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# "Magic Relation" Between the Structures of Coexisting Phases at a First-Order Phase Transition in a Hard Sphere System

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In the statistical geometry of a hard sphere system of any number of dimensions, $V_o$ and $S_o$, the so-called *available space* and the area of the interface between the *available* and *unavailable space*, respectively, can be used as surrogates for chemical potential and pressure. It is shown exactly that, if a first-order transition occurs, the relation $dV_o/dS_o = -\sigma/2D$, where $\sigma$ is the diameter of a sphere and $D$ is the dimensionality of the system, must hold for densities in the phase coexistence region. This relation is remarkable in that $-\sigma/2D$ is the ratio of the volume to the surface area of a sphere. Also, it is shown that it is possible for the system to have two successive first-order transitions, but that the occurrence of a continuous transition (even in two dimensions) is unlikely. It is argued that this unlikelihood is substantially strengthened by the absence of temperature (except as a trivial factor) as a variable in hard-sphere systems. This suggests that the findings of the KTHNY theory, recent simulations, and colloid experiments (specialized to "sticky" hard disks) can be extended to true hard disks. The fundamental physics underlying the "magic relation" is yet to be exposed. The author continues to search for the underlying reason and hopes that the present paper will stimulate others to join the search.

**KEY WORDS:** Hard spheres; statistical geometry; available space; cavities; phase transitions.

## 1. SOME STATISTICAL GEOMETRICAL FORMULAS

It has been known for some time that, for hard particle systems, the *available space* $V_o$ and the area of the *interface* $S_o$ separating the *available*

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from the *unavailable space*, quantities defined in statistical geometry,$^{(2)}$ can be used in statistical thermodynamic analyses as surrogates for the chemical potential and pressure. $V_o$ is the possibly multiply connected volume within the system at which the center of an additional hard particle may be placed and is closely connected to the well known insertion probability$^{(3-5)}$ while $S_o$ is the area of the complex extended interface separating $V_o$ from the remaining volume of the system. Both $V_o$ and $S_o$ are "average" quantities but, in the thermodynamic limit, the following relations have been shown to be exact.$^{(6-10)}$

$$\mu = kT \ln \frac{\Lambda^D N}{V_o} \tag{1}$$

$$P = \frac{NkT}{V}\left[1 + \frac{\sigma S_o}{2DV_o}\right] \tag{2}$$

$$F = NkT\left[\ln \frac{\Lambda^D}{V_o} - 1 - \frac{\sigma S_o}{2DV_o}\right] \tag{3}$$

In these equations $\mu$ is the chemical potential, $P$ is the pressure of the system, $F$ is the Helmholtz free energy of the system, $k$ is the Boltzmann constant, $T$ is the temperature, $\Lambda$ is the thermal de Broglie wavelength of a particle, $N$ is the number of particles in the system, $V$ is the volume of the system, $\sigma$ is the diameter of a particle, and $D$ is the dimensionality of the system. Eqs. (1) and (2) are the basis for the statement that $S_o$ and $V_o$ can be used as surrogates for $\mu$ and $P$.

In spite of the beautiful simplicity of these equations, workers have apparently not yet been able to exploit them as fully as might be expected upon first sight. There is of course the successful use of the "insertion probability," embodied in Eq. (1), in simulation and in theory (for example in *scaled particle theory*$^{(6, 11)}$) as well as in the demonstration that the free volume equation of state holds in the limit of high density$^{(12-15)}$), but the geometrical and structural intuition, implicit in the equations, has certainly not been yet been fully utilized. There has been some tentative application$^{(16)}$ in an attempt to estimate the density at which a freezing transition should occur, but even this approach has not been fully developed. In addition, there has been a partially successful effort to show that the equations can be derived for a lattice system.$^{(17)}$ One might conclude because of this limited progress, that the equations are "pretty" but not very useful. In the present author's opinion, however, the final returns on this issue are not yet in, and in this paper we will present still another incarnation of the equations that seems remarkable enough to be dubbed a "magic relation."

## 2. THE MAGIC RELATION

We now consider the "hard sphere" fluid-solid phase transition.(18) In order to proceed we will introduce a simple expansion of notation, appending a subscript f to quantities referring to the fluid and a subscript s to those referring to the solid. The only variable of significance in the hard sphere system is the density $\rho = N/V$, and we will *assume* that the system undergoes a first-order transition such that the fluid freezes at a density $\rho_f$ and melts at $\rho_s$ where $\rho_s \neq \rho_f$. Between these densities the fluid and solid phases coexist. It is simplest to hold $V$ fixed and to vary $\rho$ by varying $N$. Then, for $N = N_f$ and $N = N_s$ we have

$$\mu_f = \mu_s \tag{4}$$

and

$$P_f = P_s \tag{5}$$

Substitution of Eqs. (1) and (2) into these equations yields

$$\frac{V_{os}}{V_{of}} = \frac{N_s}{N_f} > 1 \tag{6}$$

and

$$N_f \left[ 1 + \frac{\sigma S_{of}}{2DV_{of}} \right] = N_s \left[ \frac{\sigma S_{os}}{2DV_{os}} \right] \tag{7}$$

Eq. (7) can be rearranged into the form

$$\frac{N_f S_{of}}{V_{of}} - \frac{N_s S_{os}}{V_{os}} = \frac{2D}{\sigma} \ (N_s - N_f) > 0 \tag{8}$$

The inequalities in Eqs. (6) and (8) follow from the fact that the density of the solid exceeds that of the fluid. Thus, since $V_{os} > V_{of}$, $V_o$ increases during the transit of the coexistence region. Substitution of the equality in Eq. (6) into Eq. (8) yields

$$S_{of} > S_{os} \tag{10}$$

Thus, whereas $V_o$ increases during the transition, $S_o$ decreases. These various *exact* results have been derived previously,(10) and they are presented in order to set the stage for the derivation of the new result, Eq. (11) below.

Substitution of the equality in Eq. (6) into Eq. (7) yields the exact result

$$\frac{V_{\mathrm{os}} - V_{\mathrm{of}}}{S_{\mathrm{os}} - S_{\mathrm{of}}} = -\frac{\sigma}{2D} \tag{11}$$

This is the “magic relation.” It was derived by the author several years ago, but never published, although discussed with various colleagues. The formula is remarkable on several counts. Before proceeding to explore these features, we again stress the fact that the derivation of Eq. (11) is based on the assumption that the system *does* undergo a first-order transition. Thus, the magic relation is an exact, *necessary* consequence of the occurrence of such a transition. As such, it represents a sensitive test for the first-order nature of a transition. On the other hand, it is not a *sufficient* condition for the occurrence of a transition. Having made this point, it is appropriate to emphasize the fact that the relation *does not contain the density explicitly*, i.e. it does not contain $N$, $N_{\mathrm{f}}$, $N_{\mathrm{s}}$. We return to this point later.

In one sense, Eq. (11), being only a single condition, is not as restrictive as the combination of the two conditions, Eqs. (4) and (5). However, in a structural and *geometric sense* it is quite restrictive, and raises the question as to what pair of *average* fluid and solid structures can satisfy it.

## 3. MORE ABOUT THE RELATION

If $N$ lies in the phase coexistence range, it follows quite simply (as a lever rule) that

$$V_{\mathrm{o}} = \left(\frac{N_{\mathrm{s}} - N}{N_{\mathrm{s}} - N_{\mathrm{f}}}\right) V_{\mathrm{of}} + \left(\frac{N - N_{\mathrm{f}}}{N_{\mathrm{s}} - N_{\mathrm{f}}}\right) V_{\mathrm{os}} \tag{12}$$

and

$$S_{\mathrm{o}} = \left(\frac{N_{\mathrm{s}} - N}{N_{\mathrm{s}} - N_{\mathrm{f}}}\right) S_{\mathrm{of}} + \left(\frac{N - N_{\mathrm{f}}}{N_{\mathrm{s}} - N_{\mathrm{f}}}\right) S_{\mathrm{os}} \tag{13}$$

Differentiating both of these equations with respect to $N$, and taking the ratio of the results, gives

$$\frac{dV_{\mathrm{o}}}{dS_{\mathrm{o}}} = \frac{V_{\mathrm{os}} - V_{\mathrm{of}}}{S_{\mathrm{os}} - S_{\mathrm{of}}} = -\frac{\sigma}{2D} \tag{14}$$

Where the second equality is simply Eq. (11). This equation is a more compact form of the magic relation. Thus, in the coexistence region, the derivative of the total available space with respect to the total interface area is a negative constant equal to $-\sigma/2D$. That constant which also appears in Eq. (11), is just the negative of the ratio of the volume to the surface area of a hard sphere.

The fundamental reason for this is, at present, unclear, but the following feature may be related to it. For simplicity, consider a three dimensional system. The actual volume in the system not covered by spheres, at any value of $N$, is

$$\tilde{V}_{\mathrm{o}} = V - \frac{\pi\sigma^3 N}{6} \tag{15}$$

and the total surface area of the spheres is

$$\tilde{S}_{\mathrm{o}} = \pi\sigma^2 N \tag{16}$$

Since $N$ is the only variable in Eqs. (15) and (16), it follows that

$$\frac{d\tilde{V}_{\mathrm{o}}}{d\tilde{S}_{\mathrm{o}}} = -\frac{\sigma}{6} = -\frac{\sigma}{2D} = \left(\frac{dV_{\mathrm{o}}}{dS_{\mathrm{o}}}\right)_{\mathrm{coex}} \tag{17}$$

where the subscript "coex" indicates that the derivative refers only to values of $N$ in the coexistence range. In contrast, the derivative at the left corresponds to any value of $N$. We have used the symbols $\tilde{V}_{\mathrm{o}}$ and $\tilde{S}_{\mathrm{o}}$ to denote the geometric properties of the volume not covered by spheres, i.e. symbols similar to those associated with the available space, because the noncovered volume can be regarded as the available space for a single *point* "solute" in a "solvent" of hard spheres. Stillinger(19) has examined the available space for solutes intermediate in size between a point and a sphere of diameter $\sigma$ and has shown that the magic relation does not apply to these intermediate spheres. It is therefore limited to spheres having radii equal to zero or $\sigma$ only. This limitation is reasonable. The ratio in Eqs. (11) or (16) has the dimension of length, and in the two extreme systems there is only one fundamental length, namely $\sigma$. Thus $\sigma$ must appear on the right side of Eq. (11) and in the middle of Eq. (17), and the only thing to be explained is the coefficient, $-1/2D$. On the other hand, in an intermediate system having a solute sphere larger than a point, there are two lengths corresponding to the diameters of the solute and solvent, respectively. Hence Eq. (17) need not apply. However, recently, Corti and Bowles(20, 21) have derived the equivalent of Eq. (14) for mixtures of hard spheres (including a mixture in which there is only one solute sphere) and have shown that a similar relation can hold for such a mixture. However, in this case, the available space is a weighted sum of the available spaces of the various components, and not merely the space available to the solute.

Now the changes in both $\tilde{V}_o$ and $\tilde{S}_o$, upon the addition of a sphere, depend only on the added sphere, and the ratio of these changes is in fact constant. In the case of $V_o$ and $S_o$, in the coexistence region, the addition of a sphere will only induce additional freezing without altering the intensive properties of the individual phases. The amount of additional freezing will clearly be the same for each sphere that is added. Thus, the ratio of the change in $V_o$ to the change in $S_o$ may be expected to remain constant, as in the case of $\tilde{V}_o$ and $\tilde{S}_0$, but the physical reason for its equaling $-\sigma/2D$, or at least the coefficient, $-1/2D$, remains to be understood. It should also be noted that the minus sign in the magic relation for $V_o$ and $S_o$ is a result of an *increase* in $V_o$ and a *decrease* in $S_o$, upon the addition of a sphere, whereas in the case of $\tilde{V}_o$ and $\tilde{S}_o$ the reverse is true; $\tilde{V}_o$ *decreases* while $\tilde{S}_o$ *increases*!

## 4. CAN THE MAGIC RELATION BE SATISFIED?

Figure 1 constitutes one sort of graphic description of Eq. (17). It exhibits a schematic plot of $dV_o/dS_o$ versus $N$ (i.e. versus density, since $V$ is constant) whose qualitative features are consistent with whatever precise knowledge is available concerning $V_o$ and $S_o$ (at least for a 3 dimensional system, so that it is most appropriate to consider the figure in terms of such a system). We know that at low densities $V_o$ decreases with increasing $N$ while $S_o$ increases. Thus, at small $N$, the derivative is negative as in the figure. Ultimately, as $N$ is increased, $V_o$ becomes multiply connected and is contained in many isolated cavities. As $N$ is increased further, a point will be reached at which $S_o$ will decrease while $V_o$ will continue to decrease. At this point, $S_o$ will pass through a maximum so that the derivative will pass through zero and exhibit positive values, again as in Fig. 1. It can be proved *exactly*(2, 10) that the maximum must occur at densities lower than those at which any first-order freezing transition occurs. We can guess that the positive values of the derivative themselves pass through a maximum as the density is increased, and this guess has been incorporated into the plot in the figure. The guess is based on the assumption that the cavities remain compact and roughly spherical as they become smaller, so that the derivative will scale roughly as the decreasing average radius of a cavity.(14, 15) When $N$ reaches $N_f$ corresponding to the freezing density (assuming that a first-order transition occurs), Eq. (17) must be obeyed, and the derivative jumps discontinuously to the negative value, $-\sigma/2D$, as shown in the figure. It retains this negative constant value until $N$ reaches $N_s$, corresponding to the melting density, at which point it

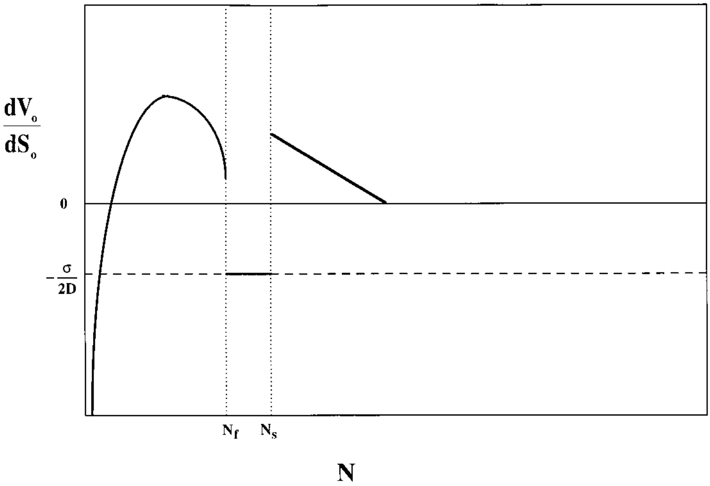

Fig. 1. Schematic plot of $dV_o/dS_o$ versus $N$ (at fixed $V$) for a hard sphere system. The discontinuities appearing at the extremes of the coexistence region are demanded by the magic relation together with the fact that the derivative must be positive at any density larger than that at which the available space becomes distributed over compact cavities. It can be proved, exactly, that the maximum in the derivative must occur at a density lower than that of a first-order transition.

jumps discontinuously to a positive value characteristic of the solid. Thereafter, assuming the cavities to be compact, it decreases toward zero at close packing.

We have emphasized that Eqs. (11) and (17) do not depend explicitly on density. At the same time, $V_{\text{os}}$ and $S_{\text{os}}$ as well as $V_{\text{of}}$ and $S_{\text{of}}$ depend uniquely on $N_s$ and $N_f$ (or densities), respectively, and in each phase they have no knowledge of the density-independent magic relation which they are supposed to satisfy. This raises the question of how that relation *can* be satisfied. Even if it is satisfied, a phase transition is not assured unless Eq. (6) is simultaneously satisfied. To gain some insight into this matter we refer to Fig. 2. In this figure it is convenient to deal with the dimensionless variables $\hat{V}_o = V_o/\sigma^D$ and $\hat{S}_o = S_o/\sigma^{D-1}$, in terms of which Eq. (17) can be expressed as

$$\frac{d\hat{S}_o}{d\hat{V}_o} = -2D \tag{18}$$

Figure 2 contains, as parts A, B, C, three different totally schematic sets of plots of $\hat{S}_o$ versus $\hat{V}_o$. (Note that these plots are almost entirely schematic

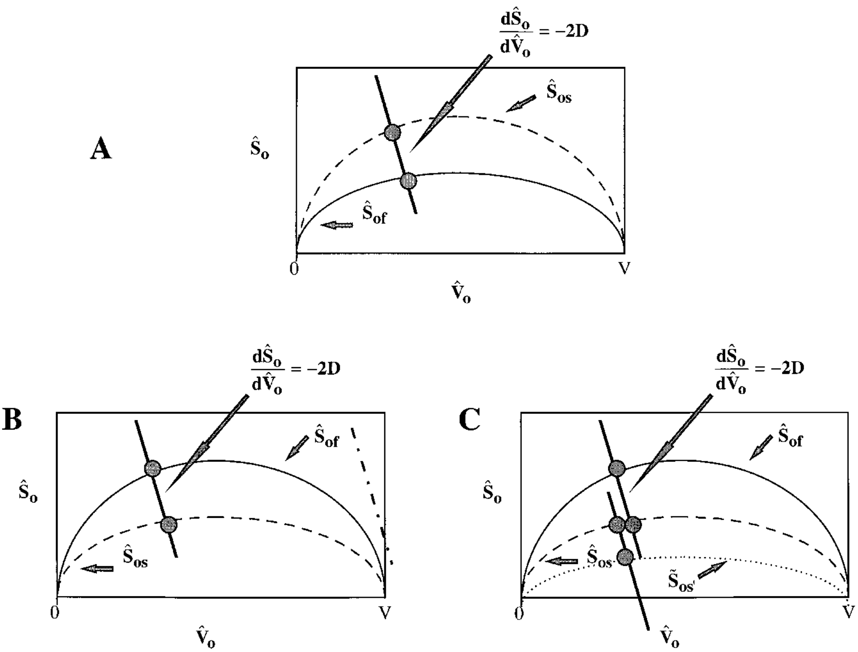

Fig. 2. Various plots of $\hat{S}_o$ versus $\hat{V}_o$. The straight line of negative slope corresponds to Eq. (18), and the occurrence of a first-order phase transition requires that Eqs. (6) and (10) be simultaneously satisfied by the points of intersection of the straight line with the curves for the fluid and solid that appear in each part of the figure. On this basis, first-order transitions are possible in parts B and C. In part C, conditions are such that two successive first-order transitions are possible.

and presented only for the purpose of facilitating the associated discussion. However, the curves do conform to the requirements that $S_o$ and $V_o$ vanish at close packing while $S_o$ vanishes at zero density while $V_o$ becomes equal to $V$.) A and B each contain a supposed plot for the fluid phase (solid line) together with a supposed one for the solid phase (dashed line). Superimposed on these curves is a heavy solid straight line of slope, $-2D$, representing a possible plot of Eq. (18). The intersections of this line with the curves are represented by small shaded spheres. It should be emphasized that, although the plots are schematic, in any actual case they are determined by the physics of the system and in this sense they are invariant and beyond our control.

First, consider part A. The curves for solid and liquid are denoted respectively by $\hat{S}_{os}$ and $\hat{S}_{of}$. In this case the curve for the solid lies above that for the fluid. *Note that points on the two curves corresponding to the* *same value of $\hat{V}_o$ will generally correspond to different densities.* (Again, density does not appear explicitly in the magic relation.) The straight line of slope, $-2D$, can be translated, parallel to itself, over the two curves, and it is clear that at any translated position, the points of intersection must satisfy the magic relation, Eq. (18), since they lie on a line whose slope is prescribed by that equation. The question then arises as to which position of the straight line is the correct one. Normally, the correct position would be determined by the need for the points of intersection to simultaneously satisfy Eq. (6). But this can never be the case for the curves in part A of the figure. Equation (6) can never be satisfied because it requires $\hat{V}_{os} > \hat{V}_{of}$, and in part A the point of intersection on the fluid curve has $\hat{V}_{of}$ greater than $\tilde{V}_{os}$ on the solid curve. It also has $\hat{S}_{of}$ less than $\hat{S}_{os}$ on the solid curve, and this is a violation of Eq. (10). Note that $\hat{V}_o$ on the abscissa runs from $V$ corresponding to zero density to 0 corresponding to a close packed density. In part A, Eq. (6) cannot be satisfied because the curve for the solid lies *above* that for the fluid. With such an arrangement the system cannot have a first-order transition. This result provides a graphic example of our earlier statement that satisfaction of the magic relation is a *necessary* but not a *sufficient* condition for the existence of a first-order transition.

In part B of Fig. 2 the situation is reversed, and the fluid curve lies above the solid curve. It is easy to see that, in this case, both Eqs. (6) and (10), as well as the magic relation, Eq. (18), could now be satisfied simultaneously. Of course, this is not guaranteed and the straight line might be translated to a position like that of the dot-dash line, where it fails to intersect either curve, without satisfying both Eqs. (6) and (10). Everything depends on manner in which $\hat{S}_o$ and $\hat{V}_o$ depend on the density, not explicitly shown in the figure. However, it is unlikely that a satisfactory translation of the straight line will not be found, given the infinite continuum set of possible locations available to it.

Part C of Fig. 2 illustrates another situation. Here there are three curves respectively denoted by the subscripts of, os, and os', and represented by solid, dashed and dotted lines. Those denoted by of and os may again be regarded as belonging to a fluid and solid phase, respectively, while os' designates a possible second nonfluid (solid) phase. Since the dotted curve lies below the dashed one, it offers the possibility of a second first-order phase transition as the density is increased. This is implied by the second magic relation line that intersects the two curves to the left of the one that intersects the solid and dashed curves. Thus the system might exhibit two first-order transitions.

Now, phase transitions in 2-dimensional systems have been the subject of intense scrutiny during the last two decades.(22–31) An important advance in understanding took place with the development of the theory of

Kosterlitz and Thouless,(23, 24) augmented by the modifications introduced by Halperin, Nelson, and Young.(24–26) The theory is now identified by the acronym KTHNY. The original work of Kosterlitz and Thouless focused on the dissociation of vortices, but later work dealt with the dissociation of dislocation pairs in an elastic solid to form disclinations and ultimately a disordered fluid phase. The theory indicated that the melting of the 2-dimensional solid involved two continuous phase transitions. Starting at a high enough density so that the solid hexagonal phase with very long range order, both positional and orientational, was stable, a decrease of density was predicted to induce a phase transition (via dislocation pair dissociation) to a hexatic phase where only orientational order was very long ranged. A further reduction in density predicts a second transition, driven by the dissociation of individual dislocations into disclinations and results in a fluid in which neither positional or orientational order is long ranged. The two transitions are not only supposed to be continuous but are supposed to lie close together on the density axis. It is important to indicate that the argument loses currency for true hard disks, but should hold for disks that have attached to them, a narrow attractive potential well.

Bladon and Frenkel(28) performed a convincing simulation, using disks with narrow square wells (or with narrow potential steps), and argued that their results make it highly plausible that *both* transitions are actually discontinuous and first-order. The KTHNY theory has been modified to include this possibility. Furthermore, in a tour de force experiment involving micron size monodisperse polymethylmethacrylate (PMMA) spheres confined in a narrow space between two plates, Marcus and Rice(31) seem to have demonstrated the first-order nature of both transitions.

The question that remains concerns whether this scenario applies to true hard disks, e.g. to disks that do not have narrow potential wells. The analysis of the present paper is suggestive in this respect, and to proceed further we consider the possibility of the occurrence of continuous transitions. Figure 3 is relevant to this purpose. The two curves in the figure refer to the solid and the fluid, and again we note that, although they are schematic, they are determined by the system and are beyond our control. On the right, the solid curve lies above the fluid one so that, in this interval, there can be no first-order phase transition. On the left, beyond the intersection, the situation is reversed and there *could* be a first-order transition. However, as we explain below, there could be a continuous transition at the intersection so that a stable fluid phase would not exist beyond that intersection.

That there could be a continuous transition at the point of intersection follows from the fact that, at such a transition, $\partial P/\partial \mu = N/V = \rho$ is continuous across the transition,(32) so that with $V$ constant, $N$ must be the

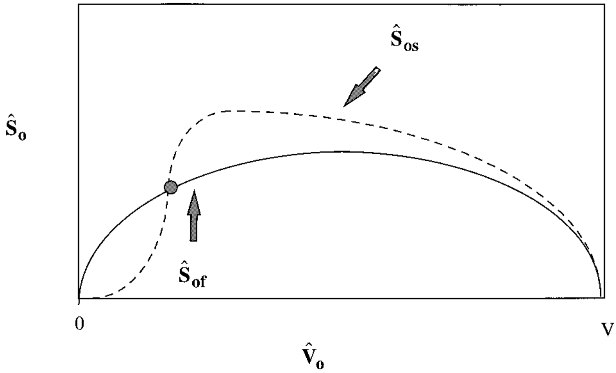

Fig. 3. Plots of $\hat{S}_o$ versus $\hat{V}_o$ that allow a continuous transition, at the intersection between the two curves, provided that, at the intersection, $N$ is the same on the two curves.

same on either side of the transition. The simultaneous solution of Eqs. (1) and (2), with $N$, $\mu$, and $P$ the same, for the phases on either side of the transition, shows that $\hat{S}_o$ and $\hat{V}_o$ must each be the same on either side, and this is just the case at such a point. Note that, because there are no changes in $\hat{S}_o$ and $\hat{V}_o$, the derivative in Eq. (18) is indeterminate and the magic relation is irrelevant.

Note also that the mere existence of the point of intersection does not guarantee the occurrence of a continuous transition anymore than the satisfaction of the magic relation alone, in Fig. 2B, guarantees a first-order transition. There must also be a special relation between the $N$'s in the two phases. In this case the two $N$'s must be equal. But now, presented by the system with two intersecting curves, we do not have the freedom, as we had with the magic relation in regard to the satisfaction of Eq. (6), of sliding that intersection along the $\hat{V}_o$ axis until the $N$'s match. Put in another way, the "intersection" requirement can only be satisfied at a single point whereas the "magic relation" can be satisfied almost everywhere within the range of the two curves. Thus the mathematical requirement has become much less flexible and it might seem that a continuous transition is far less likely.

However, when the argument of the last paragraph is considered from the purely *mathematical* point of view, both types of transition are subject to the *same* degree of restriction. This is because, for *both* types of transition, there are *two* mathematical steps or conditions that have to be satisfied, and therefore it could be argued that either transition is subject to the same level of restriction! In each case, a first step involves finding a unique relation between the $\hat{S}_{of}$ and $\hat{S}_{os}$ curves. In the case of the first-order transition, this relation is simply the "magic relation" while, for the continuous transition it is the "intersection" of the curves. The second step involves the satisfaction of a particular relation between the $N$'s in the pair of curves. For the first-order transition, that relation is Eq (6) while, for the continuous transition, it is the requirement that each member of the pair have the *same* value of $N$ at the intersection.

A difference in the degree of restriction, although not apparent when the problem is considered from the *mathematical* point of view, is more evident when it is looked at from the *physical* point of view. Then we have to consider the situation in terms of the *pairs* of particle configurations that represent the two phases between which a transition takes place. In the case of a first-order transition, the "magic relation" can be satisfied over an extensive range of $\hat{V}_o$, or in other words, by a very large number of configurational pairs. In contrast, in the case of a continuous transition, the "intersection" is limited to just *one* value of $\hat{V}_o$. Furthermore, at this single value of $\hat{V}_o$, the pair of configurations must be such that each member refers to the same value of $N$. The *physical* likelihood that a physical system will have configurational pairs that submit to these conditions is not very good. On the other hand, as has already been noted, there is an abundance of configurational pairs that satisfy the magic relation. So, in the case of a first-order transition, the system has a large number of pairs to choose from in satisfying Eq. (6). Consequently, a first-order transition must be regarded as considerably more likely than a continuous one. Indeed, on this *physical* basis the occurrence of a continuous transition might be considered to be almost excluded.

This suggests that the findings of Bladon and Frenkel(28) and Marcus and Rice(31) can be extended to true hard disk systems.

It has been brought to the author's attention(33) that a continuous transition always requires more special conditions than a first-order one. However, because of the absence of the temperature variable, the situation is more compelling in the case of hard spheres. Up to now, the analysis in this paper has been developed in terms of $V_o$ and $S_o$, in the interest of focussing on structural geometry. But is somewhat easier to make to make the argument about the role of temperature if we return to $\mu$, $P$ space. In fact, since we want to feature the role of temperature, it is best to work in a three dimensional $\mu$, $P$, $N$ space (at constant $V$... so that, in effect, $N$ behaves like an intensive variable). Only two of these three intensive variables is independent in a single component system, and in the case of hard spheres in the subspace of $\mu$ and $P$, only $\mu$ or $P$ is independent. In $\mu$, $P$, $N$ space, the behaviors of the two phases (each identified by a suitable order parameter) between which a continuous transition is supposed to take place could be represented by two parametric curves with say $N$ as the parameter, and for a continuous transition to take place these curves will have to intersect... or at least meet. With an additional degree of freedom, e.g. temperature (not available to hard spheres) this improbable event need not be so improbable. For example, when a supercritical fluid is cooled to just below the critical temperature, the curves for the two phases that result from the symmetry breaking have, in a sense, already met... they are already together... metaphorically, they are nonidentical twins of a common mother. It is therefore not hard to understand how these "siblings" can be in contact and differ only at of some high order derivative.

In contrast, it is hard to see, in the case of hard spheres, lacking the temperature variable (so that no common "mother" exists), how two such curves can get together, especially if they are not broadened into lines of nonzero thickness by fluctuations (which of course will occur to a degree in the vicinity of a transition). Thus one could argue that hard spheres constitute a very special case because of the absence of the temperature variable, and that for these systems in particular, a higher order transition should be virtually impossible.

Recently Karnchanaphanurach, Lin, and Rice(34) have performed additional experiments in the style of Marcus and Rice,(31) but have varied the interaction potential between colloid particles. They still only find a first-order transition (in this case only a single transition) and therefore provide strong evidence that the character (even of the first-order transition) is sensitive to the potential.

In closing this section, it is appropriate to call attention to the fact that none of the phase transition studies, theory or experiment, include an awareness of the cavities that constitute the available space at the high densities in question. Indeed, these cavities and the associated available space form such a small part of the system (at high densities) that it is reasonable to ignore them. On the other hand the available space is a "thermometer" for the equilibrium properties of the system, i.e. it is a "weak probe," whose behavior is subject to many known exact conditions, and for this reason alone, it should not be ignored. In an experiment such as that of Marcus and Rice,(31) both $V_o$ and $S_o$ are exceedingly small and would be very difficult to measure. On the other hand, at lower densities, e.g. in the fluid phase, such measurements may be possible. These could be facilitated by a beautiful technique recently devised by Sastry, Truskett, Debenedetti, Torquato, and Stillinger.(35, 36) The measured $V_o$ and $S_o$ could be substituted into the so-called geometric Gibbs equation (obtained by substituting Eqs. (1) and (2) into $dP = \rho d\mu$), and the degree to which the Gibbs equation was satisfied would constitute a measure of the hard sphere-like nature of the PMMA spheres.

## 5. CONCLUDING REMARKS

We can conclude this paper by emphasizing that the "magic" in the magic relation lies not so much in the fact that the derivative in Eq. (14) equals $\sigma$ times a negative coefficient, but in that the coefficient is the negative of the ratio of the volume of a hard sphere to its surface area. This very special result must have a nontrivial significance, the understanding of which could reveal much about the fundamental basis of the phase transition. The author will continue to search for this understanding, but he hopes that this paper will stimulate others to join the search.

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