only an ad hoc attempt at explanation was offered. Indeed what appears to be the correct explanation is connected with the virial theorem, and it is elaborated in the following section.

In closing this section it is worthwhile to explain the origin of a nonzero γ in the case of a *nonspherical* volume containing a single hard drop. $Q(N, V, A, T)$ for such a system would be given by a formula similar to that in eq 10, in fact by $Q(N, V, A, T) = V_d q_d / \lambda_d$. Except when initiating a variation at the spherical shape, when the derivative in eq 10 is implemented, the thermodynamic volume V can be held constant but V_d will vary as the thermodynamic surface area A is varied. Thus, $\gamma = -kT(\partial \ln Q / \partial A)_{T, N, V}$ will be nonzero because $(\partial V_d / \partial A)_{T, N, V}$ is nonzero.

5. The Pressure Derived from the Virial

A well-known form of the virial theorem may be expressed as¹⁷

$$P_M V_M = NkT + \frac{1}{3} \langle \Omega_{\text{int}} \rangle_t \quad (20)$$

in which P_M is the equilibrium pressure of N molecules whose centers of mass are confined to a volume V_M and $\langle \Omega_{\text{int}} \rangle_t$ is the long time average of the *internal* virial specified by

$$\Omega_{\text{int}} = \sum_{i=1}^N \mathbf{r}_i(t) \mathbf{F}_i(t) \quad (21)$$

where t is time and \mathbf{r}_i is the vector position of the i th molecule while \mathbf{F}_i is the force exerted on the i th molecule by the remaining $N - 1$ molecules, but not by the container.

[Equation 20 implicitly defines the interaction of the centers of mass of the molecules with the boundary of V_M as *exerting a hard wall potential*, since all $\mathbf{F}_i(t)$ represent only forces *between molecules* and not between molecules and the wall. One could of course include such wall forces in eq 21 with the penalty of complicating the analysis.]

The subscript M appearing in eq 20 indicates that the equation applies to the N molecules, regardless of how they are configured within V_M , i.e., independent of how they are correlated in clusters, phases, etc. It is important to note that \mathbf{r}_i refers to the position of the center of mass of the molecule and that V_M in eq 20 is the volume available to the center of masses of the N molecules. For example, if the walls of the container are hard and the molecules have hard cores, V_M must be smaller than V , the “thermodynamic” volume of the system, since a

hard core can be in contact with a hard wall, but the molecule’s center of mass cannot. This difference between V and V_M is of negligible consequence when V is in the thermodynamic limit, but it can be extremely important in a nanosystem. If the value of the pressure is obtained from a simulation using the virial, then P_M is also the simulated pressure.

To set the stage for the analysis in this section, we return to Figure 4 and focus on the sharp rise in pressure with decreasing volume that occurs at small volumes. The solid MC curve shows this rise, which is due to the repulsive cores of the individual argon molecules. However, the dashed EMLD curve shows the rise, primarily, because of the confinement of the hard incompressible drop. In fact, for the EMLD, there will be very few, if any, single molecules in the container at such small values of V . [Note that the dot-dash curve (that does not take the pressure $p_{\text{drop}}(T, V)$ due to the drop into account but only $p_1(T, V)$ due to the single molecules) does not exhibit the sharp rise.] The question that emerges is then, how is it possible for the simulated pressure, based on N individual molecules interacting according to a Lennard-Jones potential, to predict the same pressure as that due to a single ideal gas molecule represented by an incompressible drop consisting of N molecules?

By use of the virial theorem, we will now show that at sufficiently small values of V , where the volume of the container is similar to that of the drop, i.e., when V can be well approximated by

$$V \cong N v_l \quad (22)$$

the pressure exerted by the N molecules coincides with the pressure that would be exerted by a single ideal hard drop consisting of these N molecules.

Let us assume that the cores of the individual molecules can be approximated as hard spheres of volume v . We define the ratio of v_l , the molecular volume in the liquid, to v by g so that

$$v_l = g v \quad (23)$$

The radius of the molecular hard core is given by

$$\xi = \left(\frac{3v}{4\pi} \right)^{1/3} \quad (24)$$

Then the radius of V_M the volume available to the centers of mass of the N molecules is $R - \xi$, and V_M itself is given by

$$V_M = \frac{4\pi}{3} (R - \xi)^3 = \frac{4\pi}{3} \left(R - \left(\frac{3v}{4\pi} \right)^{1/3} \right)^3 \quad (25)$$

When V is small enough, there are essentially no single molecules inside the container, since practically all of them are condensed into the drop. Hence, we can just focus on the pressure exerted by the drop. In the MLD or the EMLD its contribution P_{drop} to the total pressure, designed to match the simulated pressure, is given by the following ideal gas relation.

$$P_{\text{drop}} V_d = kT \quad (26)$$

(see eq 3).

In the EMLD, as opposed to the MLD, P_{drop} is averaged over the free energy landscape, but at small volumes this landscape is very limited, since the drop is very stable (there is a very deep minimum in the free energy).

Taking the ratio of eq 20 to eq 26, we find

$$\frac{P_M}{P_{\text{drop}}} = \left[N + \frac{\langle \Omega_{\text{int}} \rangle_t}{3kT} \right] \frac{V_d}{V_M} = \left[N + \frac{\langle \Omega_{\text{int}} \rangle_t}{3kT} \right] \left\{ \frac{R - \left(\frac{3gV}{4\pi} \right)^{1/3} N^{1/3}}{R - \left(\frac{3V}{4\pi} \right)^{1/3}} \right\}^3 = \left[N + \frac{\langle \Omega_{\text{int}} \rangle_t}{3kT} \right] \left\{ \frac{R - \xi g^{1/3} N^{1/3}}{R - \xi} \right\}^3 \quad (27)$$

In order for the simulated pressure P_M and the pressure due to the drop whose center is limited to V_d to be identical, the ratio on the left of eq 27 must be unity. Setting that ratio equal to unity in eq 27 yields the relation

$$\frac{R}{\xi} \left[\left(N + \frac{\langle \Omega_{\text{int}} \rangle_t}{3kT} \right)^{1/3} - 1 \right] + 1 = \left(N + \frac{\langle \Omega_{\text{int}} \rangle_t}{3kT} \right)^{1/3} g^{1/3} N^{1/3} \quad (28)$$

Now N is considerably larger than unity and $\langle \Omega_{\text{int}} \rangle_t$ is large and positive when V is small, i.e., on the rapidly rising branch of the isotherm in Figure 4. Thus, the unities in eq 28 can be neglected so that $(N + \langle \Omega_{\text{int}} \rangle_t / 3kT)^{1/3}$ will cancel out of eq 28, leaving the result

$$\frac{R^3}{\xi^3} = \frac{V}{v} = Ng \quad \text{or} \quad \frac{V}{N} = gv \quad \text{or} \quad V = Nv_1 \quad (29)$$

the last form of which is eq 22. But we have already agreed that eq 22 holds at small enough V on the rapidly rising branch of the isotherm in Figure 4, so this shows that, at small enough V , the pressure estimated by the MLD or EMLD will be essentially equal to the simulated pressure, since the result is predicated on setting the ratio on the left of eq 27 equal to unity.

Thus, the puzzle seems to have been, at least partially solved. The solution rests on the discovery that the pressure predicted by the model and that obtained by means of simulation are essentially equal at small values of V , even though P_{drop} in eq 26 is evaluated with the center of the drop confined to the smaller volume V_d rather than to V .

As V is increased on the sharply rising branch of the isotherm, single molecules will evaporate and coexist with the drop within V (at least within the model). As a result, both individual molecules and the drop will contribute to the total pressure, and the conditions supporting eq 29 will no longer hold since V will exceed Nv_1 . Therefore, the isotherm can follow the course appearing in Figure 4. At larger V , the drop will not contribute much to the total pressure and the isotherm will be determined largely by p_1 , i.e., by the Kelvin relation for which there is evidence that it can hold into the nanometer-size range.¹⁸

It is worth stressing that, from what has been said in the previous section, neither the virial pressure P_M nor the model yield the thermodynamic pressure. Because of the finite size of the molecules, P_M appearing in eq 20 is not the thermodynamic pressure P^{th} but should be related to that pressure by

$$P_M = \frac{R^2}{(R - \xi)^2} P^{\text{th}} \quad (30)$$

where this correction will usually be small because of the smallness of ξ .

Since the model is able to reproduce the simulated pressure, both approaches can be made to yield the thermodynamic pressure through the application of eq 30. Note also that,

although eq 8 would be rigorously valid for the thermodynamic pressure of a *single* hard molecule of the size of the drop, eq 30 is actually the most appropriate to model the pressure exerted by a drop consisting of n molecules.

Even though the puzzle seems to have been, at least partially solved, we have as yet to prove that $\gamma = 0$ for the drop in a spherical container. This proof underlies the validity of eq 11', a relation that is essential to the identification of the thermodynamic pressure with the internal pressure. This proof is presented in the Appendix.

6. Concluding Remarks

The main focus of this paper has been an analysis of the use of the virial in the simulation of the pressure in a nanosized N, V, T system. The problem with the use of the virial in the simulation of very small systems lies in the observation that the pressure evaluated in this way represents the pressure due to molecules confined, not to the thermodynamic volume V but rather to a smaller volume V_M available to their center of masses. The difference between these two pressures is due to the finite size of the molecules. This problem is of negligible importance in macroscopic systems and, for this reason, has gone mostly unnoticed in prior simulations. However it can become extremely important in nanosystems.

In such systems, simulation of the pressure by way of the virial, does not yield the desired thermodynamic pressure, but it is possible to use the simulated pressure to obtain the thermodynamic pressure through the use of a fairly exact correction when the molecules have hard cores and interact with the hard walls of the thermodynamic volume only through these hard cores. Any other form of interaction with the wall will involve a difficult correction.

Most of the argument concerning the failure of the virial approach in nanosystems is documented by a fairly exact analysis in the present paper.

It is important to understand the generality of this result in future studies of fluid nanosystems.²¹

The other main goal of the paper was to present a clear, almost magically simple, argument that justifies the excellent agreement, for small volumes, between the MLD/EMLD model and simulation. The derivation in section 5 clearly shows that, when the volume of the container becomes comparable to that of the drop, the pressure exerted by this drop can be surprisingly well represented by that of an ideal gas consisting of a single drop "molecule".

The reader will recognize, in the puzzle of this paper, a similarity to a long standing puzzle that has not been fully resolved in the molecular theory of surface tension.¹⁶ There, a theory based on stress (and use of the virial) and one based on free energy yield disparate results. It is possible that the resolution of the problem will be found in a phenomenon similar to that which we have used to resolve the puzzle on which the present paper is focused, especially since an interface is a nanosystem in at least one direction.

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Appendix

We wish to show that, in eq 12, $\gamma = 0$ when the container of volume V is spherical, and all N molecules are in an incom-

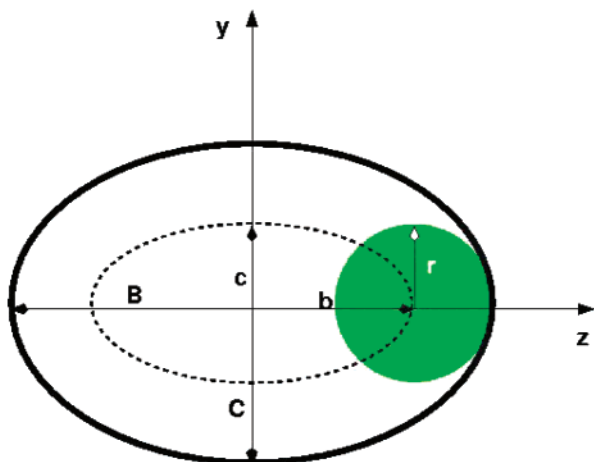


Figure 5. Section at $x = 0$ of a prolate spheroidal container, illustrating all the definitions used in the Appendix.

pressible drop of radius r . To accomplish this, we begin with a container that is a prolate spheroid (see Figure 5). In rectangular coordinates X, Y, Z the equation for this object is

$$X^2 + Y^2 + \frac{C^2}{B^2}Z^2 = C^2 \quad (\text{A1})$$

where C and B are constants. The volume of this spheroid is given by²²

$$V = \frac{4\pi}{3}C^2B \quad (\text{A2})$$

and the area of its surface is²²

$$A = 2\pi C^2 + \frac{2\pi CB^2}{\sqrt{B^2 - C^2}} \sin^{-1} \left(\frac{\sqrt{B^2 - C^2}}{B} \right) \quad (\text{A3})$$

Note that when $C = B = R$, these equations reduce to those for a simple sphere of radius R .

In Figure 5, a spherical drop of radius r is shown in contact with the spheroid's interior surface. By rolling the drop along this surface, its center is made to trace out a smaller closed surface A_d to which the center of the drop is confined. This surface is not a spheroid. However, if B and C are only infinitesimally different from R the radius of a sphere, so that the spheroid is an infinitesimally deformed sphere, it can be shown²³ that both the surface area A_d and the volume V_d of the smaller closed surface differ from those of a spheroid in the second and higher orders in the infinitesimals, but not in the first order. Since we shall be concerned with the limit in which the spheroid converges on a sphere we can therefore treat the smaller closed surface as a spheroid. The equation of this spheroid is

$$x^2 + y^2 + \frac{c^2}{b^2}z^2 = c^2 \quad (\text{A4})$$

where the constants c and b take the place of C and B in eq A1.

Equation A1 shows that, on the larger spheroid, $Z = B$ at the point where the Z axis pierces its surface. By the same argument, the z axis pierces the smaller spheroid at $z = b$. The point of intersection of the z axis with the spheroid is also the center of the drop of radius r shown in Figure 5, while the point of intersection with the larger spheroid is the point of contact

between it and the surface of the drop. Thus, it is clear that

$$b = B - r \quad (\text{A5})$$

A similar argument, using the x or y axis, yields

$$c = C - r \quad (\text{A6})$$

The volume V_d through which the center of the drop can move and its corresponding surface area A_d are given by relations eqs A2 and 3 with c and b substituted for C and B . Thus, using eqs A5 and A6, we find

$$V_d = \frac{4\pi}{3}(C - r)^2(B - r) \quad (\text{A7})$$

and

$$A_d = 2\pi(C - r)^2 + \frac{2\pi(C - r)(B - r)^2}{\sqrt{(B - r)^2 - (C - r)^2}} \sin^{-1} \left(\frac{\sqrt{(B - r)^2 - (C - r)^2}}{B - r} \right) \quad (\text{A8})$$

The \sin^{-1} function is difficult to work with, and matters can be simplified by taking advantage of the fact that our goal is to be able to vary the volume and surface area of the container independently so as to be able to implement eq 12. In this process we want to start with a spherical container of radius R and deform it into a prolate spheroid in such a way that either its volume is held constant while the area of its surface is varied or vice versa. However, as already indicated, for our purpose the deformation can be very small. Thus, we can choose C and B to be

$$C = R + \epsilon \quad \text{and} \quad B = R + \zeta \quad (\text{A9})$$

where ϵ and ζ are infinitesimal. Substitution of these equations into eqs A2 and A3, followed by expansion in terms of ϵ and ζ and retaining only linear terms leads to the relations

$$V = \frac{4\pi}{3}R^3 + \frac{4\pi}{3}R^2(\zeta + 2\epsilon) \quad (\text{A10})$$

and

$$A = 4\pi R^2 + 2\pi R(3\epsilon + \zeta) \quad (\text{A11})$$

Starting with a spherical container and deforming it into a prolate spheroid, the differential change in volume can be expressed as

$$dV = V - \frac{4\pi}{3}R^3 = \frac{4\pi}{3}R^2(\zeta + 2\epsilon) \quad (\text{A12})$$

and

$$dA = A - 4\pi R^2 = 2\pi R(3\epsilon + \zeta) \quad (\text{A13})$$

where we have used eqs A10 and A11 and have relied on the infinitesimal natures of ϵ and ζ .

Equation A12 shows that, for a deformation in which V is constant, i.e., in which $dV = 0$,

$$\zeta = -2\epsilon \quad (\text{A14})$$

Substituting this result into eq A13 shows that for this deformation we can write

$$(dA)_V = 2\pi R\epsilon \quad (\text{A15})$$

The analogue of eq 10 can be written for the spheroid containing a drop consisting of n molecules, but no single molecules. A little thought will show that

$$Q(N, C, B, T) = \frac{\left(\frac{4\pi}{3}\right)(C-r)^2(B-r)q_d}{\lambda_d^3} = \frac{\left(\frac{4\pi}{3}\right)(R-r+\epsilon)^2(R-r+\zeta)q_d}{\lambda_d^3} \quad (\text{A16})$$

where eqs A5, A6, A7, and A9 have been used. Now, reference to eq 12 shows that

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{T,V,N} \quad (\text{A17})$$

Making use of eq A16, and noting eq A14, which allows Q in eq A15 to be expressed in terms of ϵ alone, leads to

$$\gamma = -kT\left(\frac{\partial \ln Q}{\partial A}\right)_{T,V,N} = -kT\left(\frac{\partial \ln Q}{\partial \epsilon}\right)_{T,V,N}\left(\frac{\partial \epsilon}{\partial A}\right)_{T,V,N} = -kT\left(\frac{\partial \ln Q}{\partial \epsilon}\right)_{T,V,N}\left(\frac{\epsilon}{\partial A}\right)_{T,V,N} \quad (\text{A18})$$

where in the last step we recognize that ϵ and $\partial \epsilon$ are the same since ϵ is infinitesimal and the deformation is initiated at $\epsilon = 0$. Substitution of eq A15 into eq A18 yields

$$\gamma = -\frac{kT}{2\pi R}\left(\frac{\partial \ln Q}{\partial \epsilon}\right)_{T,V,N} \quad (\text{A19})$$

Then, eliminating ζ from eq A16 with the help of eq A14 and substituting the result into eq A19 gives

$$\gamma = -\frac{kT}{2\pi R}\left\{\frac{2}{R-r+2\epsilon} - \frac{2}{R-r-\epsilon}\right\} \quad (\text{A20})$$

Thus, for the prolate spheroid container, γ is nonzero. However, for a spherical container, which is obtained by setting $\epsilon = 0$, eq 20 yields the result $\gamma = 0$. This is what we set out to prove. Note that r determines n and vice versa.

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