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Howard Reiss: In Memoriam

With the passing of Howard Reiss (December, 2015) the international community of chemists and physicists has lost one of its most original and versatile researchers.

Howard was one of the all-too-rare examples of a scientist who, from his first days to his last, worked on whatever aroused his intellectual curiosity, whether it was the fundamentals of nucleation phenomena or what makes one-dimensional systems special or what might be the best dose protocol for administering a drug. No problem was "off-bounds" for him—he was the consummate problem-solver, armed with a great imagination and facile mastery of theoretical modeling—and yet he became the world's expert in several different mainstreams of chemistry and physics.

Howard was born (1922) and grew up in New York City, completing his public school, college (NYU, 1943) and graduate (Columbia, 1949) studies there, with brief stints during the war at Princeton (1943–1944) and at Oak Ridge (1944–1946). Already in his PhD thesis work he was started on his lifelong fascination with and contributions to nucleation phenomena and droplet growth. This work was continued during his two years on the faculty at Boston University, before he moved in 1952 (after a year as a staff researcher at the Celanese Research Laboratory) to Bell Laboratories where he remained through 1960. These were extremely productive and influential years for Howard, when he established the research mode that suited him so well—working simultaneously in several different areas, so that he was always an "outsider" in each, even as he did fundamental work and contributed vitally to each. There he published his first papers on semiconductor physics, dealing with hydrogen and lithium impurities in silicon and germanium, and on zone melting. Still more significantly, he began his study of liquids and wrote his seminal paper on "scaled particle" theory, launching his sixty year love affair with hard-sphere fluids.

In 1960, while Bell Laboratories was still in its prime as the world's premier center for solid-state physics and chemistry, Howard moved to the west coast to pursue a unique opportunity at what would become the North American Rockwell "Science Center", in Thousand Oaks, just north of Los Angeles. Those who knew Howard know that—while he was many things—he was not a manager. And yet, in the post-Sputnik 1960s when basic science was (all-too-briefly) being encouraged and supported without pressure to be immediately profitable, Howard was the perfect recruiter and director of an expanding collection of outstanding physicists, chemists and mathematicians. Instead of managing, he led with his ideas, enthusiasm, and good instincts about ambitious-yet-feasible new problems and areas. Even as

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Director, he found time to work and write several papers on fused salts, stressed solid solutions, and the statistics of random sequential addition phenomena. After about eight years, when the 1960s bubble broke, he moved (1968) to the UCLA Chemistry Department, where he was to spend more than 35 years.

At UCLA, in his late 40s, Howard became a professor for the first time, a role that he moved into easily and happily. He returned to nucleation phenomena as his focus, building up an experimental group to investigate photooxidation and polymerization in pure and binary systems using diffusion cloud chambers. On the theory side he complemented the classical phenomenological models with molecular formulations and simulations of "physical clusters". He also continued his earlier work on "statistical geometry" and hard particle systems, and moved into many completely new areas including conducting polymers, the glass transition, and ion-selective membranes. And he taught undergraduate and graduate courses across the full spectrum of physical chemistry.

Throughout his several decades at UCLA, Howard was greatly appreciated for the interest and enthusiasm he showed in the work of his many friends and colleagues there, always ready to wrestle with a tough, conceptual, thermodynamics or statistical mechanics problem that arose in their work, or to help by making connections to other problems and fields. From his two decades at Bell Labs and at the Science Center, and his many years of consulting in industry and serving on government advisory panels—but, mostly, from his insatiable curiosity and lively imagination—he was a veritable fount of ideas and knowledge on just about any scientific subject, a "renaissance man" of physical science.

Howard's work has been recognized by many awards and honors, including election to the National Academy of Sciences (1977), a Guggenheim Fellowship (1978), the Colloid and Surface Chemistry (1980) and Liquids (1991) Prizes of the American Chemical Society, and numerous endowed lectureships and visiting professorships throughout the States and Europe. He was also a member of the editorial boards of many journals, and the founding editor (1968-78) of the Journal of Statistical Physics. We will remember and miss sorely his self-effacing sense of humor and modesty, and his great intellect and originality.

William M. Gelbart, Dept. of Chemistry UCLA

It is with great sadness that I write these lines in memory of Howard Reiss. Howard was a friend, a mentor, and the founding editor of the Journal of Statistical Physics. It was Howard who chose me as his successor editor of the journal. Howard was also a wonderful scientist and human being. As noted by Bill Gelbart in the article above, he was interested and creative in a great variety of fields. It was he who, with his idea of sealed particle theory, got me interested in the study of hard spheres. His latest article on this topic, joint work with José Manzanares is published in this issue of the journal. His insight and enthusiasm for the subject will continue to be an inspiration to all working in this field.

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Statistical Thermodynamics of an "Open" Hard Sphere System on the Equilibrium Fluid Isotherm: Study of Properties of the Freezing Transition Without Direct Involvement of the Equilibrium Solid Phase

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Abstract Using several theoretical tools… (i) the nucleation theorem, (ii) an equivalent cavity, (iii) the reversible work of adding a cavity to an open hard sphere system, and (iv) the theory of "stability"… the authors estimated the density at which the hard sphere freezing transition occurs. No direct involvement of the equilibrium solid phase is involved. The reduced density $\pi a^3 \rho_f/6$ (where a is the hard sphere diameter and ρ_f is the actual density at which freezing occurs) is found to be 0.4937 while the value obtained by computer simulation is 0.494. The agreement is good, but the new method still contains some approximation. However, the approximation is based on the idea that at a density just below ρ_f the fluid adopts a distorted structure resembling the solid, but different enough so that long-range order vanishes. Initial loss of stability may not be involved in every fluid–solid transition, but it may be an early step in the hard sphere and related systems.

Keywords Hard sphere freezing transition · Nucleation theorem · Equivalent cavity · Open hard sphere system · Statistical geometry

1 Sphere Packings

Hard sphere packings in thermodynamic equilibrium and nonequilibrium [1–14] have been an issue of considerable interest in recent years. Theory and simulation have addressed the problem and yielded interesting but incomplete results. The present authors attempted to study the *metastable* fluid pressure-volume isotherm in the density range where the *stable* system was a solid. In this effort they used (i) an equivalent cavity [10], (ii) the nucleation

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theorem [15], (iii) the reversible work involved in adding the cavity to the system [8,9], and (iv) the theory of stability [16].

The present paper considers the density range where the system can be in *stable* equilibrium, and involves a study of the concentration and fluctuation of hard spheres in an *open* system of hard spheres in a fixed volume as the system responds, at constant chemical potential, to the reversible addition of a cavity. However, the size of the number fluctuation of spheres is essentially infinitesimal since it is tied to the relatively infinitesimal size of the added cavity. But the standard rules [17] of the bridge between thermodynamics and statistical mechanics should not be affected, since the *total* number of spheres in the system is assumed to lie in the thermodynamic limit. Instead, we will adopt the currently standard rules to develop a closed theory whose accuracy will be at least internally consistent!

2 Relevant Statistical Mechanics

We begin with a classical equilibrium system of Nhard spheres at temperature T in a "box" of volume V *at rest in the laboratory coordinate system*. For this system, the configuration integral in the canonical ensemble phase integral or partition function Q is given by [17]

$$Z = \int_V \mathrm{d}\boldsymbol{r}_1 \int_V \mathrm{d}\boldsymbol{r}_2 \ldots \int_V \mathrm{d}\boldsymbol{r}_N \exp\left[-\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)/kT\right], \tag{1}$$

where Φ is the potential energy of the system, $d\boldsymbol{r}_i$ is the volume element associated with the ith molecule and $\boldsymbol{r}_i$ is its vector position. Actually, in the case of hard spheres, Φ must be zero in all "allowed" configurations but its spatial derivative need not be zero when the impulsive force between particles is considered.

In *some* situations we could demand that the system satisfies Eq. (2) below. This might include a wide range of molecular configurations without having to detail them beyond the requirement that the system is in the thermodynamic limit and Φ is a sum of short-range pair potentials such that, in the integral of Eq. (2), below, the space near the surface of V could be ignored. Then, Z could normally be expressed as

$$\begin{aligned} Z &= \int_V \mathrm{d}\boldsymbol{r}_1 \left\{ \int_V \mathrm{d}\boldsymbol{r}_2 \ldots \int_V \mathrm{d}\boldsymbol{r}_N \exp\left[-\Phi(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)/kT\right] \right\} \\ &= V \int_V \mathrm{d}\boldsymbol{r}_2 \ldots \int_V \mathrm{d}\boldsymbol{r}_N \exp\left[-\Phi(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)/kT\right] \end{aligned} \tag{2}$$

since the quantity in braces would be independent of $\boldsymbol{r}_1$ [17]. We should indicate that Eq. (2) forms a principal basis for many statistical mechanical studies of the thermodynamic behavior of the hard sphere fluid. This would not be the case if the system evidenced any kind of long-range order and exhibited a singlet distribution function that varied with position in the laboratory frame.

But the theory developed in this paper will be restricted to the use of periodic boundary conditions since the behavior of an *equivalent cavity* (see below) will be used as a tool, and this entity is so small that its properties might not overwhelm system surface effects. This could sufficiently compromise the analysis of the phase transition that constitutes one of the features of the present paper.

It should be noted that there is a simulative computational procedure in which, superficially, Eq. (2) can seem to apply, even in the case of an ordered system… for example in the case of a crystal. This involves the use of *periodic boundary conditions*. Thus, consider a simulation within a two dimensional "volume" e.g. a surface containing hard disks. The 1D boundary of

this 2D volume could be eliminated by wrapping the 2D system onto the "surface" of a torus. Then, there would be no boundaries *within* the surface…in effect it would exhibit periodic boundaries in respect to the disks.

Our theory will use a few analytical tools. These include (i) the *nucleation* theorem [15], (ii) a so-called *equivalent cavity* [10] as an analytical "probe" of the structural properties of the system, (iii) W_μ the reversible work involved in adding a cavity to an *open* system [8,9], and (iv) the theory of stability [16]. Several following sections elaborate the use of these tools.

In simple mechanics, center of mass motion or system translation is exactly separable from the internal degrees of freedom of a system. However, there are numerous studies, other than those involving periodic boundary conditions, where the role of translational motion has required special consideration. The phenomenon of nucleation provides an example [18].

3 Constraints, Thermodynamic Potentials, Equivalent Cavities, and Stability

The independent thermodynamic variables of a system can be viewed as external constraints [16,17,19–21] that determine the state of a system. This view is often not elaborated, but it can be very helpful in understanding some of the subtle aspects of the thermodynamic discipline. Corresponding to a given set of constraints, maintained constant, one can introduce a *thermodynamic potential* [16] whose change along a reversible path becomes a measure of the reversible work exchanged between the system and its surroundings. This process is generally familiar for a *closed* system having the potentials… U,H,F, and G… i.e. *internal energy*, *enthalpy*, *Helmholtz free energy*, and *Gibbs free energy*, … for paths of constant (S,V), (S,p), (T,V), and (T,p), respectively. However, the methods for developing and using thermodynamic potentials in general are not so familiar. This is true for *open* systems among others. Since an open system will be used in this paper it is appropriate to adopt it to demonstrate the method of developing and using the relevant potential. We will use an *equivalent cavity* as a treatable object and proceed to this task.

A "cavity" is defined as a spherical region from which the centers of hard spheres are excluded, and as we have indicated we will focus on an (immobile) *equivalent* cavity. Furthermore we shall be interested in an *open* thermodynamic system whose molecular content can fluctuate. Thus, we shall often denote that content by $\langle N\rangle$ rather than Nsuch that the angle brackets indicate an *average* value. The stable equilibrium structure of the system surrounding an immobile equivalent cavity is identical to that surrounding a hard sphere of diameter a. The *radius* of an equivalent cavity is equal to the *diameter* of a hard sphere.

Consider a reversible process involving an attempt to add a hard sphere to an *open* stable equilibrated system of $\langle N\rangle$ spheres in a fixed volume Vwhile the chemical potential μ is maintained constant. What would W_μ, the reversible work of addition be? In this example, μ could only remain constant if the open system caused the expulsion of spheres to the surrounding reservoir such that $\langle N\rangle$ remained constant. But then the final state would be the same as the initial state, and from the thermodynamic point of view there would not have been a process and W_μ would equal zero. Although the "process" satisfies the requirement that it should be closely associated with a hard sphere, it is really a nonprocess and not useful to the *nucleation theorem* discussed in the following section.

An alternative process closely associated with a hard sphere, and for which W_μ is not zero, is the addition of an equivalent cavity. The statistical mechanics of W_μ is simple enough that

its theory does not constitute a difficult additional problem and the work of formation of an equivalent cavity entails only modest analysis beyond the work of adding a hard sphere.

The reversible work of formation of the equivalent cavity, at constant μ, has been defined by W_μ. If the number of hard spheres in the system is Nwhile the volume of the system is $V$and the chemical potential of a sphere is μ, the fundamental equation of thermodynamics corresponding to this system is

$$\Delta U = \int T\mathrm{d}S - \int p\mathrm{d}V + \int \mu\mathrm{d}N + W_\mu, \tag{3}$$

where $p\mathrm{d}V$ is infinitesimal reversible volume work performed *by* the system. Additional kinds of reversible work will have to be represented by additional terms. W_μ is one such term. The increment sign Δ is used to represent a finite change and the integrals cover the interval to which Δ applies. As already indicated, $U$and Srepresent internal energy and entropy respectively while $T$is temperature. It is convenient to rearrange Eq. (3) to obtain

$$\Delta U - \int T\mathrm{d}S + \int p\mathrm{d}V - \int \mu\mathrm{d}N = W_\mu \tag{4}$$

and to define a quantity

$$\Delta\phi = W_\mu. \tag{5}$$

In this equation ϕ is not meant to be a function of state and $\Delta\phi$ is just a symbol that indicates the sum of terms on the left side of Eq. (4). For an infinitesimal process we can write that equation as

$$\mathrm{D}\phi = \mathrm{d}U - T\mathrm{d}S + p\mathrm{d}V - \mu\mathrm{d}N = \mathrm{D}W_\mu, \tag{6}$$

where D indicates an inexact differential.

Now we wish to invent a thermodynamic state function that can be tabulated and whose differential will *imitate* the sum of terms represented by $\mathrm{D}\phi = \mathrm{D}W_\mu$ for a change conducted at constant μ, V, T. As a suitable choice we employ the *grand potential*

$$\Omega = F - N\mu = U - TS - N\mu, \tag{7}$$

where $F = U - TS$ is the *Helmholtz free energy* of the system. According to Eq. (6)

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N + \mathrm{D}W_\mu \tag{8}$$

and from Eq. (7) we then have

$$\mathrm{d}\Omega = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T - \mu\mathrm{d}N - N\mathrm{d}\mu. \tag{9}$$

Substitution of Eq. (8) into Eq. (9) yields

$$\mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu + \mathrm{D}W_\mu. \tag{10}$$

From this it is clear that, over a path of constant μ, V, T, $\mathrm{d}\Omega = \mathrm{D}W_\mu$, while for a finite change of state, when work is performed *on* the system,

$$(\Delta\Omega)_{\mu,V,T} = W_\mu = (\Delta\phi)_{\mu,V,T} \geq 0. \tag{11}$$

The work W_μ is performed by constraints additional to those confining the initial state of the system and, if we use the subscripts i and f to identify the initial and final states respectively, the work may be expressed as

$$W_\mu = (\Delta\Omega)_{\mu,V,T} = \Omega_\mathrm{f} - \Omega_\mathrm{i}. \tag{12}$$

Thus, the reversible work may be expressed in terms of a tabulatable function of state of the system.

Although we have demonstrated a relation between reversible work and a particular thermodynamic potential…in this case a potential for an open system, the form of the result is quite general for all types of reversible work and corresponding thermodynamic potentials. The particular reversible work…positive or negative… performed *on* a system will be equal to the increment of the thermodynamic potential…positive or negative… in the associated process!

This principle can be considered in connection with the *nucleation theorem* that forms an important feature of the present paper and is most clearly understood in connection with an *open* system where the independent variables are μ, V, T for which the preceding analysis is especially relevant. The "theorem" is elaborated in the following section, but first the present section is closed with a discussion of *thermodynamic stability* [16].

It is known that, in a unary hard sphere μ, V, T system at stable equilibrium, the density increases with increasing chemical potential. It is useful to repeat a standard proof of this behavior. However, now we include the case where the system is so small that fluctuations are important. We introduce the grand partition function

$$\Xi = \sum_{N=0}^{\infty} Q(N, V, T)\mathrm{e}^{\mu N/kT} \tag{13}$$

that allows us to write the *average* molecular content as

$$\langle N(\mu, V, T)\rangle = \frac{\sum_{N=0}^{\infty} N Q(N, V, T)\mathrm{e}^{\mu N/kT}}{\sum_{N=0}^{\infty} Q(N, V, T)\mathrm{e}^{\mu N/kT}}. \tag{14}$$

Differentiation of both sides of this equation with respect to μ, followed by some rearrangement, gives

$$kT\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = \left\langle N^2\right\rangle - \langle N\rangle^2 = \left\langle (N - \langle N\rangle)^2\right\rangle \geq 0$$

or

$$\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} \geq 0 \tag{15}$$

which shows that $\langle N\rangle$, at constant T,V, must increase or remain unchanged with an increase of μ. Clearly, work must be performed *on* the system in this process in order to increase its molecular content at constant V. Since Eq. (15) has been derived for an *open* system at full *thermodynamic equilibrium* it represents a "stability" relation, i.e. it represents a prerequisite for the thermodynamic stability of the *open* system. For a *closed* system a particular stability condition is quite familiar and is represented by [16]

$$\left(\frac{\partial p}{\partial V}\right)_{T,N} < 0. \tag{16}$$

It is almost trivial to know that increasing the volume of a single-phase system while maintaining N constant reduces its pressure as Eq. (16) requires. Again, the system performs work *on* its environment. Thus the system is behaving in a stable way. It is important to note that because Eq. (16) corresponds to the system performing mechanical work *on* its environment it can be referred to as a condition *mechanical stability*. We return to the stability question in Sect. 8 where we prefer to use Eq. (15) appropriate for an open system.

4 The Nucleation Theorem

The nucleation theorem acquired its name by having first been used in connection with "nucleation". This is somewhat unfortunate since it has now been used in the study of many other *phenomena*. It may be represented by the relation

$$\left(\frac{\partial W_\mu}{\partial \mu}\right)_{T,V} = -(\langle N\rangle_\mathrm{f} - \langle N\rangle_\mathrm{i}) = -\Delta\langle N\rangle\,. \tag{17}$$

Here, we consider a reversible process in an *open* unary system, described by the variables μ, V, T, consisting initially of $\langle N\rangle_\mathrm{i}$ molecules, and subjected to a constraint that performs the reversible work W_μ *on* the system while μ, V, T are held constant. Since the system is open, the process may change its molecular content to $\langle N\rangle_\mathrm{f}$ so that $(\langle N\rangle_\mathrm{f} - \langle N\rangle_\mathrm{i}) = \Delta\langle N\rangle$ represents the positive or negative *global* molecular "excess" of molecules generated by the process.

As indicated earlier, the angle brackets in Eq. (17) emphasize that molecular contents may fluctuate since the system is open. The subscripts f and i stand for final and initial states, respectively, while $\langle\rangle_\mathrm{f}$ and $\langle\rangle_\mathrm{i}$ indicate averages of the fluctuating quantity based on the probability distributions of the fluctuations in the final and initial states. In the thermodynamic limit, these distributions are extremely narrow.

In statistical mechanics, the μ, V, T system is treated by the grand ensemble and Eq. (17) can be derived within this ensemble. We proceed to this derivation. We start with an open system in an initial macroscopic state having a spectrum of microstates such that $\zeta(i, N)$ is the energy of the ith quantum state in a system of Nmolecules. Next, with μ being held constant, we introduce a constraint that limits the system to the final state characterized by another spectrum of microstates such that $\chi(i, N)$ is the energy of the ith quantum state when N molecules are present. The grand partition function for the initial state will be denoted by Ξ_i while, for the final state, it will be Ξ_f. Then, the reversible work of a constant μ process is given by

$$W_\mu = -kT\ln(\Xi_\mathrm{f}/\Xi_\mathrm{i}). \tag{18}$$

Also,

$$\Xi_\mathrm{i} = \sum_N Q_i(N, V, T)\mathrm{e}^{N\mu/kT} \tag{19}$$

where the sum over Nbegins with $N = 0$ and where Q_i, the canonical ensemble partition function, may be written as

$$Q_\mathrm{i}(N, V, T) = \sum_\mathrm{i} \mathrm{e}^{-\zeta(i,N)/kT} \tag{20}$$

while

$$\Xi_\mathrm{f} = \sum_N Q_\mathrm{f}(N, V, T)\mathrm{e}^{N\mu/kT} \tag{21}$$

where Q_f is given by

$$Q_\mathrm{f}(N, V, T) = \sum_i \mathrm{e}^{-\chi(i,N)/kT}. \tag{22}$$

[Although the development in this section is general, we shall, among other things, be interested as was previously indicated (also see below) in a system of hard spheres of *diameter a*, and in a constraint that limits the molecular configurations in $V$to those that allow a spherical cavity of at least *radius a* to exist at a fixed point in V. As indicated in Sect. 3, a cavity is

defined as a region from which the centers of hard spheres are excluded. The structure of the equilibrium system surrounding such a cavity is identical to that surrounding a hard sphere so that the cavity can be denoted as an *equivalent* cavity. Furthermore, the process of interest will be the formation of the cavity while μ is held constant by a reservoir outside of the open system.]

Equations (19) and (21), substituted into (18), yield

$$W_\mu = -kT \ln \sum_N Q_\mathrm{f}(N, V, T)\mathrm{e}^{N\mu/kT} + kT \ln \sum_N Q_\mathrm{i}(N, V, T)\mathrm{e}^{N\mu/kT}. \tag{23}$$

Taking the derivative of W_μ with respect to μ at constant T, V we obtain

$$\begin{aligned}\left(\frac{\partial W_\mu}{\partial \mu}\right)_{T,V} &= -\frac{\sum_N N Q_\mathrm{f}(N, V, T)\mathrm{e}^{N\mu/kT}}{\sum_N Q_\mathrm{f}(N, V, T)\mathrm{e}^{N\mu/kT}} + \frac{\sum_N N Q_\mathrm{i}(N, V, T)\mathrm{e}^{N\mu/kT}}{\sum_N Q_\mathrm{i}(N, V, T)\mathrm{e}^{N\mu/kT}} \\ &= -\langle N\rangle_\mathrm{f} + \langle N\rangle_\mathrm{i} = -\Delta\langle N\rangle .\end{aligned} \tag{24}$$

This is the nucleation theorem. Again, the angle brackets, indicate *average* numbers, and emphasize the fact that in the grand ensemble the molecular numbers can fluctuate! Correspondingly, in the thermodynamic limit, these fluctuations will be very small and, in a development involving the formation of a single cavity, $\langle N\rangle_\mathrm{f}$ and $\langle N\rangle_\mathrm{i}$ could differ by as little as a single molecule or less. Furthermore, since these numbers are averages, they need not be integers.

We return to this issue below, but it is worth remarking that fluctuations will be especially significant at a value of μ corresponding to a phase transition. It is important to note that $(\partial W_\mu/\partial\mu)_{T,V}$, and W_μ itself, may *normally* be discontinuous and undefined at the value of μ corresponding to a phase transition, since they must be defined in one phase *before* the transition and in another phase *after* the transition. We comment further on this issue below, but at this point it should be noted that if, in some application, it should arise that $\langle N\rangle_\mathrm{f}$ was predicted to exceed $\langle N\rangle_\mathrm{i}$, Eq. (24) would require $(\partial W_\mu/\partial\mu)_{T,V}$ to be negative.

5 Conventional Derivation of the Reversible Work Involved in Cavity Insertion

In the most common use of the grand ensemble, especially in the thermodynamic limit, the actual fluctuation of the molecular content of the open system is disregarded. However, since the cavities of interest, as well as the corresponding density inhomogeneities, are of molecular dimensions, we must now be aware of fluctuations. Normally, the grand potential Ω is written simply as $\Omega = F - N\mu = U - TS - N\mu$ whereas in fact U and $N$are respectively the averages, $\langle U\rangle$ and $\langle N\rangle$ over a fluctuating internal energy and fluctuating molecular content. The entropy $S$is subject to another interpretation. It measures all possible states of the system *including those that correspond to fluctuations*. It is therefore not an average. Still, there are other averaged quantities; for example pressure p, and we should write $\langle p\rangle$ in place of$p$.

The connection between thermodynamics and mechanics (classical or quantum) using ensemble theory has received considerable study over the years. In particular, for a one-component system, three relations from which the full connection in the grand ensemble can be derived [17] are

$$\langle p\rangle = kT\left(\frac{\partial \ln \Xi}{\partial V}\right)_{T,\mu} \tag{25}$$

$$S(\mu, V, T) = k \ln \Xi + kT \left(\frac{\partial \ln \Xi}{\partial T} \right)_{V,\mu} \tag{26}$$

$$\langle N \rangle = kT \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{T,V}. \tag{27}$$

In these equations the averages indicated by the angle brackets are taken over N.

As an example of how these relations allow the derivation of other bridges between thermodynamics and statistical mechanics we may derive $\langle F \rangle$. In the grand canonical ensemble we write the expression for

$$\langle U \rangle = kT^2 \left(\frac{\partial \ln \Xi}{\partial T} \right)_{V,\mu/T} = kT^2 \frac{\sum_N (\partial Q_N / \partial T)_{N,V} \mathrm{e}^{\mu N/kT}}{\sum_N Q_N \mathrm{e}^{\mu N/kT}} \tag{28}$$

where $Q_N = Q(N, V, T)$ is the canonical ensemble partition function. Equation (26) may be written as

$$S(\mu, V, T) = k \ln \sum_N Q_N \mathrm{e}^{\mu N/kT} + kT \left(\frac{\partial}{\partial T} \ln \sum_N Q_N \mathrm{e}^{\mu N/kT} \right)_{V,\mu} \tag{29}$$

where the sums over Nstill begin with $N = 0$. Substitution of Eqs. (28) and (29) into $\langle F \rangle = \langle U \rangle - TS$ yields

$$\langle F \rangle = -kT \ln \sum_N Q_N e^{\mu N/kT} + \frac{\sum_N \mu N Q_N \mathrm{e}^{\mu N/kT}}{\sum_N Q_N \mathrm{e}^{\mu N/kT}}. \tag{30}$$

Then, with the aid of Eqs. (23) and (26), we find

$$\langle \Omega \rangle = \langle F \rangle - \mu \langle N \rangle = -kT \ln \sum_N Q_N \mathrm{e}^{\mu N/kT} = -kT \ln \Xi(\mu, V, T). \tag{31}$$

In this derivation, the fluctuation of Nhas been properly included. However, it should be remarked that this equation refers to a case where the system has only three independent variables, for example μ, V, T. If there are other kinds of work and corresponding constraints there will be additional independent variables. We discuss this below.

It is instructive to return to Eq. (3). The process to which that equation refers is one of constant μ. Then, combining Eqs. (12) and (31), we find

$$W_\mu = (\Delta\Omega)_{\mu,V,T} = \Omega_\mathrm{f} - \Omega_\mathrm{i} = -kT \ln(\Xi_\mathrm{f}/\Xi_\mathrm{i}) \tag{32}$$

that repeats Eq. (18).

Now consider how the work of formation of a stationary *equivalent* cavity in a hard sphere system is related to the chemical potential μ of a sphere. We consider an open unary hard sphere system in an initial state at chemical potential μ, volume V, and temperature T, and also the same system in a final state containing a stationary *equivalent* cavity [10].

A generally accepted derivation of W_μ has been the following [22]. First add a hard sphere to the *open* system at constant V. The reversible work involved in this step is μ itself. However one correct definition of μ is $(\partial F/\partial N)_{T,V}$. Ignoring fluctuations it is equally described by $(\partial G/\partial N)_{T,p}$. In both cases the system is *open* since a molecule is being added. However, in the first step just described, we are concerned with $(\partial\Omega/\partial N)_{T,V}$. Ultimately, this approach, together with a second step seems to yield a correct final expression. The second step involves the work of subtraction of the translational entropy of the mobile sphere, to which μ refers,

to obtain the entropy of the immobile sphere involved in W_μ and the sum of these two works leads to

$$W_\mu = \mu - kT \ln \frac{\langle N \rangle_{\mathrm{i}} \Lambda^3}{V} = \mu - kT \ln \left(\Lambda^3 \langle \rho \rangle_{\mathrm{i}} \right). \tag{33}$$

However, implicitly, we have mixed ideas from two different ensembles. Thus the use of a more "consistent" argument is suggested and we offer it in the following section.

6 Consistent Derivation of the Reversible Work Involved in Cavity Insertion

A modest increase of notation is convenient for the discussion of the present section. We introduce the quantity $\bar{Z}(N)$ to denote the configuration integral of the N hard spheres surrounding a hard sphere with center *fixed* in an arbitrary volume element $\mathrm{d}\boldsymbol{r}_1$ within the system volume V. The reader should remember that our system is assumed to be subject to periodic boundary conditions and that the normal rules connecting statistical mechanical quantities to thermodynamic quantities are in force.

The N spheres together with the fixed one constitute a system containing $N + 1$ spheres and, when the position of the fixed sphere is integrated over V, we obtain the relation

$$Z(N + 1, V, T) = V \bar{Z}(N, V, T). \tag{34}$$

Now, with V containing N mobile spheres, the initial canonical ensemble partition function may be expressed as

$$Q_{\mathrm{i}}(N) = \frac{Z(N)}{\Lambda^{3N} N!} \tag{35}$$

where we have not shown the dependence on T, V since these quantities will always be present and constant. If we now add an immobile (and *distinguishable*) sphere to the system that can serve as a fixed cavity we obtain the *final* configuration for which the final canonical partition function can be represented as

$$Q_{\mathrm{f}}(N) = \frac{\bar{Z}(N)}{\Lambda^{3N} N!} = \frac{Z(N + 1)}{V \Lambda^{3N} N!} \tag{36}$$

where we have used Eq. (34). $N!$ appears in the denominator instead of $(N + 1)!$ because the fixed sphere (or cavity) is distinguishable.

We can express the initial and final grand partition functions as

$$\Xi_{\mathrm{i}}(\mu, T, V) = \sum_{N=0} Q_i(N) \mathrm{e}^{\mu N/kT} = \sum_{N=0} \frac{Z(N)}{\Lambda^{3N} N!} \mathrm{e}^{\mu N/kT} \tag{37}$$

and

$$\Xi_{\mathrm{f}}(\mu, T, V) = \sum_{N=0} Q_{\mathrm{f}}(N) \mathrm{e}^{\mu N/kT} = \sum_{N=0} \frac{Z(N + 1)}{V \Lambda^{3N} N!} \mathrm{e}^{\mu N/kT} \tag{38}$$

where Eqs. (35) and (36) have been used. Substituting Eqs. (37) and (38) into (32) we obtain

$$W_\mu = kT \ln \left(\sum_{N=0} \frac{Z(N)}{\Lambda^{3N} N!} \mathrm{e}^{\mu N/kT} \right) - kT \ln \left(\sum_{N=0} \frac{Z(N + 1)}{V \Lambda^{3N} N!} \mathrm{e}^{\mu N/kT} \right). \tag{39}$$

Now, it is well known that when N in the sums in Eq. (39) extends to infinity, i.e. when the system is in the thermodynamic limit, each sum is adequately represented by its maximum

term. For example, the maximum term in the first sum of Eq. (37) satisfies the condition

$$\left(\frac{\partial \ln Q_{\mathrm{i}}(N)}{\partial N}\right)_{T,V} = -\frac{\mu}{kT}. \tag{40}$$

Applying this kind of relation to Eq. (39) results in

$$W_\mu = \mu - kT \ln \frac{\Lambda^3 \langle N\rangle_{\mathrm{f}}}{V} = \mu - kT \ln\left(\Lambda^3 \langle \rho\rangle_{\mathrm{f}}\right) \tag{41}$$

which is to be compared to Eq. (33). However, Eq. (41) has been derived in a more thermodynamically consistent manner whereas Eq. (33) is based on a method that relies on an argument involving several leaps of inconsistency. Nevertheless, it can be shown that although the two relations are nearly the same, Eq. (33) can lead to some unphysical conclusions if substituted into an argument where Eq. (41) avoids such an outcome.

We have come far enough to know that both $\langle N\rangle_{\mathrm{i}}$ and $\langle N\rangle_{\mathrm{f}}$ depend on μ (or p) and it is obviously important to understand these dependences as well as their inverses. This problem is addressed in the following section.

7 Relation Between $\langle N\rangle_{\mathrm{f}}$ and $\langle N\rangle_{\mathrm{i}}$ as μ is Varied

It is known that, in a unary hard sphere system at stable equilibrium, the density $\rho = \langle N\rangle / V$ in a μ, V, T system increases with increasing chemical potential. As already mentioned, a standard proof of this behavior is worthwhile (see Eq. (15)). However, we now introduce the subscripts i into the proof (see Eq. (14))

$$\langle N(T,V,\mu)\rangle_{\mathrm{i}} \sum_N Q(N,V,T)\mathrm{e}^{\mu N/kT} = \sum_N N Q(N,V,T)\mathrm{e}^{\mu N/kT}. \tag{42}$$

Differentiation of both sides of this equation with respect to μ, followed by some rearrangement, gives

$$kT\left(\frac{\partial \langle N\rangle_{\mathrm{i}}}{\partial \mu}\right)_{T,V} = \left\langle N^2\right\rangle_{\mathrm{i}} - \langle N\rangle_{\mathrm{i}}^2 = \left\langle (N - \langle N\rangle_{\mathrm{i}})^2\right\rangle_{\mathrm{i}} \geq 0 \tag{43}$$

which of course confirms the result that $\langle N\rangle_{\mathrm{i}}$ at constant T,V must increase with μ.

Differentiating Eq. (41) with respect to μ gives

$$\left(\frac{\partial W_\mu}{\partial \mu}\right)_{T,V} = 1 - \frac{kT}{\langle N\rangle_{\mathrm{f}}}\left(\frac{\partial \langle N\rangle_{\mathrm{f}}}{\partial \mu}\right)_{T,V} = \langle N\rangle_{\mathrm{i}} - \langle N\rangle_{\mathrm{f}} \tag{44}$$

where, in the last step we have made use of the *nucleation theorem.* The second equality in this equation can be rearranged to yield

$$\frac{kT}{\langle N\rangle_{\mathrm{f}}}\left(\frac{\partial \langle N\rangle_{\mathrm{f}}}{\partial \mu}\right)_{T,V} = \langle N\rangle_{\mathrm{f}} - \langle N\rangle_{\mathrm{i}} + 1 \geq 0 \tag{45}$$

where the inequality stems from the fact that $(\partial \langle N\rangle_{\mathrm{f}} / \partial\mu)_{T,V}$ like $(\partial \langle N\rangle_{\mathrm{i}} / \partial\mu)_{T,V}$ can be shown (by the same procedure) to be positive. But, clearly, this can only be the case if

$$\langle N\rangle_{\mathrm{f}} > \langle N\rangle_{\mathrm{i}} - 1. \tag{46}$$

Thus Eq. (46) establishes a lower limit to$\langle N\rangle_{\mathrm{f}}$.

In addition we *already* possess a somewhat concealed upper limit in Eq. (24)! This relation shows that, if $\langle N\rangle_{\mathrm{f}}$ exceeds $\langle N\rangle_{\mathrm{i}}$, $(\partial W_\mu / \partial\mu)$ must be negative. This implies that reversible

work is performed *by* the system on its environment and is therefore a violation of the mechanical stability relation. Thus, the upper limit is

$$\langle N\rangle_{\mathrm{f}} = \langle N\rangle_{\mathrm{i}} \tag{47}$$

and we can write

$$\langle N\rangle_{\mathrm{i}} \geq \langle N\rangle_{\mathrm{f}} \geq \langle N\rangle_{\mathrm{i}} - 1. \tag{48}$$

Thus, not surprisingly, $\langle N\rangle_{\mathrm{f}}$ is limited to the *unit interval*, Eq. (48), since the perturbation of the system is subject to the insertion of only a *single* cavity!

The mention of this relation generates an interesting perspective on the significance of $\langle N\rangle_{\mathrm{f}}$. From one point of view, its location in the interval, $\langle N\rangle_{\mathrm{i}} - 1$ to $\langle N\rangle_{\mathrm{i}}$, allows it to serve as a vernier even though it is itself essentially infinite. On the other hand, it is a measure of the final number of hard spheres accompanying the insertion process. The critical measure in this application is Eq. (48). Both $\langle N\rangle_{\mathrm{i}}$ and $\langle N\rangle_{\mathrm{f}}$ are functions of μ and we need to find the value of μ at which Eq. (48) is satisfied. If that value exceeds the value at which the equilibrated system "freezes", it may be of little use since our analysis thus far (most of our equations) is predicated on the system being in the *stable* equilibrated *fluid* state. However, our focus is on the relative motion, of $\langle N\rangle_{\mathrm{f}}$ and $\langle N\rangle_{\mathrm{i}}$ as μ is varied. Equation (48) shows that $\langle N\rangle_{\mathrm{f}}$ is "trapped" between $\langle N\rangle_{\mathrm{i}} - 1$ and $\langle N\rangle_{\mathrm{i}}$. Thus, if μ and therefore $\langle N\rangle_{\mathrm{i}}$ is increased, $\langle N\rangle_{\mathrm{f}}$ must still be less than or equal to $\langle N\rangle_{\mathrm{i}}$.

8 Stability Condition and the Hard Sphere Freezing Transition

The experimental dependences of p on μ or ρ can, in principle, be determined by a molecular dynamics computation subject to periodic boundary conditions. The fluid branch of the $p - \rho$ isotherm, determined thus far in this manner, *appears* to rise continuously with ρ until the freezing density of the system is reached! However, if this monotone behavior in the fluid continues *right up* to the density of the *equilibrium* solid phase, a question arises concerning how the equilibrium fluid finds the appropriate equilibrium crystalline structure. In this connection it is well known that, from the viewpoint of thermodynamics, the transition is driven by the increase of entropy associated with the larger number of configurations available to the system in the solid even at a higher density. This mechanism has currently received increased attention in a number of situations beyond the freezing of the hard sphere system [23,24].

Of course, time is not an issue in equilibrium thermodynamics, and the discussion of the previous paragraph uses the language of time as a rhetorical tool rather than a physical reality. Recently, Professor R. L. Scott asked one of us (HR) "how, in a molecular dynamics experiment, does the freezing system find the correct lattice?" Again, this is a *rhetorical* rather than a *physical* question!

A possible answer is that the hunt for the lattice takes place in the fluid phase, at a density very slightly below that of the solid, but where mobility far exceeds that in the solid. In such a domain the equilibrium structure of the fluid might then resemble a distorted version of the targeted equilibrium solid phase in which long range order has disappeared as a result of the distortion. In fact, several authors have mentioned this idea in casual discussions dealing with second order transitions and related phenomena.However, in this case, experiment would be hard pressed to demonstrate such behavior, given the difficulty of simulating the system in the limited density range in the neighborhood of the phase transition. Nevertheless, assuming such *pretransition* behavior, instead of p continuing to rapidly rise with increasing ρ, the

$p - \rho$ isotherm should bend to the right (in the thermodynamic limit) and eventually exhibit $(\partial \langle N \rangle / \partial \mu)_{T,V} \to 0$ so that it reaches the stability limit implied by Eq. (15). This behavior is expected since at constant V there must be a packing limit to $\langle N \rangle$ while μ could increase indefinitely. Thus the stability condition would play a role in the phase transition.

9 Analytical Estimate of the Freezing Density

Based on the scenario of the preceding section, a theoretical estimate of the freezing density has been made (without the full justification presented in the present paper). The reader can find that estimate and its details, such as they are, in [25]. Here we only present the estimate as well as an abbreviated description of its details, some of which are exact:

a. We assume at the outset that a fluid–solid freezing transition does occur.
b. We require the fluid system to configure itself so that, at any density V_0, the *available space* is as large as possible. (The "available space" was first introduced by Boltzmann and in more recent times has been used in the statistical mechanics of hard particles and often confused with the *free volume* that is related but different. In the case of hard spheres the chemical potential can be exactly represented by $\mu = kT \ln(\Lambda^3 N / V_0)$.)
c. The system should be as uniform as possible.
d. It is assumed that in the fluid, very close to the freezing density, V_0 is maximally small.
e. V_0 cannot vanish on the stable fluid isotherm. This requirement is discussed in detail in Sect. 5 of [25].

Based on these requirements, the *distorted* hard sphere fluid at the density just below that of freezing could have a structure comparable to that obtained by stacking honeycomb lattice planes in place of simple hexagonal planes (see Fig. 4 of [25]). This produces a cubic closepacked (ccp) three dimensional lattice. For this three dimensional lattice, V_0 will vanish when the honeycomb structures become closepacked and the reduced density $y = \pi a^3 \rho / 6$ is chosen as

$$y = y_0 = \sqrt{2}\,\pi / 9 \approx 0.4937. \tag{49}$$

For comparison, the value of the freezing density obtained by means of computer simulation is

$$y = y_f = 0.494. \tag{50}$$

Although this comparison is satisfying the mechanistic picture of the phase transition rather than the successful numerical prediction should be regarded as the most important result of our analysis.

It should be noted that our method of estimate of y_f differs from previous methods in a somewhat fundamental way from those based on determining the density at which the pressure and chemical potential in model fluid and solid phases are equal. *In the present method, the particular properties of the solid are never specified!* Still, the method in general is based on some approximation and the results may not be as accurate for systems besides the important one dealing with hard spheres.

As far as the mechanistic features of the method are concerned, a successful molecular dynamics study of the system at the freezing density would be invaluable but we know that such studies are extremely difficult although several admirable approaches are described and applied in the literature.

Actually, according to our view, y_0 should exceed $y_f \ldots$ by a small amount. If it did not, the fluid would be *unstable* before it froze and our theory would not apply. The fundamental

idea is that the system should be in the *equilibrium fluid state*, where its structure is easily adjusted while it is establishing a structure close to that of the solid (this would partially answer Professor Scott's query). Since our estimates of y_0 and y_f are close it remains a viable possibility that y_0 exceeds y_f However, as a cautionary note, and as indicated earlier (see Sect. 7), the stability condition derived for a region where $(\partial W_N/\partial \mu)$ is negative would not be valid since the system might be metastable in that region where there are constraints not taken into account (for example cavity surface tension as in nucleation theory).

Given the argument of the last few paragraphs, it would be desirable to design an attempt to perform a *super* molecular dynamics simulation…one that still doesn't exist… with the goal of displaying the equilibrium structure of the hard sphere fluid at a density extremely close to the freezing density. We recognize that the freezing density itself may not now be known with the required accuracy, but if the indicated goal could be reached, the result might confirm that $y_f < y_0$.

In closing, it is worth repeating that our analysis is based on the study of successive *stable* equilibrium states of the *open* system as density is increased. The "openess" of the system is important. Thus, since V is held constant, density may be increased by the addition of hard spheres until $y$reaches and surpasses y_f. Beyond that point the fluid, if it persisted, would no longer be in *stable* but rather in *metastable* equilibrium. If it does not persist, y_f would be identified!

In a normal study of nucleation and solidification, embryonic fragments of the solid would appear first such that the system would have been constrained into *metastable* equilibrium while these fragments grew into *stable* equilibrium. Our thought experiment and the essentially kinetic experiment, just described, would have different natures.

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