Phase Transitions in Two-Dimensional Lattice Gases of Hard-Core Molecules with Long-Range Attractions*

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We have investigated the phase behavior that results when an infinitely weak and long-range attractive potential is added to the following hard-core lattice gases: the triangular-lattice gases with exclusions up to first, second, third, and fourth neighbors, and the square-lattice gases with exclusions up to first, second and third neighbors. Three of the systems considered have realistic (i.e., argonlike) phase diagrams, complete with a first-order solid-fluid phase change, a first-order liquid-gas phase change (with a critical point), and a triple point. Three other systems have a first-order solid-fluid phase change. The remaining system has a first-order liquid-gas phase change along with a higher-order transition that is not of the typical solid-fluid type. We find that when the hard-core system has a second-order or first-order phase change to begin with, the addition of the attractive potential spreads the transition out into a first-order phase change with temperature-dependent coexistence densities that bracket the density at which (or density interval over which) the original transition takes place. We also find that the presence or absence of realistic phase behavior for the combined system appears to be dependent upon the shape of the hard core as well as its range.

I. INTRODUCTION

In order to better understand how the existence of phase transitions depends on the nature of the intermolecular potential in systems of real molecules, we have calculated the equation of state for several lattice-gas systems of particles defined by a pair potential that includes a hard-core repulsion and an infinitely weak long-range attraction.[1,2] These models have many of the essential features of real systems and are reasonably tractable to analyze with high precision. We particularly address ourselves to the two complementary questions: In what ways does the inclusion of long-range attractions between molecules modify the phase-change behavior already existing in lattice gases of hard-core molecules, and in what ways does the inclusion of hard-core repulsions modify the phase-change behavior already existing in simple lattice gases with single-site cores and long-range attractions?

In a lattice-gas model, molecular positions can be thought of as being restricted to the sites of a regular lattice, and multiple occupancy of sites is forbidden. This exclusion of multiple occupancy provides a hard core in the simplest version of the model. The repulsive part of the potential between real molecules may be approximated by an extended hard-core potential in which a certain number of surrounding sites (in addition to the occupied site) are forbidden to other particles. Alternatively, the lattice gas may be thought of in terms of a cell picture in which molecules move freely on the lattice of Wigner–Seitz cells associated with the lattice structure. The potential energy between two molecules is a function of the distance between the cells that contain the two molecular centers. The extended hard core of the site picture corresponds to an exclusion volume in the cell picture, which is the volume of those cells that are forbidden to other particles. The correspondence is shown in Fig. 1 for the examples we treat in this paper. We shall have occasion to refer to both pictures.

Calculations by many authors indicate that extended hard-core lattice gases have order-disorder phase transitions and also suggest that if the exclusion range is sufficiently large the transition becomes first order of the solid-fluid type.[3–11] If, on the other hand, only multiple occupancy of sites is forbidden and there are either finite attractions between nearest neighbors or very long-range weak attractions, there will be only a single first-order phase transition of the liquid-gas type (i.e., with a critical point).[12,13] It would seem reasonable to expect therefore, that if one were to consider a lattice gas with a pair potential that includes both an extended hard core and suitable attractions beyond the core, one would find a realistic phase diagram with two phase transitions, one of the solid-fluid type due to the repulsions and the other of the liquid-gas type due to the attractions. The extent to which that expectation is realized in some appropriate models is the central concern of this paper.

One model of interest in this regard has already been considered by Runnels, Salvant, and Streiffer,[14] who studied a square lattice gas with first-neighbor exclusions and a second-neighbor finite attraction of strength w. They found a single phase transition of the solid-fluid type that is second-order for high enough values of the reduced temperature kT/w and is first order for lower values of the reduced temperature. They found no evidence of a liquid-gas type phase transition with a critical point. Another model has been studied by Runnels, Craig, and Streiffer,[10] who looked at the triangular lattice with first-and-second-neighbor exclusions and third-neighbor attractions and found a first-order solid-fluid type phase transition but no liquid-gas transition. Orban, Van Craen, and Bellemans[15] considered a square lattice with exclusions up to third neighbors and fourth-and-fifth-neighbor attractions, $-g\epsilon$ and $-\epsilon$, with $g>1$. They found a realistic (i.e., argonlike) phase diagram but their results were somewhat limited by the considerable numerical uncertainty associated with treating such a complicated Hamiltonian by approximation methods. From these studies it is difficult to draw any general conclusions as to how the interplay between the repulsions and attractions in a real system affects the presence and nature of the phase transitions.

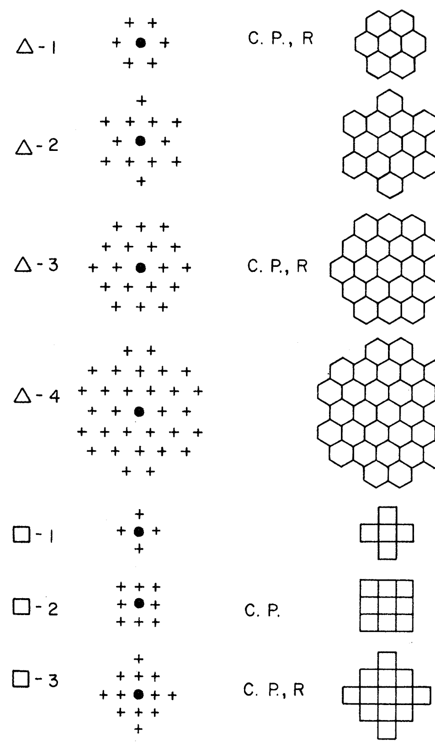

FIG. 1. Extended hard cores and the corresponding exclusion volumes for the hard-core reference systems that we consider. • denotes an occupied site, while + denotes all neighboring sites upon which occupancy is forbidden. C. P. indicates that when a weak long-range attractive potential is added to this system a critical point will appear. R indicates that a realistic coexistence curve will result.

In this article we consider the way certain variations in the repulsive and the attractive parts of the potential affect the macroscopic behavior of a lattice gas. We have added an infinitely weak and long-range attractive Kac potential to the following two-dimensional hard-core lattice gases (see Fig. 1): the triangular lattice with exclusions up to first, second, third, and fourth neighbors and the square lattice with exclusions up to first, second, and third neighbors; these hard-core lattice gases will be referred to as Δ-1, Δ-2, Δ-3, Δ-4, □-1, □-2, and □-3. The Kac potential was chosen because it is thought to be a good first approximation to more realistic potentials and because its effect can be analyzed exactly.[16-18] Using the equations of state of the hard-core lattice gases already given in the literature,[3-9] along with the work of Lebowitz and Penrose,[16] we determine the equations of state for several hard-core lattice gases with weak long-range attractive potentials. From an examination of the coexistence curves we find:

(a) In three of the systems considered, the coexistence curves are remarkably like those of a system of simple real molecules such as argon molecules, having a first-order solid-fluid phase change, a first-order liquid-gas phase change with a critical point, and a triple point.

(b) The addition of the attractive potential to the potential of the hard-core lattice system acts to spread out the solid-fluid type phase transition that exists in the hard-core lattice system alone. If it is second order before the attractive potential is added it becomes first order. If it is initially of first order it remains first order but spreads out further to have temperature-dependent coexistence densities that bracket the density interval over which the original transition took place.

(c) It appears that the existence of a realistic coexistence curve with a critical point depends not only on the range of the core but also on the "roughness" of the exclusion volume.

In Sec. II we describe in general terms the methods used to obtain the coexistence curves and in Sec. III we discuss the details of the calculation for each model giving in particular the coexistence curves in ρ-T space. In Sec. IV we present our conclusions.

II. METHOD

The thermodynamic properties of systems of molecules with hard repulsive cores and weak long-range attractions can be deduced from the properties of the hard-core system alone using a result of Lebowitz and Penrose.[16] They considered a classical system of particles with two-body interaction potentials of the form

$$v(\vec{r}) = q(\vec{r}) + \gamma^\nu \Phi(\gamma \vec{r}) , \tag{1}$$

where $\vec{r}$ is the distance between particles, ν is the dimensionality, γ is a positive parameter, and $\Phi(\vec{r})$ satisfies certain restrictions, one of which is that it be nonpositive. The term $q(\vec{r})$ is called a reference potential (which for the models considered in this paper will be the potential energy of the hard-core system alone) and the term $\gamma^\nu \Phi(\gamma \vec{r})$ is often called the Kac or Kac–Baker potential in acknowledgment of its initial use.[17] The Kac potential, whose range is proportional to γ^{-1}, has the property that in the limit as $\gamma \to 0$ it becomes an infinitely weak and long-range attractive potential. It is sometimes referred to as a "weak and long-range tail" term. Lebowitz and Penrose found that in the Van der Waals limit, $\gamma \to 0$, the equation of state is given by

$$P(\rho, T) = \mathrm{M.C.}\,[P_{\mathrm{ref}}(\rho, T) - \tfrac{1}{2}\alpha\rho^2] , \tag{2a}$$

where M.C. denotes the well known Maxwell construction, $P_{\mathrm{ref}}(\rho, T)$ is the pressure of the reference system, ρ is the density, T is the temperature, and

$$\alpha = -\lim_{\gamma \to 0} \gamma^\nu \int \Phi(\gamma \vec{r}) d^\nu \vec{r} . \tag{2b}$$

Similarly, the free-energy density $a(\rho, T)$ and the chemical potential $\mu(\rho, T)$ are given by

$$a(\rho, T) = \mathrm{C.E.}\,[a_{\mathrm{ref}}(\rho, T) - \tfrac{1}{2}\alpha\rho^2] \tag{3}$$

and

$$\mu(\rho, T) = \mathrm{Inf}[\mu_{\mathrm{ref}}(\rho, T) - \alpha\rho] , \tag{4}$$

where C.E. denotes the convex envelope and Inf denotes the infimum, which is the lowest value of a function taken by that function when it is multivalued.

As Lebowitz and Penrose point out,[16,18] these results can be applied to lattice systems and in particular are applicable to the two-dimensional lattice-gas systems studied here which have pair potentials of the form

$$v(\vec{r}_{ij}) = q(\vec{r}_{ij}) + \lim_{\gamma \to 0} \gamma^2 \, \Phi(\gamma \vec{r}_{ij}) , \tag{5}$$

where the reference potential $q(\vec{r}_{ij})$ is given by

$$\begin{aligned} q(\vec{r}_{ij}) &= \infty \quad \text{for particles occupying the same site or sites within a certain neighborhood,} \\ q(\vec{r}_{ij}) &= 0 \quad \text{otherwise,} \end{aligned} \tag{6}$$

and $\Phi(\vec{x})$ is nonpositive. We assume it is also smoothly behaved (e.g., bounded and monotonically decaying) as $|x| \to \infty$ to avoid any behavior in our model that depends upon oscillatory structure in the potential. In treating a lattice system the integrals of continuum systems go over into sums over cells or equivalently sums over lattice sites. Equation (2b) becomes

$$\alpha = -\lim_{\gamma \to 0} \gamma^\nu \sum_i \Phi(\gamma \vec{r}_{ij}) , \tag{7}$$

where $\sum_i$ denotes a summation over all cells or sites. Information on the equation of state $P_{\mathrm{ref}}(\rho, T)$ for each choice of reference system is obtained from accurate although nonrigorous calculations previously made by other authors. Thus, we see that if the equation of state for a lattice-gas (or continuum) system is known, the equation of state for that system with an infinitely weak long-range attractive potential is readily determined.

We find that much useful qualitative information as well as some exact information on the full system can be obtained from an inspection of graphs of simple thermodynamic functions of the reference system. We will illustrate this using as examples two of our simplest reference models, the triangular lattice gas with nearest-neighbor exclusions (Δ-1) and the square lattice gas with nearest-neighbor exclusions ($\square$-1). We will see that by inspecting a graph of $(\partial \beta P_{\mathrm{ref}}/\partial\rho)_T$ vs ρ ($\beta = 1/kT$) for each of these reference systems we will be able to tell at a glance that $\square$-1 with long-range attractions will have a first-order solid-fluid transition but cannot possibly have a liquid-gas transition with a critical point and that Δ-1 with long-range attractions will also have a first-order solid-fluid transition, while a liquid-gas transition with a critical point is not ruled out.

Both of these reference models possess a second-order continuous phase transition with an inflection point in the P vs ρ isotherm at the transition point $\rho = \rho_t$. The evidence of Refs. 3–5 suggests that at the inflection point the isotherms of both these models are horizontal, implying that the compressibility is infinite. This can be seen by the sharp spike to zero in Fig. 2(a) (Δ-1) and Fig. 2(b) ($\square$-1), which show plots of $(\partial \beta P_{\mathrm{ref}}/\partial\rho)_\beta$ vs ρ for the two models. This function is simply related to the compressibility at constant temperature K_T by

$$\left(\frac{\partial \beta P}{\partial \rho}\right)_T = \left(\frac{\rho K_T}{\beta}\right)^{-1} . \tag{8}$$

Referring to Eq. (2a) we see that if the quantity $[P_{\mathrm{ref}}(\rho, T) - \frac{1}{2}\alpha\rho^2]$ is a decreasing function of the density ρ over some interval then the Maxwell construction will yield a first-order phase transition. If a critical point is associated with this transition then it is clear that the critical density ρ_c and reduced critical temperature $(kT/\alpha)_c$ are the solutions to the equations

$$\left(\frac{\partial \beta P_{\rm ref}}{\partial \rho}\right)_\beta = \beta\alpha\rho \,, \tag{9a}$$

$$\left(\frac{\partial^2 \beta P_{\rm ref}}{\partial \rho^2}\right)_\beta = \beta\alpha \,, \tag{9b}$$

where k is Boltzmann's constant. It should be noted that although a solution to Eqs. (9a) and (9b) must exist in order for a critical point to exist, these equations are not sufficient conditions for the existence of a critical point because of further constraints imposed by the Maxwell construction. Thus, the solution to Eqs. (9a) and (9b) represents only a *possible* critical point.

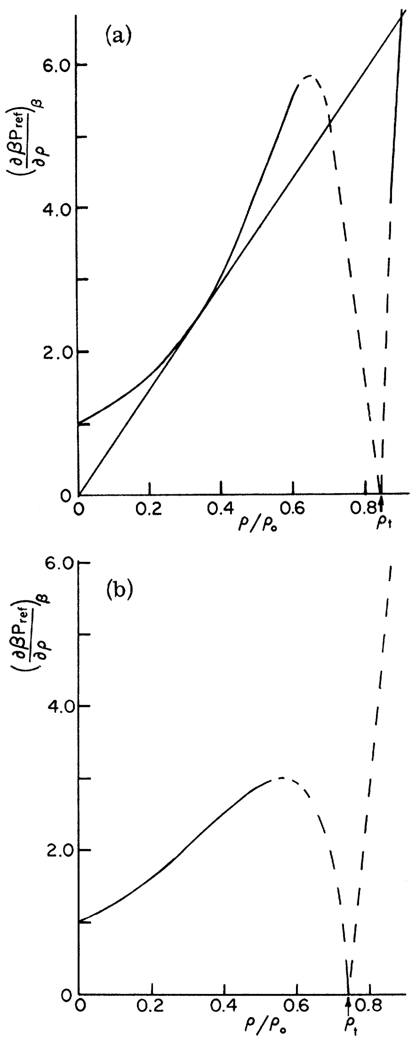

FIG. 2. (a) Plot of $(\partial \beta P_{\rm ref}/\partial\rho)_\beta$ vs ρ for Δ-1. When a weak long-range attraction is added to this reference system a critical point is found. The critical point will be located by the point of tangency between the curve and a straight line through the origin. (b) Same plot for □-1 which cannot have a critical point when a long-range attraction is added as a result of the absence of a point of tangency. In each plot the sharp minimum at ρ_t marks the second-order solid-fluid transition of the reference system. (Dashed lines indicate our best estimate of the behavior of the curve in this region on the basis of the data of Runnels and Combs.)

Throughout this paper we shall characterize a solution of Eqs. (9a) and (9b) as a tangency point because we may interpret graphically the solutions to these equations as the point at which the curve $(\partial \beta P_{\rm ref}/\partial\rho)_\beta$ vs ρ and a straight line through the origin with slope $\beta\alpha$ are tangent to each other. Thus we can say that a hard-core reference system with attractions may possibly have a critical point if there is a sagging "belly" in a plot of $(\partial \beta P_{\rm ref}/\partial\rho)_\beta$ vs ρ which allows the point of tangency to be located. We illustrate this point for Δ-1 with long-range attractions and show in Fig. 2(a) how the location of the tangency point (potential critical point) is determined. In contrast we see from Fig. 2(b) that for □-1 with long-range attractions it is impossible to find a critical point because no point of tangency exists.

Since many workers plot their results on a graph of $(\partial\rho/\partial\beta\mu_{\rm ref})_\beta$ vs $\beta\mu_{\rm ref}$ it is also useful to see how the presence or absence of a solution to Eqs. (9a) and (9b) is reflected in such a graph. Because $\rho(\partial\rho/\partial P)_\beta = (\partial\rho/\partial\mu)_\beta$, it follows from Eqs. (9a) and (9b) that the possible critical point will be located at the point where $(\partial^2\rho/\partial\beta\mu^2_{\rm ref})_\beta = 0$ and $\partial\rho/\partial\beta\mu_{\rm ref}$ is a maximum. At this point the values of $\rho, (\partial\rho/\partial\beta\mu_{\rm ref})_\beta$, and $P_{\rm ref}(\rho, T) - \frac{1}{2}\alpha\rho^2$ will be the possible critical values ρ_c, $(\alpha\beta)_c^{-1}$, and $P_c(\rho_c, T_c)$. Thus we can say that a hard-core reference system with attractions may have a critical point if there is a maximum followed by a minimum in a plot of $(\partial\rho/\partial\beta\mu_{\rm ref})_\beta$ vs $\beta\mu_{\rm ref}$. As an example of this point we see that the maximum followed by a minimum in Fig. 3(a) is evidence of the possible existence of a critical point for Δ-1 with long-range attractions. The lack of this behavior in Fig. 3(b) shows that there is no possible critical point for □-1 with long-range attractions.

An examination of these reference-system graphs can also tell us something about the phase behavior of the full system by allowing us to read off the location of the spinodal points for each isotherm. Since the coexistence densities will bracket the spinodal point densities, the location of the spinodal points gives us a good indication of where the coexistence densities will lie. The spinodal points are the maximum and minimum points of the van der Waals loops at which $(\partial\beta P/\partial\rho)_\beta = 0$ or $(\partial\beta P_{\rm ref}/\partial\rho)_\beta = \alpha\beta\rho$, which is just Eq. (9a). [Thus the critical point is a special spinodal point at which $(\partial^2\beta P/\partial\rho^2)_\beta = 0$.] Graphically the spinodal points for each reduced temperature, kT/α, may be determined by the intersection of the curve $(\partial\beta P_{\rm ref}/\partial\rho)_\beta$ vs ρ and a straight line through the origin with slope $\beta\alpha$. The use of this technique will be made clearer by using as an example Δ-1 with long-range attractions [Fig. 2(a)]. A straight line through the origin with slopé $\beta\alpha < (\beta\alpha)_c$ will intersect the curve at two spinodal points to the right and left of $\rho = \rho_t$, indicating a first-order transition with infinite critical temperature (i.e., a solid-fluid phase transition). At $\beta\alpha = (\beta\alpha)_c$ there are three spinodal points corresponding to a critical point and a first-order phase transition. For $\beta\alpha > (\beta\alpha)_c$ there will be four spinodal points corresponding to two first-order phase transitions and for $\beta\alpha \gg (\beta\alpha)_c$ (temperature below the triple point) there will be two spinodal points corresponding to one first-order phase transition.

From an examination of this type we can see what happens to the phase transitions of the reference systems when the long-range attractions are added. In general, if the reference system has a second-order phase transition it will spread out to

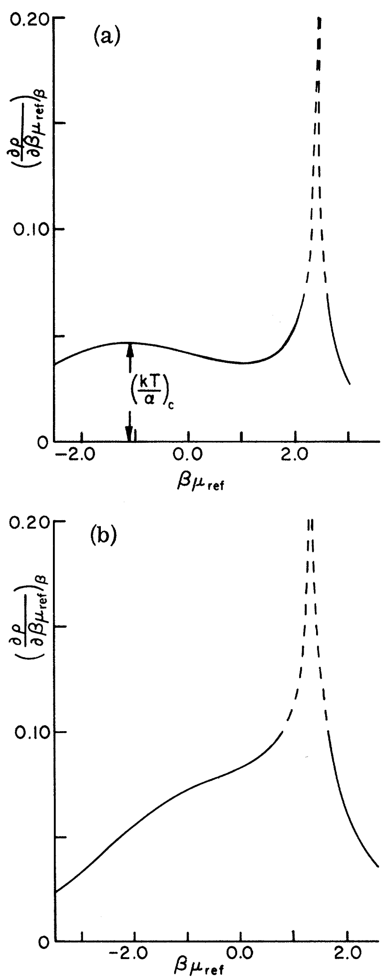

FIG. 3. Plots of $(\partial\rho/\partial\beta\mu_{ref})_\beta$ vs $\beta\mu_{ref}$ for (a) Δ-1 and (b)□-1. Such plots typify the way matrix workers display hard-core lattice-gas results. The critical value of kT/α can be read in the case (a) as shown.

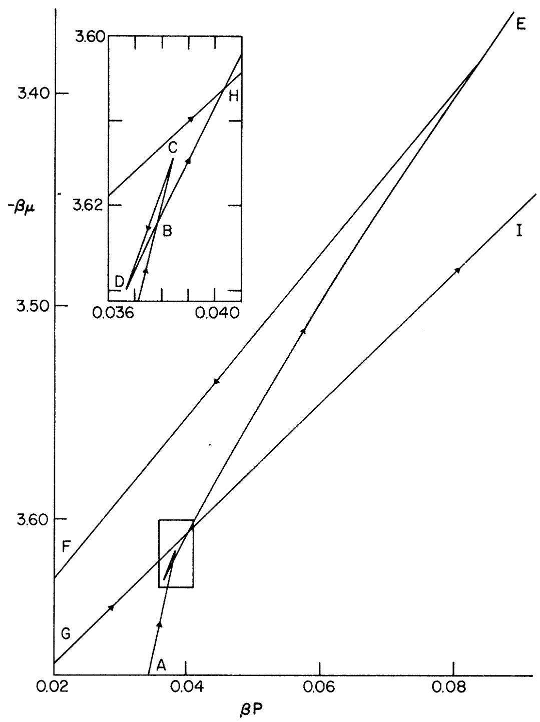

FIG. 4. Plot of $\beta\mu$ vs βP for Δ-1 with long-range attractions for a temperature $kT/\alpha = 0.0472$ which is below the critical temperature and above the triple-point temperature. The density increases in alphabetical order. The crossover point B marks the first-order liquid-gas transition and the crossover point H marks the first-order solid-fluid phase transition. The stable isotherm for this system is ABHI. High- and low-temperature behavior is not shown.

become first order when an attractive potential is added. If the reference system already has a first-order transition, i.e., $(\partial\beta P_{ref}/\partial\rho)_\beta$ is zero over a finite density interval with coexistence densities $\rho_{solid\,ref}$ and $\rho_{liquid\,ref}$, then that system with the addition of the attractive potential will have temperature-dependent coexistence densities, $\rho_{solid}(T)$ and $\rho_{liquid}(T)$, whose minimum difference $[\rho_{solid}(T) - \rho_{liquid}(T)]$ occurring at $T = \infty$ is equal to $[\rho_{solid\,ref} - \rho_{liquid\,ref}]$.

The above considerations give us a necessary condition for a critical point and a qualitative indication of the thermodynamic behavior of systems of hard-core molecules with attractive interactions. In order to obtain the coexistence curves and phase diagrams it is necessary to make a Maxwell equal-area construction on the equation of state or an equivalent construction on some other thermodynamic function. We choose to find the coexistence curve by graphing the chemical potential versus the pressure for each value of the reduced temperature and thereby finding the stable isotherm which minimizes the free energy. We choose to use this

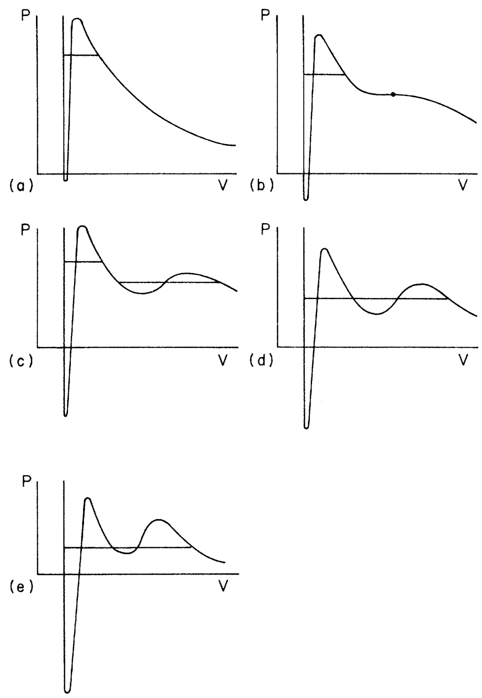

FIG. 5. Schematic plot of the relevant Maxwell constructions according to Eq. (2a) in the P-V plane for a system with a realistic phase diagram such as Δ-1 with long-range attractions. (a) $T > T_c$, (b) $T = T_c$, (c) $T < T_c$, (d) $T = T_{\text{triple point}}$, (e) $T < T_{\text{triple point}}$.

construction rather than the Maxwell equal-area construction because in this way the uncertain data around $\rho = \rho_t$ are avoided. The coexistence densities are determined by the crossover point on this graph (see Fig. 4). In Fig. 5 we illustrate schematically the behavior of isotherms found from Eq. (2a) before and after the Maxwell construction is made for the case of Δ-1 with long-range attractions.

We have emphasized that the conditions stated in Eqs. (9a) and (9b) are necessary for the existence of a critical point but not sufficient. We find that in some of our cases the tangency point never appears as a critical point because it is lost within the Maxwell construction on the other (solid-fluid) phase transition. In Fig. 6 we illustrate schematically this behavior for the case of Δ-2 with long-range attractions. This "critical point that never appears" also occurs in Δ-4 with long-range attractions.

We have seen that if we know the equation of state for a hard-core lattice gas we can calculate the equation of state for the same hard-core lattice gas but with an additional infinitely weak long-range attractive potential. A consideration of graphs of $(\partial\beta P_{\text{ref}}/\partial\rho)_\beta$ vs ρ and $(\partial\rho/\partial\beta\mu_{\text{ref}})_\beta$ vs $\beta\mu_{\text{ref}}$ tells us qualitatively the behavior to be found in the full system and enables us to see if a necessary condition for the existence of a critical point is satisfied. In order to complete the picture quantitatively it is necessary to make a Maxwell construction. In the manner described in this section we examine qualitatively and quantitatively in the next section a number of different hard-core reference systems to which we add long-range attractive potentials.

III. SPECIFIC MODELS AND RESULTS

In this section we discuss the results obtained for each model by the methods described in Sec. II.

A. Triangular Lattice Gas with First-Neighbor Exclusions and Weak Long-Range Attractions (Δ-1)

Gaunt[4] investigated the reference system for this case by deriving exact low-density and high-density series expansions which he studied and extrapolated using ratio and Padé approximant techniques. Runnels and Combs[3] studied the same system independently by using a computerized transfer-matrix method to find exact solutions for systems of infinite length and finite widths of up to 21 lattice sites and then extrapolating their results to infinite width. The two sets of results proved to be in excellent agreement. In both studies it was found that at $\rho \approx 0.84\ \rho_0$ (where ρ_0, the close packing density, is $\frac{1}{3}$), the hard hexagons exhibit an order-disorder transition, at which point the compressibility $\rho^{-1}(\partial\rho/\partial P)_T$ appears to become infinite [see Fig. 2(a)].

An analysis of the data of Gaunt and of Runnels

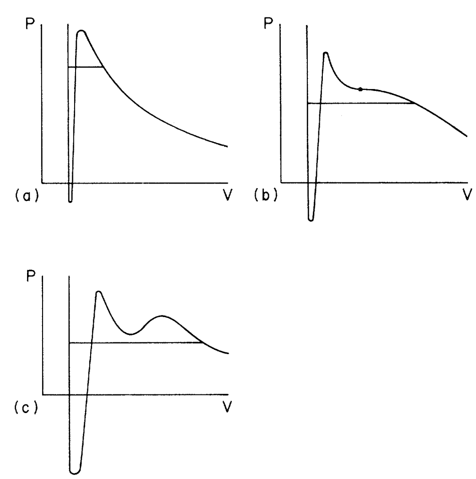

FIG. 6. Schematic plot of the relevant Maxwell construction in the P-V plane showing how a "possible critical point" [i.e., the distinguished point of tangency on a graph of $(\partial\beta\rho_{\text{ref}}/\partial\rho)_\beta$ vs ρ] can be lost within the Maxwell construction. This behavior occurs when long-range attractions are added to Δ-2 and to Δ-4. (a) $T > T_c$, (b) $T = T_c$, (c) $T < T_c$.

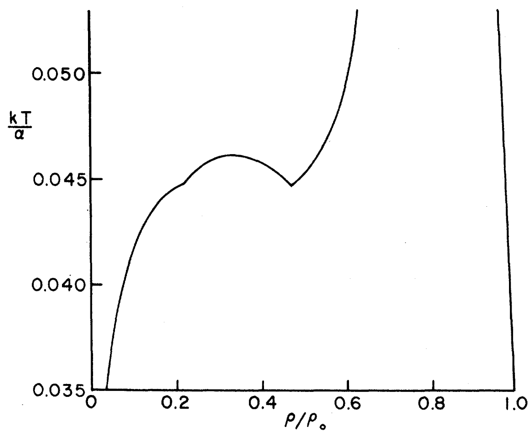

FIG. 7. Coexistence curve for Δ-1 and weak long-range attractions.

and Combs in the manner described in Sec. II showed that a possible critical point exists at $\rho/\rho_0 = 0.333 \pm 0.002$. Since the data of Gaunt and of Runnels and Combs are in agreement and are both extremely reliable except in the vicinity of ρ_t, these combined data were used to find the equation of state and the coexistence curves for the system when a long-range attractive potential was added. By plotting the chemical potential versus the pressure, the coexistence curve was obtained. The coexistence curve is shown in Fig. 7. The second-order phase transition of the reference system has spread out to become the first-order solid-fluid transition of the full system. A liquid-gas transition with a critical point has developed, and there is a triple point. (Notice the kink on the left-hand side of the coexistence curve at the triple-point temperature. This is to be expected in all model systems in which a Maxwell construction is used.) The critical quantities are

$$\rho_c = (0.333 \pm 0.002)\rho_0 ,$$

$$(kT/\alpha)_c = 0.046\,166 \pm 0.000\,001 ,$$

$$(P/\alpha)_c = 0.001\,894 \pm 0.000\,004 ,$$

$$(\beta P/\rho)_c = 0.370 \pm 0.002 .$$

Here and throughout our paper the uncertainties represent informal estimates rather than standard deviations or other formal measures of error.

B. Triangular Lattice Gas with First- and Second-Neighbor Exclusions and Weak Long-Range Attractions (Δ-2)

The reference system for this model was studied by Runnels, Craig, and Streiffer,[10] who used the transfer-matrix techniques for lattices with widths of up to 14 sites, and by Orban and Bellemans,[7] who also used the transfer-matrix techniques for widths of up to 14 sites as well as low-density and high-density (and activity) series expansions and Padé approximant techniques. Both groups concluded that a single first-order phase transition occurs. Orban and Bellemans found the coexistence densities to be $\rho_{\text{fluid}} \approx 0.68\,\rho_0$ and $\rho_{\text{solid}} \approx 0.80\,\rho_0$. Although a construction for this model similar to that of Fig. 2(a) does not rule out the possibility of a critical point (i.e., there is a point of tangency), we find that once the Maxwell construction is made, a critical point never appears (see Fig. 5). The resulting coexistence curve is shown in Fig. 8.

C. Triangular Lattice Gas with First-, Second-, and Third-Neighbor Exclusions and Weak Long-Range Attractions (Δ-3)

Using the same methods that they applied to the preceding case, Orban and Bellemans[7] investigated this reference system and found a first-order phase transition with coexistence densities $\rho_{\text{fluid}} \approx 0.81\,\rho_0$ and $\rho_{\text{solid}} \approx 0.98\,\rho_0$, where $\rho_0 = \frac{1}{7}$. Using the techniques discussed in Sec. II we find the possibility of a critical point. The best Padé approximants for the low- and high-density series of Orban and Bellemans were used to find the equation of state and to make the Maxwell construction. We find that the critical point persists even after the Maxwell construction is made. We were not able to map out the full coexistence curve because of a singularity in the Padé approximant for the low-density series of the chemical potential. We are certain, however, of the existence of the two-phase transitions, the location of the critical point, and of the fact that this system has a triple point. The critical quantities are

$$\rho_c = (0.303 \pm 0.002)\rho_0 ,$$

$$(kT/\alpha)_c = 0.001\,752 \pm 0.000\,001 ,$$

$$(P/\alpha)_c = 0.000\,2779 \pm 0.000\,0006 ,$$

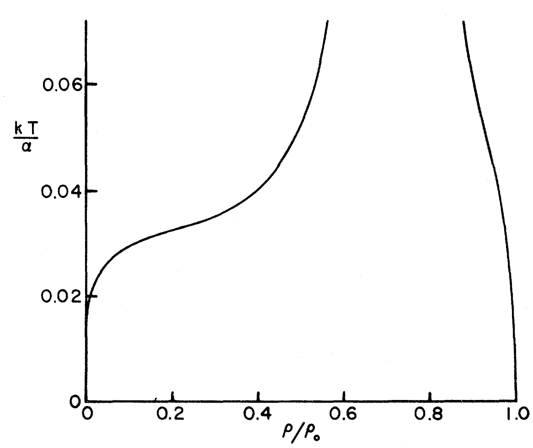

FIG. 8. Coexistence curve for Δ-2 and weak long-range attractions.

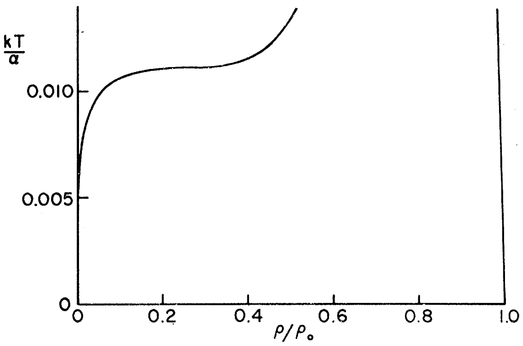

FIG. 9. Coexistence curve for Δ-4 and weak long-range attractions.

$$(\beta P/\rho)_c = 0.367 \pm 0.002 .$$

D. Triangular Lattice Gas with First-, Second-, Third-, and Fourth-Neighbor Exclusions and Long-Range Attractions (Δ-4)

Orban and Bellemans[7] also investigated this reference system and found a first-order phase transition with coexistence densities $\rho_{\text{fluid}} \approx 0.79\ \rho_0$ and $\rho_{\text{solid}} \approx 0.88\ \rho_0$, where $\rho_0 = \frac{1}{9}$. Using the best Padé approximants to their high- and low-density series expansions we calculate the equation of state and make the Maxwell construction. Although a possible critical point is found, it does not appear after the Maxwell construction is made. Thus, no liquid-gas transition occurs, although the presence of the tangency point is felt in the rapidly changing width of the coexistence curve. The coexistence curve is shown in Fig. 9.

E. Square Lattice with First-Neighbor Exclusions and Weak Long-Range Attractions (□-1)

Runnels and Combs[3] and Ree and Chestnut,[9] using transfer-matrix techniques, and Gaunt and Fisher,[5] using series-extrapolation techniques, have studied this system and have concluded that, like the triangular lattice already discussed, this system of hard-square molecules exhibits a second-order phase transition. It occurs at $\rho_t \approx 0.74\ \rho_0$, where $\rho_0 = \frac{1}{2}$, at which point the compressibility appears to become infinite. An examination of the data indicates that it is not possible for this model to exhibit a liquid-gas phase transition [see Figs. 2(b) and 3(b)]. Using Padé approximants for the series of Gaunt and Fisher and using the data of Runnels and Combs (whose widest lattice in this case was 22 sites), we obtained the equation of state and the coexistence curve. Upon addition of the long-range attractions, the second-order continuous transition found in the reference model spreads out to become first order. The coexistence curve is presented in Fig. 10. It is useful to compare this phase diagram to those of Figs. 8 and 9, in which the tangency points were suppressed by the Maxwell construction. This gives us an indication of how the bump or lack of it in plots of $(\partial\rho/\partial\beta\mu_{\text{ref}})_\beta$ vs $\beta\mu_{\text{ref}}$ [see Figs. 3(a) and 3(b)] affects the coexistence curve.

F. Square Lattice with First- and Second-Neighbor Exclusions and Weak Long-Range Attractions (□-2)

This reference system was studied by Bellemans and Nigam[6] who used the same techniques as those employed by Orban and Bellemans for the Δ-2 case as well as an approximate closed-form method originally due to Rushbrooke and Scoins. Bellemans and Nigam felt that their studies using the matrix techniques for widths of up to 12 sites suggested the possibility of a weak transition at high densities $\rho/\rho_0 = 0.92$ (where $\rho_0 = \frac{1}{4}$) and that no evidence for a transition existed using the low- and high-density series-expansion technique. Using the method of Rushbrooke and Scoins they found a second-order phase change (without a horizontal inflection point) with a discontinuity in the compressibility at $\rho/\rho_0 = 0.807$. They were able to rule out the possibility of a first-order phase change as well as a second-order one with a horizontal inflection point. This system was also studied by Ree and Chestnut[8] who used transfer-matrix techniques for widths of up to 18 lattice sites. They felt that their studies indicated that there may be a third-order phase transition with a discontinuous jump in $\partial^2\rho/\partial\beta\mu^2$ (i.e. a cusp in the compressibility) at $\rho/\rho_0 = 0.95$. Thus the studies to date on the square lattice with first- and second-neighbor exclusions are inconclusive.

We have chosen in this paper to use as our reference-model results the results of Ree and Chestnut, who found that at most there is a third-order phase transition. Since it is generally found that

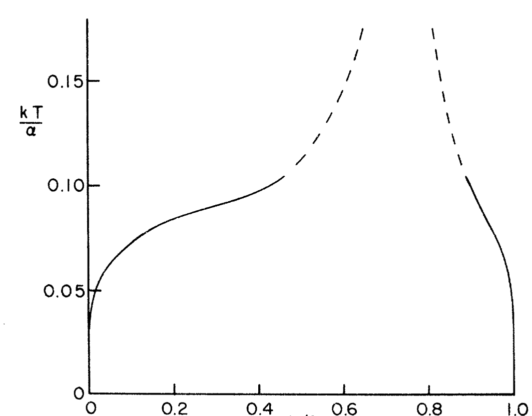

FIG. 10. Coexistence curve for □-1 and weak long-range attractions. Dashed lines indicate our best estimate of the behavior or the curve in this region based not only upon our own results but also on the results obtained by H. Narang [Masters thesis (State University of New York at Stony Brook, 1972) (unpublished)].

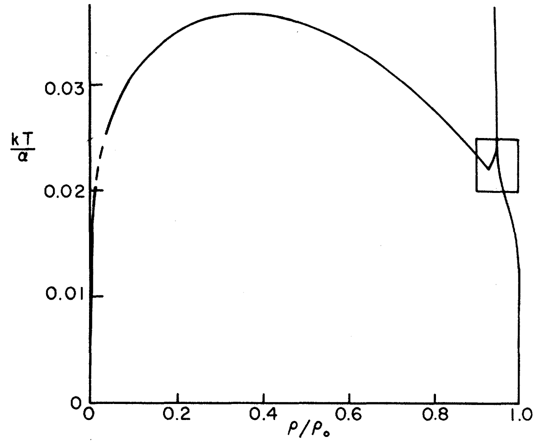

FIG. 11. Coexistence curve for □-2 and weak long-range attractions. Boxed region shows one conjectured possible form of the coexistence curve in the vicinity of $\rho/\rho_0 = 0.95$ that appears consistent with the conclusions of Ref. 8.

the matrix-method results and series-expansions results are reliable and hence reproduce one another except in regions where anomalies exist (i.e. around transition densities) we have used Padé aproximants for the high- and low-density series of Bellemans and Nigam to find the equation of state for the system when an infinitely weak long-range attractive potential is added. The existence of a pronounced "belly" in the plot of $(\partial\beta P_{ref}/\partial\rho)_\beta$ vs ρ together with the lack of a dip at any higher density (there is only a cusp in the graph at $\rho = \rho_t$) indicates that a critical point will surely be present. The Maxwell construction was made on this equation of state and as expected the resulting coexistence curve showed a liquid-gas phase transition with a critical point and no first-order solid-fluid phase change but instead a subtle higher-order transition that is not markedly different for higher temperatures than the transition that existed before the attractive potential was added. The special behavior found for this reference system can probably be attributed to the lack of a unique close-packed configuration for this system (i.e., rows of molecules are allowed to slide freely with respect to each other).

The coexistence curve for this model is shown in Fig. 11. The dashed lines denote that the computations could not be done in the temperature region indicated because of uncertain reference system data around $\rho = 0.92\,\rho_0$. The critical quantities are

$$\rho_c = (0.360 \pm 0.004)\rho_0 ,$$
$$(kT/\alpha)_c = 0.036\,833 \pm 0.000\,001 ,$$
$$(P/\alpha)_c = 0.001\,228 \pm 0.000\,001 ,$$
$$(\beta P/\rho)_c = 0.370 \pm 0.004 .$$

G. Square Lattice with First-, Second-, and Third-Neighbor Exclusions and Long-Range Attractions (□-3)

This reference system was studied by Bellemans and Nigam using the techniques that we have previously mentioned in connection with Ref. 6. They found strong indication of the existence of a first-order phase transition. On the basis of the best Padé approximants to their low-density and high-density series, the equation of state was calculated and the Maxwell construction made. Using the methods described in Sec. II the critical point on a diagram similar to that of Fig. 2(a) was located and was found to persist after the Maxwell construction was made. The realistic coexistence curve obtained is shown in Fig. 12. Critical quantities are

$$\rho_c = (0.330 \pm .003)\rho_0 \quad (\rho_0 = \tfrac{1}{5}) ,$$
$$(kT/\alpha) = 0.026\,238 \pm 0.000\,001 ,$$
$$(P/a)_c = 0.000\,6339 \pm 0.000\,0002 ,$$
$$(\beta P/\rho)_c = 0.366 \pm 0.004 .$$

IV. CONCLUSIONS

The phase behavior that results when an infinitely weak and long-range attractive potential is added to seven different lattice-gas reference systems is summarized below.

(a) In three of the systems considered, Δ-1 with attractions, Δ-3 with attractions, and □-3 with attractions the coexistence curves are realistic. By realistic we mean having a first-order solid-fluid phase change, a first-order liquid-gas phase change with a critical point, and a triple point.

(b) Three other systems, Δ-2 with attractions, Δ-4 with attractions, and □-1 with attractions fail to have a critical point and have only one first-order phase transition of the solid-fluid type.

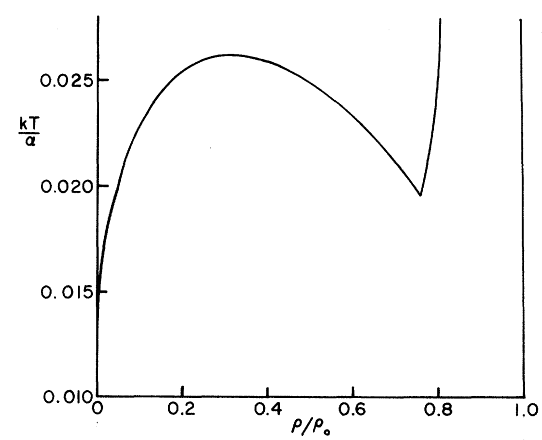

FIG. 12. Coexistence curve for □-3 and weak long-range attractions.

(c) The phase behavior of □-2 with attractions appears to be unusual but this may be a result of the fact that the phase behavior of the reference model has not been clearly established owing to problems associated with the lack of a unique close packed configuration.[19] If we assume that the reference model has at most a third-order order-disorder phase change (as suggested by Ree and Chestnut[8]) we find that the full system exhibits a typical first-order liquid-gas phase change with a critical point in addition to a higher-order phase change.

It is of interest to compare three of our specific results with those of other workers. Δ-3 with fourth- and fifth-neighbor attractions has been studied by Orban, Van Craen, and Bellemans,[15] who found a realistic phase diagram qualitatively similar to ours for Δ-3 and a long-range attractive tail. Δ-2 with third-neighbor attractions has been studied by Runnels, Craig, and Streiffer, who found a first-order solid-fluid type transition but no liquid-gas-type transition in substantial agreement with our result for Δ-2 and a long-range attractive tail. □-1 with second-neighbor attractions has been studied by Runnels, Salvant, and Streiffer,[14] who found that if the second-neighbor attractions were strong enough, the second-order phase transition of the reference system becomes first order, in agreement with our results for □-1 with long-range attractions.

It is clear at this point that the situation is much more complex than the simplest version of the expectation mentioned in the Introduction, i.e., that by including long-range attractions and extended hard-core repulsions in the same model, one will automatically obtain a first-order solid-fluid transition owing to the effect of the repulsions and a first-order liquid-gas transition due to the effect of the attractions. We have seen in this study that the inclusion of long-range attractions modifies the solid-fluid transition that is primarily associated with the hard-core repulsions and that the inclusion of the hard cores modifies the liquid-gas transition that is primarily associated with the attractions. More specifically we can conclude:

(a) The solid-fluid-type phase transition of the hard-core lattice gas is spread out by the addition of the long-range attractions. Thus, if the hard-core lattice gas has a second-order phase transition, it will spread out to become first-order when an attractive potential is added, the coexistence densities becoming functions of temperature. If the hard-core lattice gas has a first-order phase transition with coexistence densities $\rho_{\text{solid ref}}$ and $\rho_{\text{liquid ref}}$, then that system with the addition of the attractive potential will have temperature-dependent coexistence densities $\rho_{\text{solid}}(T)$ and $\rho_{\text{liquid}}(T)$ which bracket the original coexistence densities and whose minimum difference $[\rho_{\text{solid}}(T) - \rho_{\text{liquid}}(T)]$, occurring at $T=\infty$, will be equal to $(\rho_{\text{solid ref}} - \rho_{\text{liquid ref}})$.

(b) The liquid-gas transition of the simple lattice gas with long-range attractions is in some cases eliminated by the inclusion of an extended hard core, although in other cases it persists. The reasons for this behavior are not clear but some observations can be made. In this study we find that the existence of the critical point appears to depend not only on the range of the core but also on its shape.[20] Consideration of the exclusion volumes shown in Fig. 1 will indicate that those systems that have realistic diagrams are the ones with relatively smooth core perimeters. This is particularly clear in the case of the triangular-lattice structure. Although □-3 is not very smooth, it is smoother than □-1 (we discount □-2 because of the peculiarities which have already been discussed). Although the roughness of the exclusion volume as well as its range appears to be playing a role in determining the existence of the critical point, we have found no reliable theoretical means of constructing a quantitative index based on these two factors that would allow us to predict which systems would have realistic phase diagrams.

Finally, it is of interest to compare certain thermodynamic properties of our models at the critical point with results for other similar models. One index that appears remarkably insensitive to the details of the hard core, at least in a given dimension, is the critical ratio $(\beta P/\rho)_c$. The critical ratio for the models calculated in this paper vary between 0.36 and 0.37. These values are all very close to the critical ratio of 0.366 for a two dimensional continuum system with hard-disk repulsions and weak long-range attractions. In three dimensions a continuum system with hard-sphere repulsions and weak long-range attractions has a critical ratio of 0.359. A simple lattice gas with a weak long-range potential has a critical ratio of 0.386 regardless of the dimensionality[13] and the critical ratio of argon has been variously quoted as[21] 0.291 or 0.314.[22]

We have shown how the systematic study of lattice gases with hard-core repulsions and weak long-range attractions helps to further our understanding of how the phenomenon of phase transitions in systems of real molecules is dependent upon the nature of the intermolecular potential.

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We would like to thank L. K. Runnels, L. L. Combs, J. R. Craig, and H. R. Streiffer for providing us with unpublished data on the triangular lattice gases with first-neighbor, and first- and-second-neighbor exclusions, and on the square-lattice gas with the first-neighbor exclusions. We are also very much indebted to Professor Runnels and Dr. D. G. Gaunt for helpful correspondence and conversations.

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[1]A preliminary note on this work has been published: G. Stell, H. Narang, and C. K. Hall, Phys. Rev. Lett. 28, 292 (1972).

[2]Our results can be thought of as lattice-gas analogs to the results of H. C. Longuet-Higgins and B. Widom [Mol. Phys. 8, 549 (1964)] who used a hard-sphere continuum fluid as their hard-core reference system. Although the language and viewpoint that they adopt to discuss the results of adding an attractive tail to a hard-core system are somewhat different from our own (the attractive forces in their model are represented by a uniform background potential), their equations are identical to those obtained when one adds a Kac potential to the hard-sphere system and lets $\gamma \to 0$. Their viewpoint can be more easily identified with the use of the "equivalent-neighbor" potential mentioned in Ref. 18.

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[18]For applications to particular lattice systems, see, for example, Ref. 17(b) as well as G. A. Baker, Jr., Phys. Rev. 126, 2071 (1962); M. Kac and E. Helfand, J. Math. Phys. 4, 1078 (1963); J. F. Nagle, Phys. Rev. A 2, 2124 (1970); and other workers who have exactly analyzed examples of a slightly different "equivalent-neighbor" potential that becomes exactly equivalent to (1) after the thermodynamic limit and the limit $\gamma \to 0$ are both taken; see Nagle's paper for some earlier references to the "equivalent-neighbor" potential.

[19]Bellemans and Nigam (Ref. 6) have done some preliminary calculations on the square lattice with exclusions up to fourth and up to fifth neighbors (both of these systems likewise do not have unique close-packed configurations, in contrast to the case of third-neighbor exclusions). On the basis of these results and their extensive earlier studies, they conjecture that the reason for the irregularity in the nature of the transition as the exclusion range is increased in the square lattice is the absence, then the presence, then again the absence of a unique close-packed configuration as one goes from second- to fourth-neighbor exclusion. The triangular lattice, on the other hand, always has a unique close-packed configuration, and the nature of the solid-fluid phase transition changes more regularly with the increase in the exclusion range. See also R. M. Nisbet and I. E. Farquhar, Phys. Rev. A 5, 380 (1972).

[20]The shape of the core and the roughness in particular have already been discussed by Orban and Bellemans (Ref. 6) in connection with the presence and nature of the order-disorder (solid-fluid) transition in a triangular lattice gas system of hard core molecules. They found that, provided the exclusion range exceeds first-neighbor sites, the system will tend to behave at the transition more like a system of hard disks if the roughness of the core decreases, and that the roughness of the core rather than the range of the core seems, in this case, to be a better criterion for whether the hard-core lattice gas gives a reasonable approximation to the properties of continuous hard-disk systems. The critical point, when it is present at all, occurs in our models at relatively low densities and is associated with a change of state from one disordered fluid state to another, so that its dependence upon the shape of the core is not obviously hinged upon the same factors that dominate the relation between the core shape and the presence and nature of the solid-fluid transition.

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