Intermediate phase for a classical continuum model

L. Chayes* and R. Kotecký†
Erwin Schrödinger Institute, Vienna, Austria
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We consider a continuum four component model of Widom-Rowlinson type with an Ashkin-Teller symmetry. It is established that this model has two phase transitions with four distinct phases at high fugacity and two distinct phases in an intermediate fugacity regime. [S0163-1829(96)05134-X]

A number of years ago, Widom and Rowlinson[1] proposed a continuum model of interacting spherical particles and provided compelling evidence that this model has a phase transition. A rigorous proof of the existence of a two-phase regime in this model emerged shortly thereafter[2] and recently,[3,4] this phase transition has been understood in geometric terms—as a percolation phenomenon.

Nevertheless, progress in the rigorous study of phase transitions in continuum systems has been slow and primarily confined to models of the Widom-Rowlinson (WR) type. The q-component generalizations of the WR model and their perturbations have been studied in Ref. 5 and the existence of a region with multiple phases have been demonstrated at large activities.[6]

The present work does not really provide any further significant insight for the general problem of liquid-gas transition. However, we have discovered a modified type of penetrable sphere model that exhibits *two* phase transitions; the intermediate phase in this model is quite distinct from the high- or low-density phase of the usual WR systems.

The q-component WR model may be loosely described as a continuum version of the q-state Potts model (or, somewhat more accurately, the annealed dilute Potts models). In this sense, the model we study is a continuum *Ashkin-Teller* model. On the lattice, the Ashkin-Teller[7] model is known[8,9] to have an intermediate phase and, as will be demonstrated in this work, such a phase survives in the continuum version.

The reader will recall that the Ashkin-Teller model consists of four species of particles, here denoted by Y (yellow), R (red), G, and B. In the most interesting region of the phase diagram, each particle type is strongly attracted to particles of their own species, weakly attracted to one other species and repelled by the other two. In our case, we will take Y and R as allies against the G-B team. Here we will assume for simplicity that the Y-G and Y-B (repulsive) interaction are the same. In all other respects it will be assumed that the four species are identical under relabeling, e.g., $Y \rightarrow B \rightarrow R \rightarrow G \rightarrow Y$.

With this description it is not difficult to imagine that as the (common) fugacity is increased, or, in the lattice versions, as the temperature is lowered, there will come a point where one team dominates at the expense of the other. Explicitly, there will be two phases, a YR-rich phase and a GB-rich phase, within which YR and GB symmetry is still respected. Finally, at lower temperatures and/or higher fugacity, cooperation between the allied pairs is forsaken in favor of single color dominance. Here, there are four distinct (but equivalent) phases.

To implement this scheme in the continuum, we consider spherical particles with two interaction radii, a and $A > a$. The outer radius A serves as a hard-core interaction distance for phobic pairs, e.g., any G and Y particles are forbidden to come within a radius $2A$ of one another. The inner radius a then serves as a hard core for the phillic pairs. Finally, all the species are unaffected by the members of their own color group.

As is the case in the usual WR models, one can conceive of integrating out all colors save a single species, Y, and regard all of this as a machinery for generating interactions between the Y particles. (In the two-component model, the interaction can be written in a closed form.[1]) In the present context, the resulting effective interaction does not immediately yield any intuitive features and hence will not be discussed further. Nevertheless, the single species description of the model is of interest and will be used alongside the four-color picture in describing the various phases.

As in the case of the two-component model, we may describe the various phases in terms of different percolation properties. Indeed, in Refs. 3 and 4, it was shown that percolation is necessary and sufficient for the existence of distinct high-density phases. In the present context, we may envision two types of percolation: (i) inner-core percolations and (ii) outer-core percolation.

The former is analogous to the high-density phase in the usual q-component WR models; there is an infinite cluster of particles that are connected in the sense that the union of spheres of radius a surrounding each particle form an infinite component. Observe, by the (inner) hard-core rule such a cluster must be of a single color; indeed, in the usual q-component models, these particles constitute the density excess in the two-phase regime and are hence identified with the condensate.

Percolation of type (ii) constitutes the feature of the present model. Namely, consider a situation where the inner-core percolation does *not* occur and yet there is an infinite cluster of outer cores connected in the sense of overlapping spheres of radius A. Here, the outer-core rule requires only that the infinite cluster belong to one of the two teams, it thus represents the excess density of (say) YR over GB. However, the fact that there is no percolation of the inner cores indicates that within the YR infinite cluster, the densities of yellow and red particles are equal.

It turns out that by using the methods of Ref. 3, the above-described picture can (for certain values of parameters) be transformed into precise statements concerning coexisting

Gibbs states in the infinite volume system. This will be accomplished as soon as some preliminary notation has been established.

Let us start here with a concise formulation of the model. Let $\Lambda \subset \mathbb{R}^d$ be a ''regular vessel'' (e.g., a sphere or a cube) and let $x_1^y,\ldots,x_{N_y}^y,x_1^r,\ldots,x_{N_r}^r,x_1^b,\ldots,x_{N_b}^b,x_1^g,\ldots,x_{N_g}^g$, denote points in Λ. Define

$$\chi_I(x_1,x_2)=\begin{cases}0 & \text{if } |x_1-x_2|<2a,\\ 1 & \text{otherwise,}\end{cases} \tag{1}$$

$$\chi_O(x_1,x_2)=\begin{cases}0 & \text{if } |x_1-x_2|<2A,\\ 1 & \text{otherwise,}\end{cases} \tag{2}$$

and let

$$\chi_{N_y,N_r,N_b,N_g}=\left(\prod_{\substack{c=y,r\\ d=b,g}}\prod_{\substack{1\le i\le N_c\\ 1\le j\le N_d}}\chi_O(x_i^c,x_j^d)\right)\times\left(\prod_{\substack{1\le i\le N_y\\ 1\le j\le N_r}}\chi_I(x_i^y,x_j^r)\prod_{\substack{1\le i\le N_b\\ 1\le j\le N_g}}\chi_I(x_i^b,x_j^g)\right). \tag{3}$$

The grand-canonical partition function, at fugacities $z_y,\ldots,z_g$, is given by

$$\Xi_\Lambda(z_y,z_r,z_b,z_g)=\sum_{N_y,\ldots,N_g=0}^{\infty}\frac{z_y^{N_y}\cdots z_g^{N_g}}{N_y!\cdots N_g!}\times\int_\Lambda d^{N_y}x\cdots d^{N_g}x\,\chi_{N_y,\ldots,N_g}(x_1^y,\ldots,x_{N_g}^g). \tag{4}$$

Of course, here we have paid no heed to boundary conditions. (In fact, the above defined is correct for free boundary conditions.) Boundary conditions, in the present context, may be envisioned as the placement of particles of various types on or outside the boundary $\partial\Lambda$ and may be implemented by the restriction of the region of integration. For example, in the yellow boundary conditions, the region of integration for each x_i^y is all of Λ, however, the positions x_j^b and x_j^g are restricted to $\Lambda/\partial_A\Lambda$, the set of points in Λ of a distance greater than $2A$ from the boundary and, similarly, the position x_j^r lie in $\Lambda/\partial_a\Lambda$. As usual, the partition function provides the normalization constant for the probability distribution for the configurations of colored particles.

Along the line of equal fugacities $z_y=\cdots=z_g\equiv z$, the principle focus of our attention, we may introduce the *gray representation* (Ref. 3, see also Ref. 10) for the problem. In this representation, all configurations of a total of N particles are regarded as equivalent. For example (in the absence of boundary conditions), the probability density to observe only two particles, located at x_1 and x_2, is given by

$$P(x_1,x_2)=\frac{1}{\Xi}\frac{z^2}{2!}\times\begin{cases}4^2 & \text{if } |x_1-x_2|\geq 2A,\\ 2\times 2^2 & \text{if } 2a\leq|x_1-x_2|<2A,\\ 4 & \text{if } |x_1-x_2|<2a.\end{cases} \tag{5}$$

Aside from the prefactor, the interpretation of the above is obvious: if $|x_1-x_2|\geq 2A$, each particle could be any of four colors, if $2a\leq|x_1-x_2|<2A$ both particles must be on the same team, within which there are 2^2 possibilities and, finally, if $|x_1-x_2|<2a$ both particles must be of the same color, for which there are four possibilities.

More generally (albeit still for free boundary conditions) let $\omega=x_1,\ldots,x_N$ denote a particle configuration. Suppose that there is a total of $K(\omega)$ outer connected clusters of ω [so that $1\leq K(\omega)\leq N$] and let us denote these clusters by $C_1,\ldots,C_k$. Within each of these clusters there are $m_j=m(C_j)$ distinct *inner-core* connected clusters; $1\leq m_j\leq|C_j|\equiv$ number of particles in C_j. Each outer-core connected cluster can be on one of the two teams and within each C_j, all of the m_j clusters can be either of two colors. All in all, as it is not hard to see, we obtain a density, for the configuration $\omega\equiv x_1,\ldots,x_N$, given by

$$P(\omega)=\frac{1}{\Xi}\frac{z^N}{N!}2^{K(\omega)}\prod_{j=1}^{K(\omega)}2^{m[C_j(\omega)]}. \tag{6}$$

Of course, Eq. (6) must be appropriately modified [e.g., in the counting of the number $K(\omega)$] for the presence of specific boundary conditions. The boundary conditions corresponding to, say, a yellow particle at each point of the boundary, will be called the wired boundary conditions.

Remark. As to be expected, the above formula is considerably more complicated than that of the gray representation associated with the usual two-component WR models. For these models, one has a single interaction radius, that serves to define the notion of connectedness, and the right-hand side of Eq. (6) is replaced by (const)$\times[z^N/N!]2^{C(\omega)}$, where $C(\omega)$ is simply the number of connected components of ω. Notice that in the present model, as $a\to 0$, we obtain $m(C_j)=|C_j|$ which results in $P(\omega)\propto[1/N!](2z)^N 2^{K(\omega)}$, i.e., the two-component model (at twice the fugacity). The physical picture behind this equivalence to the two-component model is quite obvious: member of the same team are no longer distinguishable in any meaningful way. Nonetheless, this is quite interesting because in the lattice version, complete equivalence (indistinguishability) within the allied groups corresponds to the line along which the Ashkin-Teller model is known to degenerate into an Ising system.

It is, of course, seen that a complete knowledge of the gray measure, along with a specification of the coloring scheme employed at the boundary, allows us to reconstruct all possible statistical information of the original model.

Percolation, in the gray or colored representation, will be defined here quite simply: we will say that there is *inner-core percolation* if the probability that a particle located at any given point of Λ is connected to $\partial\Lambda$ by an inner-core connection is uniformly positive in Λ as $\Lambda\to\mathbb{R}^d$ along some prespecified sequence. *Outer-core percolation* is defined in the same way, using outer-core connectedness, subject to the proviso that there is no inner-core percolation.

Our first result relates these geometric phases in the gray model to actual phases in the four-color model.

Proposition 1. *If, in the grey representation with wired boundary conditions, there is inner-core percolation, then there are (at least) four infinite volume Gibbs states characterized by a relative abundance of Y, R, B, or G. If there is outer-core percolation (without inner-core percolation) there are (at least) two infinite volume Gibbs states characterized by a relative abundance of Y and R over B and G or vice versa. Within these states there is complete Y↔R and B↔G symmetry.*

Proof. Let f_Λ^I denote the average fraction of particles that are inner-core connected to the boundary. Let f_Λ^O denote the fraction of particle outer-core connected to the boundary that are not, of themselves, inner-core connected to $\partial\Lambda$ and let f_Λ^F denote the fraction of remaining (free) particles. We emphasize that, in counting the fraction f_Λ^O, the particle is permitted to be outer-core connected (without being inner-core connected) to a particle that is itself inner-core connected to the boundary. Suppose, then, that there is inner-core percolation. Let $f^I=\lim_{\Lambda\to\mathbb{R}^d} f_\Lambda^I$ (taken along a subsequence if necessary) and similarly for f^O and $f^F=1-(f^I+f^O)$. If, say, the wiring of the boundary corresponds to yellow boundary conditions, and $f_\Lambda^y, \ldots, f_\Lambda^g$, are the average fraction of yellow, red, blue, and green particle, respectively, then, as is easily seen,

$$f_\Lambda^y = f_\Lambda^I + \tfrac{1}{2} f_\Lambda^O + \tfrac{1}{4} f_\Lambda^F \tag{7}$$

while

$$f_\Lambda^r = \tfrac{1}{2} f_\Lambda^O + \tfrac{1}{4} f_\Lambda^F \tag{8}$$

and

$$f_\Lambda^b = f_\Lambda^g = \tfrac{1}{4} f_\Lambda^F . \tag{9}$$

Evidently, in the infinite volume limit, these quantities are distinct and satisfy $f^y > f^r \geqslant f^b = f^g \geqslant 0$. Changing the color at the boundary produces the claimed three remaining states.[11]

Finally, suppose there is outer-core percolation. In the yellow boundary conditions, equations (7) still apply, only this time we find $f^y=(1/2)f^O+(1/4)f^F=f^r>f^g=f^b=(1/4)f^F$ and similarly green boundary conditions produce a state with $f^g=f^b>f^y=f^r$.□

Remark. Back in the single species picture, it is seen that the two-phase region corresponds to two states of differing density [namely, $f=(1/2)f^O+(1/4)f^F$, and $f=(1/4)f^F$] while the four-phase regime, less interesting from the perspective of the four-component model, actually represents a region of *three* distinct Gibbs states with densities (of the privileged species) equal to $f^I+(1/2)f^O+(1/4)f^F$, $(1/2)f^O+(1/4)f^F$, and $(1/4)f^F$, respectively.

It remains to be shown that for some values of a and A, both types of percolation occur as the fugacity is raised. For this we need some elementary notation of monotonicity. Although the concepts below are borrowed from the lattice (and proved via continuum limits) they are in fact easier to state in the continuum. Let $\Lambda\subset\mathbb{R}^d$ and let $\mathcal{A}$ denote a function of particle configurations in Λ. Explicitly, for any N, if $\omega=(x_1,\ldots,x_N)$, it is possible to evaluate $\mathcal{A}(\omega)$. The function $\mathcal{A}$ is said to be *increasing* if the addition of one more particle, regardless of location, increases, or at least does not decrease the value of $\mathcal{A}$: for all N, all $\omega=(x_1,\ldots,x_N)$, and all x_{N+1}, we have $\mathcal{A}(\omega,x_{N+1})\geqslant\mathcal{A}(\omega)$. A function is said to be decreasing if it is the negative of an increasing function. Let μ_Λ and ν_Λ denote two grand-canonical measure on multiparticle configuration in Λ. Namely, measures according to which N indistinguishable particles are present with nonvanishing probability for all N and with conditional measure of the form $\rho_N(x_1,\ldots,x_N)=(1/N!)f_N(x_1,\ldots,x_N)dx_1,\ldots,dx_N$ with $f_N>0$ and $f_N<e^{bN}$ (for stability). Then the measure μ_Λ is said to *FKG-dominate* the measure ν_Λ if $\mu_\Lambda(\mathcal{A})\geqslant\nu_\Lambda(\mathcal{A})$ for any increasing function $\mathcal{A}$.

Remark. Despite the ominous tone in the above definition, the concepts involved are quite simple: increasing functions are functions that satisfy the criterion ''more is better,'' e.g., the number of particles in a specific region, and, loosely speaking, dominating measures correspond to systems with the tendency of larger particle content. In particular, and of relevance to the present work, for two ideal gases, the one with higher fugacity is FKG dominant.

As a consequence of the following domination result, the existence of the various phases is almost immediate.

Proposition 2. *Let $\Lambda\subset\mathbb{R}^d$ denote a regular vessel and let $\nu_{z,\Lambda}(-)$ denote the ideal gas (Poisson) measure at fugacity z and let $\mu^w_{z,\Lambda}(-)$ denote the previously described grey measure in wired boundary conditions. Then*

$$\nu_{4z,\Lambda}(-) \underset{\text{FKG}}{\geqslant} \mu^w_{z,\Lambda}(-) \underset{\text{FKG}}{\geqslant} \nu_{\alpha z,\Lambda}(-), \tag{10}$$

where $\underset{\text{FKG}}{\geqslant}$ denotes FKG dominance and the constant $\alpha=4^{-K(d)}\geqslant 4^{-(3^d-1)}$.

Proof. (Sketch) We will only provide the outline of the necessary ideas since the overall scheme (which, in any case, is fairly elementary) has appeared explicitly in Ref. 3 (proposition 2.1 and its corollary). The first domination follows from the fact that the gray measure is Poisson measure at fugacity $4z$, for isolated particles, augmented by a set of constraints that are specified by a decreasing function that restricts the possible coloring schemes. The second inequality follows from the fact that the addition of a new particle may tie together as many as $K(d)$ clusters (that were heretofore uncorrelated) and thus ''cost'' a factor of $4^{-K(d)}$. Thus, as is easily seen on an intuitive level, this system can be no ''worse'' than an ideal gas at fugacity $4^{-K(d)}z$. □

As an immediate corollary, we obtain the principal result of this paper.

Theorem. *In $d\geqslant2$, for any a there is value $z^*(a)$ that is independent of A, such that for all $z>z^*(a)$ there is inner-core percolation for the gray measure with wired boundary conditions (and hence four distinct Gibbs states in the four-color model). Further, for A/a sufficiently large, there is a range of fugacities, $z_1(a,A)\geqslant z\geqslant z_2(a,A)$ with $z_1(a,A)<z^*(a)$, such that for all z in this range there is outer-core percolation, and no inner-core percolation (and hence an intermediate phase with two Gibbs states in the four-color model).*

Proof. Consider independent (Poisson) spheres of radius b in dimension d. Let $z^{(b)}=z^{(b)}(d)$ denote the percolation threshold (where percolation is *defined* as discussed above) in this system. Notice that percolation, e.g., as defined here, can be expressed as (the limit of) the averages of increasing functions. Further, by simple scaling, $z^{(b)}(d)=z^{(1)}(d)b^{-d}$ where $z^{(1)}(d)$ is finite and nonzero for $d\geqslant 2$ (see, e.g., Ref. 12, Sec. 10.5). Thus regardless of A, by the second half of proposition 2, there will be inner-core percolation whenever $\alpha z > z^{(a)}(d)$.

Finally, let us suppose that $\alpha z > z^{(A)}(d)$ so there is an infinite cluster of outer cores. If, in addition, $4z < z^{(a)}(d)$, inner core percolation *cannot* occur due to the first domination in proposition 2. For a/A sufficiently small, we have $(1/4)z^{(a)}(d) > (1/\alpha)z^{(A)}(d)$ and for z in this range, an intermediate phase in the four-color model occurs.□

Concluding remarks. By considering continuum penetrable-sphere models with four species and differing interspecies interactions, we have shown that for a range of interaction parameters, there are two phase transitions as the fugacity is varied.

Finally, it is noted that by the methods of this work one can construct models with any number of phases; e.g., an eight-component model with two teams of four within which there are two subteams of two. Such a model, characterized by three interaction radii can display three different phase transitions. Similarly a model of this form with k interaction parameters will display k separate phase transitions.

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*On leave from Department of Mathematics, UCLA, Los Angeles.
†On leave from Center for Theoretical Study, Charles University, Prague.

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