Do Hard Spheres have Natural Boundaries?

Barry M. McCoy
Institute for Theoretical Physics
State University of New York
Stony Brook, N.Y. 11794

March 22, 2022

Abstract

I use recent advances in the study of the susceptibility of the Ising model to propose a new mechanism for the freezing transition which is observed in three dimensional hard spheres.

1 Introduction

Recently it has been shown [1] that the susceptibility of the two dimensional Ising model at $H = 0$ has a natural boundary in the complex temperature plane. Furthermore the first 323 terms in the high and low temperature series expansions have been generated [2],[3]. This discovery of a natural boundary gives new insights into phase transitions. In this note I explore possible consequences for the phenomenon of hard sphere freezing.

The freezing transition in the classical hard sphere system has been observed in both molecular dynamics and Monte Carlo computations since the 50’s [4],[5] and 60’s [6],[7] and by now it is well established [8] that there is a first order transition with the coexistence of a fluid phase with a dimensionless volume fraction of $\eta_f = 0.494$ and a solid phase with a volume fraction of $\eta_s = 0.545$ where $\eta$ is defined as $\eta = \rho v_{hs} = \rho \frac{4}{3} \pi r_{hs}^3$ with $r_{hs}$ the radius of the hard spheres and $\rho$ is the number density $N/V$. A non equilibrium glass transition occurs at $\eta_g = 0.58$. By comparison the volume fraction of the closest packed configuration (the FCC lattice) is $\eta_{cp} = \frac{\pi}{3\sqrt{2}} = 0.7405$ which was conjectured by Kepler in 1611 and recently proven by Hales [9]. There is also a volume fraction $\eta_{rcp} = 0.638$ at which random close packing occurs.

Because the volume fractions $\eta_f$ and $\eta_s$ lie well below the densities $\eta_g$ and $\eta_{rcp}$ where possible non ergodic behavior might occur the freezing transition is expected to be described by the partition function of the canonical ensemble. Yet, somewhat surprisingly, after more than three decades of effort the existence of this transition is still considered controversial. This is very well stated in a recent paper [10] “Theory can explain the...
transition only “afterwards”, that is, properties of the coexisting phases should be inserted into the theories in advance, and the coexisting densities follow by minimizing the free energy functional”.

The theory which is usually used to describe the transition (see for example ref. 8 and references contained therein) has remained virtually unchanged for over 30 years 6,7. Typically the high density phase is described by a cell (or free volume) approximation 11 which has the virtue that it is the exact limiting form of the free energy as \( \eta \to \eta_{cp} \). The fluid phase is described by solving a liquid integral equation 12 based on the Percus–Yevik approximation or the scaled particle approximation 13 to the fluid free energy. A more modern approach uses density functional theory 14. These high and low density expressions are then extrapolated out of their regions of validity and in this extrapolated region the densities of coexisting phases are found by a Maxwell construction. This procedure is guaranteed to give a first order transition but cannot actually be called predictive.

On the other hand this description of a first order transition has long ago been called into question by the droplet models of condensation of Fisher 15 and Langer 16 which predict an essential singularity at the coexistence density.

These two points of view of first order transitions are not in harmonious agreement and the state of knowledge is perhaps well described by ref. 10 “· · · from a fundamental viewpoint they [the existing theories of freezing] are still unsatisfactory. The splitting of a hard sphere system into a fluid and a solid branch is, evidently, hidden in the partition function of the system. A thorough theory of hard sphere freezing should therefore identify this property that leads to the observed symmetry breaking”

The purpose of this note is to use the intuition obtained from the recent Ising model computations 1]-3] to reexamine the hard sphere freezing transition and to propose that the phase transition is due to the formation of a natural boundary in the free energy in the complex density plane.

2 Natural Boundaries

Yang and Lee 17 pioneered the study of phase transitions by means of looking at the zeroes of the partition function on a finite size lattice. These zeros will in general not be on the positive real axis (fugacity, temperature or density) but may approach the axis in the limit as \( V \to \infty \). We may classify several of the possible limiting behavior of zeroes as follows:

1) The zeroes can lie on a curve in the complex plane and pinch the real axis at a point (say \( T_c \) for example). In the limit \( V \to \infty \) the curve of zeroes in the complex plane becomes a branch cut and the point of pinching becomes a branch point. This happens in the complex temperature plane for all integrable models and forms the basis of the theory of second order phase transitions. In this picture the thermodynamic functions are singular only at \( T_c \), the point of phase transition.

2) The zeroes can lie in some area of the complex plane, pinch the real axis in some line segment and cut the plane into two disconnected pieces each of which may be analytically continued into the region occupied by the zeroes in the finite size system. In this picture the thermodynamic functions such as the free energy and the pressure are
analytic at the coexistence density $\eta_f$ and the virial expansion will converge for densities greater than $\eta_f$. This picture forms the basis of the theory of first order phase transitions and is exactly the opposite of what happens in a second order transition.

3) The zeroes may pinch the real axis at either a point or a line segment and form a natural boundary in the complex plane. This is the phenomena discovered by Orrick, Nickel, Guttmann and Perk [1]-[3] in the susceptibility of the Ising model.

The first mechanism of phase transition is explicitly seen in every integrable model whose partition function has been computed. However, the computations of ref. [1]-[3] strongly lead to the conjecture that for non integrable models with a second order phase transition there will always be a natural boundary accompanying the singularity at $T_c$ which gives the usual critical exponents. In this sense it may be expected that natural boundaries are generic in second order transitions and that it is only the very special symmetries of integrability which turn the curve of zeroes into a branch cut in the case of integrable models.

For first order transitions such as hard spheres at the freezing density the situation is much less clear. First of all it may be debated whether a freezing transition in which the system undergoes a change in symmetry is the same as the vapor/fluid condensation where there is no symmetry change. Even for the liquid/vapor transition the only models which have ever been solved are mean field models with long range attractive forces such as the Kac potential model of condensation [18]. The pressure of these models is in fact analytic at the coexistence curve. However, for the Ising model at sufficiently low temperatures the free energy is not analytic at zero magnetic field [19] which in the language of the lattice gas means that there in a singularity at the coexistence boundary. This singularity is of the infinitely differentiable type discussed by Fisher [15] and Langer [16] but the additional prediction that the singularity is an isolated essential singularity has not been addressed.

Furthermore no model in a finite number of dimensions with only repulsive forces has ever been solved exactly which exhibits a freezing transition.

There is thus no compelling evidence to support the assumption that the scenario of case 2 must be correct for hard spheres and thus it is possible to raise the suggestion that case three holds for first as well as second order transitions. The difference being that for first order transitions the behavior at the coexistence density is presumably infinitely differentiable (but of course not analytic) instead of having an algebraic singularity.

This conjecture can be proven wrong if it can be demonstrated that there is a lower bound on the radius of convergence of the virial expansion which is greater than the fluid coexistence density of $\eta_f = 0.494$. However, the existing bound Lebowitz and Penrose [20] $\eta_{pl} = 0.1809$, which comes from Groeneveld’s bound [21] on the fugacity expansion of the pressure in the grand canonical ensemble, is very far less than this density so the conjecture cannot be ruled out by the existing bounds.

It is of course widely appreciated that the bound $\eta_{pl}$ is much less than $\eta_f$. However, because of the excellent agreement of the Padé approximate extrapolation of the first eight virial coefficients with the numerical simulations it is often said that “...it (the lower bound of Lebowitz and Penrose) seems to be far below the true radius of convergence” [22]. Indeed the nearest singularity in the Padé approximations is almost exactly at $\eta_{cp}$ and no sign of any kind is seen of the freezing transition in the eight term virial expansion data of ref. [22].
It is exactly at this point that the intuition obtained from the natural boundary in the Ising model is extremely useful. In ref. [1] the existence in the susceptibility of a dense set of singularities lying on the curve of zeroes of the partition function is demonstrated. But in refs. [2] - [3] where an expansion of the susceptibility is made to 323 terms only a small number (up to 8) of these dense set of singularities can be resolved out of the series expansion. We therefore conclude that unlike the power law singularities of second order transitions which are very strong and can be located with series as short as 8 or 10 terms that the singularities coming from natural boundaries require series of hundreds or thousands of terms to see. It is thus completely plausible and possible that the Padé approximate to the 8 term virial expansion is incapable of locating a natural boundary singularity at $\eta_f$ even if it does exist. Indeed it may be argued that since the kissing number (maximum number of spheres which can touch a given sphere) is 12 in three dimensions that the virial expansion cannot possibly include the effects of the geometry of hard spheres until at least the 12th coefficient has been computed. This is reminiscent of the early studies [23] on the Ising susceptibility where, based on the first 8 terms of the series expansion, a simple algebraic expression was conjectured which in fact omits almost all of the interesting structure of the true answer.

To illustrate the difficulty in seeing natural boundaries in a virial expansion consider the familiar example of the lacunary series

$$\sum_{k=1}^{\infty} a_k z^{n_k} \text{ with } \lim_{k \to \infty} k/n_k = 0,$$

which is well known to have a natural boundary. Typical examples of $n_k$ are $k^2$ and $2^k$. The rapid growth of the powers of $z$ indicate that the natural boundary will be invisible in a Padé analysis of terms up to order $z^8$. Note that this example exhibits the general feature of natural boundaries is that there is a sense in which the coefficients in the power series have oscillations which in a Padé analysis will lead to the appearance of more and more singularities in the complex plane as the number of terms in the series increases. We also note that if the coefficients $a_k$ fall off sufficiently rapidly (say as $1/k!$ for $n_k = k^2$ or $2^k$) that the singularity at $z = 1$ will be infinitely differentiable. This is the behavior found by Isakov for the Ising model [19] and we therefore conclude that this result is just as compatible with a natural boundary as it is with the essential singularity of Fisher [15] and Langer [16].

It has, of course, always been possible to assert that the convergence of the virial expansion is determined by terms which have not yet been seen and without some evidence to the contrary it is just as reasonable to ignore this possibility. What has changed with the discovery of the natural boundary in the Ising model susceptibility is that not only do we now have an example where a natural boundary does occur but the reason which it occurs seems to be connected with the fact that at $H \neq 0$ the Ising model is not integrable. Therefore it would seem that natural boundaries are features of generic models (such as hard spheres) instead of the very specialized models such as the Ising model at $H = 0$.

Finally it is perhaps useful to comment on the question of possible sign changes in the virial coefficients. The mechanism of natural boundary formation can happen if all the virial coefficients are positive as the example of the lacunary series (1) shows. However
it has been suggested as long ago as 1957 by Temperley \[24\] that “the possibility of violent oscillations [in the signs of the virial coefficients] cannot altogether be ruled out.” Furthermore Ree and Hoover \[25\] showed in dimension 8 and 9 that that the fourth virial coefficient is indeed negative but they speculated that in three dimensions the signs would not change before the ninth or tenth coefficient. Indeed the first eight coefficients for hard spheres and discs \[22\] are now known to be positive as is the Padé estimate for the ninth coefficient. Nevertheless Temperley’s suggestion of violent oscillations in sign is an appealing mechanism because random oscillations in sign almost always lead to natural boundaries.

### 3 Conclusions

The possibility of a natural boundary in the pressure as a function of density as an explanation of the freezing transition of hard spheres is unorthodox but it does in fact have a certain intrinsic charm. Not only does it put first and second order transitions in some sense on an equal footing but it gives some hope that there is some predictability to first order transitions. If the mechanism of first order transitions is in fact that there are 2 (or more) branches of the free energy which do not know about each other then it is extremely difficult to ever say if you have in fact complexly computed the phase diagram. There may always be some other phase with a lower free energy which you just never thought of. In this situation one will always be in the position described by ref. \[10\] that “theory can only explain the transition afterwards”. In the end this reduces statistical mechanics to a descriptive rather than predictive science. Indeed this may account for the fact that many physicists prefer to study second order transitions and are happy to leave first order transitions to chemists and biologists. If, on the other hand, the natural boundary mechanism proves to be correct then the existence of the phase boundary can at least in principle be determined by studying the properties of the fluid phase alone. In many ways this is a much more attractive alternative. At the very least sufficient analysis should be done on the hard sphere system to demonstrate that it does not happen.

### Acknowledgments

The author wishes to thank A. Guttmann, W. Orrick and J.H.H. Perk for discussions about their work on the Ising susceptibility. He also is indebted to R. Kamien, T. Lubensky and A. Sokal for extremely illuminating discussions about hard spheres. This work is supported in part by NSF grant DMR0073058.

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