crossed channel we see that the terms, $g(t)$, are energy independent. For all values of t such that the first Regge pole is at a value of l greater than zero, therefore, the term from $g(t)$ in Eq. (10) will be dominated by the Regge term. The conclusion of the foregoing work is that in the high-energy limit the crossed bubble diagrams of Fig. 2 will always be dominated by a Regge pole from the ladder graphs of Fig. 1.

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Spherical Lattice Gas

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The spherical model of a lattice gas has recently been treated by W. Pressman and J. B. Keller, utilizing the relationship between the grand partition function of the spherical lattice gas and the partition function of the spherical model of a ferromagnet. A phase transition in three dimensions was found for the lattice gas, but no description of the transition region was possible. Here we give some features of the canonical partition function for the same model. The equation of state is obtained for all densities and temperatures, and predicts that the pressure remains constant in the transition region. The particle correlations and fluctuations are calculated, and their behavior in this region is shown to be consistent with a phase transition. A physical interpretation of the normal modes of the spherical model indicates that the model contains the general aspects of clustering of particles. The origin of an anomalous behavior of the model, mentioned by Pressman and Keller, consisting of the pressure becoming negative for all temperatures at sufficiently large specific volumes, is described and a method for eliminating it is introduced.

I. INTRODUCTION

A RECENT paper by Pressman and Keller describes the behavior of this simplified model of an imperfect gas. The description is made by using the well-known relation between the partition function for the Ising model of a ferromagnet and the grand partition function of the lattice gas.[2] These relations hold as well for the spherical model (abbreviated SM henceforth) of both lattice gas and ferromagnet. The SM of a ferromagnet, introduced by Berlin and Kac,[3] leads to a partition function which has been evaluated by them for one, two, and three dimensions. It then becomes a straightforward matter to apply their results to the grand partition function for the SM of a lattice gas, and this was done in reference 1. Since the SM of a ferromagnet exhibits spontaneous magnetization in three dimensions below a critical temperature, a phase transition is found for the SM of a lattice gas in three dimensions. However, the transition region itself is not described by this method, so that one does not know how the pressure behaves in this region. Also this formal identification does not give any indication of the physical nature of the correspondence between lattice gas and the SM of a lattice gas.

The spherical model of a lattice gas was treated by one of us (HAG) some time ago as part of a doctoral dissertation.[4] Here, the canonical partition function was used, in order to be able to describe the behavior of the system right through the transition region and in order to have available a better understanding of the mechanism responsible for the transition. The present work is devoted to pointing out some features that were obtained in the description via the canonical ensemble which are not revealed by the work of Pressman and Keller. In particular, the canonical ensemble predicts that the *pressure remains constant inside the transition region*, and that the fluctuations and correlations have the proper over-all behavior to be expected in this region. In addition, one can see clearly the origin of the anomalous effect of the pressure going negative at sufficiently large specific volume for all temperatures and how a simple modification of the model allows removing this nonphysical behavior, without affecting the qualitative aspects of the phase transition.

In Sec. II, the canonical partition function for the SM is introduced. Some connections between the lattice gas and the SM of the lattice gas are discussed. Section III contains the evaluation of the partition function for all densities by the method of steepest descents. Since the formal development parallels that already re-

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ported[3,5] only an abbreviated version is given. Section IV is devoted to the behavior of the fluctuations and correlations in the transition region. In Sec. V we indicate the origin of the nonphysical negative pressure at large specific volumes for all temperatures, and indicate a method for eliminating it.

II. CANONICAL ENSEMBLE FOR SPHERICAL LATTICE GAS

The lattice gas is a cell model of an imperfect gas in which the volume V containing N particles is subdivided into K cells, each of fixed volume τ, $\tau=V/K$. The volume τ has to be chosen sufficiently small to reproduce the essential features of the interparticle potential energy. For gas condensation these properties are supposed to be a short range attraction outside of a repulsive core. The simplest choice consistent with these characteristics is to take τ small enough so that configurations having more than one particle per cell contribute negligibly to the partition function. This amounts to assuming the interaction between particles in the same cell to be infinite. The short-range attraction may then be represented by taking $U(R_{km})$ the interaction between particles in cells k and m equal to $-\epsilon$ if km are nearest neighbors, and zero otherwise. In this way one gets the configurational partition function (c.p.f.) for the lattice gas to be

$$\frac{Z_N}{N!}=\tau^N \sum_{\{n_j\}} \exp\left(\frac{\beta\epsilon}{2}\sum_{j,k} a_{jk}n_jn_k\right) \tag{1}$$

where $\beta=1/kT$, the sum is over all sets of integers $\{n_j\}$, n_j zero or one, subject to the restriction $\sum_{j=1}^{K}n_j=N$, and a_{jk} is given by

$$\begin{aligned} &a_{jk}=1, \text{ if } j, k \text{ are nearest neighbors;}\\ &a_{jk}=0, \text{ otherwise.}\end{aligned} \tag{2}$$

It is a convenience to introduce new variables x_j defined by

$$x_j=2n_j-1 \tag{3}$$

In terms of these variables, the c.p.f. for the lattice gas can then be written in the form

$$\frac{Z_N}{N!}=\tau^N \exp(Nz\beta\epsilon) \sum_{\{x_j\}} \exp\left[-\frac{\beta\epsilon}{16}\sum_{j,k} a_{jk}(x_j-x_k)^2\right], \tag{4}$$

where $2z$ is the number of nearest neighbors.

The spherical model of the lattice gas is obtained by treating the discrete variables x_j as if they were continuous, and replacing the sum over the coordinates x_j by an integration throughout the volume Ω of the $K-1$ dimensional figure described by $-1\leq x_j\leq +1$ and $\sum_{j=1}^{K}x_j=2N-K$. Thus, the c.p.f. for this model is

$$\frac{Z_N}{N!}=A\tau^N \exp(NZ\beta\epsilon)\int_\Omega\cdots\int dx_1\cdots dx_K \times\exp\left[-\frac{\beta\epsilon}{16}\sum_{j,k} a_{jk}(x_j-x_k)^2\right], \tag{5}$$

where A is a normalization constant.

Finally, the region of integration over Ω is replaced by the intersection of the hyperplane $\sum_{j=1}^{K}x_j=2N-K$ with the K dimensional sphere $\sum_{j=1}^{K}x_j^2=K$. This now gives the partition function for the spherical model as

$$\frac{Z_N}{N!}=A\tau^N \exp(NZ\beta\epsilon)\int_{\Sigma x_j=2N-K,\,\Sigma x_j^2=K}\cdots\int dx_1\cdots dx_K \times\exp\left[-\frac{\beta\epsilon}{16}\sum_{j,k} a_{jk}(x_j-x_k)^2\right]. \tag{6}$$

In details, the system described by this c.p.f. cannot agree with that for the lattice gas, since the statistical variables, the x_j, are now allowed to be continuous, whereas for the lattice gas they are discrete variables. However, in general aspects, some important features of the model seem to be quite similar to those attributable to the real gas. Such a feature is the interpretation of the normal modes which enter in when the quadratic form $\sum_{j,k}a_{jk}x_jx_k$ is diagonalized. As shown in reference 3, the diagonalization of the quadratic form in the exponential of Eq. (6) is affected by the transformation to normal coordinates $\{y_j\}$ defined by

$$x_j=\sum_k t_{jk}y_k \tag{7}$$

The quadratic form in the exponential now becomes

$$\frac{\epsilon}{16}\sum_{i,j} a_{ij}(x_i-x_j)^2=\sum_j \nu_j^2y_j^2. \tag{8}$$

The characteristic vectors t_{jk} and characteristic values ν_j^2 have been determined by Berlin and Kac in reference 3. In three dimensions their results are equivalent in the limit $K\to\infty$ to the simple forms

$$t_{jk}=K^{-\frac{1}{2}}\left[\cos\frac{2\pi}{K^{\frac{1}{3}}}(j_1k_1+j_2k_2+j_3k_3) +\sin\frac{2\pi}{K^{\frac{1}{3}}}(j_1k_1+j_2k_2+j_3k_3)\right] \tag{9}$$

and

$$\nu_j^2=\frac{\epsilon}{4}\left[3-\cos\frac{2\pi j_1}{K^{\frac{1}{3}}}-\cos\frac{2\pi j_2}{K^{\frac{1}{3}}}-\cos\frac{2\pi j_3}{K^{\frac{1}{3}}}\right], \tag{10}$$

where for simplicity, we let j and k on the left sides of these last two equations stand for the triples (j_1,j_2,j_3)

[5] T. H. Berlin, L. Witten, and H. A. Gersch, Phys. Rev. **92**, 189 (1953).

and (k_1,k_2,k_3). The SM c.p.f. now reads

$$\frac{Z_N}{N!}=A\tau^N \exp(3N\beta\epsilon)\int\cdots\int_{\Omega'} dy_1\cdots dy_K \times\exp\left[-\beta\sum_{j=1}^{K}\nu_j^2y_j^2\right], \quad (11)$$

where the volume Ω' is defined by $\sum_{j=1}^{K}y_j^2=K$, $K^{\frac{1}{2}}y_K=(2N-K)$ or

$$\sum_{j=1}^{K-1} y_j^2=4N(1-N/K)=R^2. \quad (12)$$

Concerning the physical content of the model, we can note the following expression for the total potential energy $\langle U\rangle$,

$$\langle U\rangle=-3N\epsilon+\sum_{j=1}^{K}\nu_j^2\langle y_j^2\rangle. \quad (13)$$

For given N, K, and temperature T there will be a certain distribution of mean square amplitudes $\langle y_j^2\rangle$ among the normal modes. Large values of $\langle y_j^2\rangle$ for a particular mode imply a large expectation for the corresponding configuration of the x_j. We will briefly consider the correspondence between lattice gas configurations and those which correspond to the various normal modes.

For the three-dimensional lattice gas, every face of a cubic cell which separates two opposite values for x_j contributes one unit to the nodal surface area (taking the lattice spacing as unity). A configuration having total nodal surface area equal to L has energy $\frac{1}{4}\epsilon L$ above the minimum value $-3N\epsilon$. For the SM the energy is given by $U=-3N\epsilon+\sum_j\nu_j^2y_j^2$. For the modes with small j, the energy for a fixed amplitude y_j is small, and the nodal surface area is small. Thus, there are large groups of cells for which each cell of the group has the same sign for the variable x_j. These variables are continuous; we do not have $x_j=\pm1$ only. If we identify $x_j>0$ with $x_j=1$ and $x_j<0$ with $x_j=1$, then for these configurations there are large groups of cells containing particles and large groups of empty cells. As j increases, the energy for a fixed y_j increases, and the nodal surface area increases, so that the regions for which the x_j are all of the same sign become smaller. Clearly, long wavelength modes correspond to lattice gas configurations having only a small number of boundaries separating cells containing one particle and cells containing none; that is, long wavelength modes correspond to large clusters.

The expectation values for the mean square amplitudes are determined as by-products in the solution of the c.p.f. given by Eq. (11), to which we now turn.

III. STEEPEST DESCENT EVALUATION OF PARTITION FUNCTION

The restriction on the region of integration of the variables $\{y_j\}$ expressed by Eq. (12) may be relaxed by means of the delta function, using the representation

$$\delta[R-(\sum y_j^2)^{\frac{1}{2}}]=\frac{2R}{2\pi i}\int_{S_0-i\infty}^{S_0+i\infty}dS \times\exp\left[S\left(R^2-\sum_{j=1}^{K-1}y_j^2\right)\right]. \quad (14)$$

Because R is positive, we may write

$$\frac{Z_N}{N!}=\frac{B}{2\pi i}\int_{S_0-i\infty}^{S_0+i\infty}dS\, e^{SR^2}\left\{\prod_{j=1}^{K-1}\left[\pi^{\frac{1}{2}}(S+\beta\nu_j^2)^{-\frac{1}{2}}\right]\right\}, \quad (15)$$

where $B=A\tau^N \exp 3N\beta\epsilon$.

For the limit $N,K\rightarrow\infty$, $K/N=v/\tau$ the limiting form of the integrand in Eq. (15) is required. The product may be written

$$\prod_{j=1}^{K-1}(S+\beta\nu_j^2)^{-\frac{1}{2}}=\exp\left[-\tfrac{1}{2}\sum_{j=1}^{K-1}\ln(S+\beta\nu_j^2)\right]. \quad (16)$$

Let

$$G_3(S)=\lim_{K\rightarrow\infty}\frac{1}{K}\sum_{i=1}^{K-1}\ln(S+\beta\nu_j^2). \quad (17)$$

Then, as shown in reference 3,

$$G_3(S)=(2\pi)^{-3}\int\int\int_0^{2\pi}d\omega_1d\omega_2d\omega_3\ln[S+\beta\nu^2(\omega_1,\omega_2,\omega_3)] =\int_0^{\nu_{\max}}f_3(\nu)\ln(S+\beta\nu^2)d\nu. \quad (18)$$

Here

$$\nu^2(\omega_1,\omega_2,\omega_3)=\tfrac{1}{4}\epsilon(3-\cos\omega_1-\cos\omega_2-\cos\omega_3)$$

and $f_3(\nu)$ is the density of normal modes for three dimensions, given by

$$f_3(\nu)=\int_\nu\frac{dS_3}{|\mathrm{grad}\nu|_3}, \quad (19)$$

where dS_3 is the element of area on the surface $\nu(\omega_1,\omega_2,\omega_3)=\text{constant}$, and

$$|\mathrm{grad}\nu|_3=[(\partial\nu/\partial\omega_1)^2+(\partial\nu/\partial\omega_2)^2+(\partial\nu/\partial\omega_3)^2]^{\frac{1}{2}}.$$

Let $\tilde{s}$ denote the algebraically smallest value of $\beta\nu^2$. If the s plane is cut from $s=-\infty$ to $s=-\tilde{s}$ along the real axis, then the integrand in Eq. (18) is analytic in the cut plane. To correctly describe the behavior of the integral in Eq. (15) in the neighborhood of $s=-\tilde{s}$, we must separate out from the sum in Eq. (17) the terms

for which $\beta\nu^2$ is equal to $\tilde{s}$. As shown in reference 5 there are two such terms, because the algebraically smallest eigenvalue is doubly degenerate. This gives,

$$G_3(S)=\frac{2}{K}\ln(s+\tilde{s})+\int_0^{\nu_{\max}} f_3(\nu)\ln(s+\beta\nu^2)d\nu. \quad (20)$$

Therefore, we must evaluate the integral

$$\frac{Z_N}{N!}=\frac{B}{2\pi i}\pi^{\frac{1}{2}K-\frac{1}{2}}\int_{S_0-i\infty}^{S_0+i\infty}\frac{dS}{(s+\tilde{s})}\exp[Ng_3(s)], \quad (21)$$

where

$$g_3(S)=4(1-N/K)s-\frac{K}{2N}\int_0^{\nu_{\max}} f_3(\nu)\ln(s+\beta\nu^2)d\nu. \quad (22)$$

The method of steepest descents gives the result

$$\frac{Z_N}{N!}=\frac{B\pi^{\frac{1}{2}K-\frac{1}{2}}\exp[Ng_3(s_s)]}{(s_s+\tilde{s})[\pi K(\partial^2 g_3/\partial s^2)_{s_s}]^{\frac{1}{2}}} \quad (23)$$

if a saddle point s_s can be found such that s_s is real, positive, to the right of the singularities of the integrand, and with

$$(\partial g_3/\partial s]_{s_s}=0 \quad [\partial^2 g_3/\partial s^2]_{s_s}>0. \quad (24)$$

The constant A in $B=A\tau^N\exp 3N\beta\epsilon$ shall be determined by normalizing to the lattice gas when $\epsilon=0$ and $N=K/2$, for which case $Z_{N/N!}=\tau^N K!/[(K/2)!]^2$. For the model, we have $a_{jk}=0$ for all j, k, so that $\nu_j=0$ for all j. Then one finds

$$\begin{aligned} g_3(s)&=4(1-\tau\rho)s-\frac{1}{2\tau\rho}\ln s,\\ (\partial g_3/\partial s)_{s_s}&=4(1-\tau\rho)-(2\tau\rho s_s)^{-1}=0,\\ (\partial^2 g_3/\partial s^2)_{s_s}&=(2\tau\rho s_s^2)^{-1}>0. \end{aligned} \quad (25)$$

The solution of the saddle point equation is

$$s_s=[8\tau\rho(1-\tau\rho)]^{-1}. \quad (26)$$

It is found, that for $N, K, \rightarrow\infty$, $K/N=v/\tau$,

$$\frac{1}{N}\ln A=\frac{v}{2\tau}\ln(2/\pi e). \quad (27)$$

This yields for the limiting free energy per particle the result

$$-\beta\psi_3=\ln\tau(2\pi m/\beta h^2)^{3/2}+\frac{v}{2\tau}\ln\frac{2}{e}+g_3(s_s)+3\beta\epsilon. \quad (28)$$

We now investigate the existence of a solution to the saddle point equation

$$8\tau\rho(1-\tau\rho)=\int_0^{\nu_{\max}}(s_s+\beta\nu^2)^{-1}f_3(\nu)d\nu\equiv I(s_s,T), \quad (29)$$

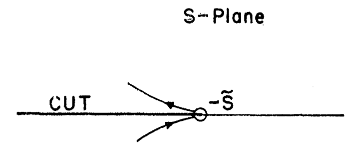

FIG. 1. Path of steepest descent in the transition region.

where $\nu_{\max}{}^2=3\epsilon/2$. This equation determines the distribution of mean square amplitudes among the normal modes. It is clear from Eqs. (11) and (15) that

$$\langle y_j^2\rangle=[2(s_s+\beta\nu_j^2)]^{-1}, \quad (30)$$

so that the saddle point equation may be written

$$8\tau\rho(1-\tau\rho)=2\int_0^{\nu_{\max}} d\nu\, f_3(\nu)\langle y^2(\nu)\rangle. \quad (31)$$

The integral $I(s_s,T)$ is a monotone decreasing function of s_s which is finite for $s_s=-\tilde{s}=0$. In fact,[3]

$$I(0,T)=\frac{1}{\beta}\int_0^{\nu_{\max}}\frac{f_3(\nu)}{\nu^2}d\nu=\frac{4}{\beta\epsilon}(0.50546). \quad (32)$$

The integral is finite because $f_3(\nu)\sim\nu^2$ as $\nu\rightarrow 0$. The corresponding integrals for one and two dimensions would diverge, because, in general, if z is the number of dimensions, $f_z(\nu)\sim\nu^{z-1}$ as ν goes to zero.

The consequence is that the three-dimensional gas exhibits a transition for temperatures below the critical temperature given by

$$kT_c/\epsilon=[2(0.50546)]^{-1}. \quad (33)$$

The density at which the transition occurs are the two solutions of the equation

$$8\tau\rho(1-\tau\rho)=(4/\beta\epsilon)(0.50546) \quad (34)$$

The critical density is $\rho_c=1/2\tau$, and the two solutions ρ_G, ρ_L for the transition densities are given by $\rho_G+\rho_L=2\rho_c$. These relations are characteristics of the lattice gas.

Supposing that $\rho_G<\rho_L$, we must now find Z_N for $\rho_G<\rho<\rho_L$, i.e., inside the transition region. The integrand in Eq. (21) has a branch point at $s=-\tilde{s}=0$. A path of steepest descents can still be found in the neighborhood of the branch point. To find this path, the behavior of $g_3(s)$ near the pole is required. The following expansion for $g_3(s)$ in the neighborhood of $s=0$ can be obtained. (Details are given in reference 4.)

$$\begin{gathered} g_3(s)=g_3(0)+\gamma s+\delta s^{\frac{3}{2}}+O(s^2),\\ \gamma=4(1-\tau\rho)-(2\tau\rho)^{-1}I(0,T),\quad \delta=-(6\pi)^{-1}(8/\beta\epsilon)^{\frac{3}{2}}. \end{gathered} \quad (35)$$

The integrand in Eq. (21) falls off rapidly from its value at $s=0$ for the real part of s negative, since $\gamma>0$. On a path as shown qualitatively in Fig. 1, the imaginary part of $g_3(s)$ is zero, and the path does not cross the branch cut. The contributions to the integral coming from the partial paths on opposite sides of the cut

cancel in the limit $N, K \to \infty$, and only the residue at the pole contributes to the integral. We get

$$Z_N/N! = B\pi^{\frac{1}{2}K-\frac{1}{2}} \exp[Ng_3(0)] \tag{36}$$

if $\rho_G < \rho < \rho_L$, $T < T_c$.
The limiting free energy per particle is then given by

$$-\beta\psi_3 = \ln \tau (2\pi m/\beta h^2)^{\frac{3}{2}} + \frac{v}{2\tau} \ln(2/e) + g_3(0) + 3\beta\epsilon. \tag{37}$$

The behavior for $T < T_c$ as the density is increased toward $\rho = \rho_G$ consists in the saddle point s_s decreasing to zero. Equation (30) shows that this implies that the mean square amplitudes for the modes with small j increase rapidly as the density ρ_G is approached. The configurations of the x_j which correspond to these modes have very long wavelength, and have an increasing expectation value as the density ρ_G is approached. According to the previous discussion, these configurations correspond to large clusters. The model then predicts the rapid formation of such large clusters as the transition density is approached.

The pressure may be obtained from Eqs. (28) and (37) using the relation $p = -(\partial\psi/\partial v)_T$. In the normal region, specified by $0 \leq \rho \leq \rho_G$ and $\rho_L < \rho \leq 1/\tau$ for $T < T_c$, or for all densities if $T > T_c$, from Eq. (28) we have

$$\frac{P}{kT} = \frac{1}{2\tau} \ln \frac{2}{e} + 4\tau s_s/v^2 - G_3(s_s)/2\tau, \tag{38}$$

with the saddle point s_s determined from Eq. (29). From inspection of the saddle point equation, it is easy to show that $(\partial p/\partial v)_T \leq 0$, so that we always have stability in this region. In the transition region, defined by $\rho_G < \rho < \rho_L$, $T < T_c$, from Eq. (37) we have

$$P/kT = \frac{1}{2\tau} \ln(2/e) - \frac{1}{2\tau} \int_0^{\nu_{\max}} d\nu\, f_3(\nu) \ln(\nu^2/kT). \tag{39}$$

Since there is no dependence of the pressure on volume, we see that the canonical ensemble predicts that the pressure is constant in the transition region. The isotherms for the three dimensional SM are then completely similar to those shown by Pressman and Keller in their Fig. 9. However, as noted by these authors, the pressure given by Eq. (39) will become negative at sufficiently low temperatures. This nonphysical behavior comes in from the term in Eq. (39) logarithmic in the temperature. As the temperature decreases, the pressure at any density decreases, but the decrease predicted is too rapid. The appearance of the logarithmic term seems to be a direct result of having replaced the sum over discrete variables n_j by an integral over continuous variables n_j, i.e., it appears to be an unavoidable characteristic of a pure continuum model.

At the transition volumes v_L and v_G, the saddle point $S_s = 0$, and it follows from Eqs. (38) and (39) that the pressure is continuous at the transitions. The first derivative of the pressure with respect to volume is also continuous at the transition points; however, there is a discontinuity in the second derivative. These statements are proved in the Appendix.

IV. FLUCTUATIONS AND CORRELATIONS

The equation of state is not itself a critical indicator of the validity of a statistical model, so we turn to a more detailed description of the physical system. Such a description is proved by the correlation function between two cells j and k, $\langle n_j n_k \rangle$. This plays the role of the molecular pair distribution function $n_2(r_1,r_2) = N(N-L)P_2(r_1,r_2)$. $P_2(r_1,r_2)$ is the probability for a specified particle to be in the volume element $d\tau_1$ surrounding $\mathbf{r}_1$, and another specified particle to be in the volume element $d\tau_2$ surrounding $\mathbf{r}_2$. From their definitions, it follows that

$$\langle n_j n_k \rangle = \int\int_\tau d\tau_{1k} d\tau_{2j}\, n_2(\mathbf{r}_{1k}, \mathbf{r}_{2j}), \tag{40}$$

where the position vector $\mathbf{r}_{1k}$ for one particle is integrated over cell k, that for the other particle over cell j.

In terms of the normal coordinates y_j, the correlation function is given by

$$\langle n_j n_k \rangle = (\tau\rho)^2 + \tfrac{1}{4} \sum_{l=1}^{K-1} t_{jl} t_{kl} \langle y_l^2 \rangle, \tag{41}$$

where again we use a single index like j to stand for the triple $(j_1 . j_2\, j_3)$. Making use of Eq. (8) for the components t_{jl} of the characteristic vectors and Eq. (30) for the mean square amplitudes $\langle y_l^2 \rangle$ this becomes

$$\langle n_j n_k \rangle = (\tau\rho)^2 + \cos\left[\frac{2\pi}{K}(k-j)\right] \left\langle \frac{1}{4K(s+\tilde{s})} \right\rangle + \frac{1}{4K} \sum_{m=1}^{\frac{1}{2}(K-1)} \frac{\cos[(2\pi/K)(k-j)(m-1)]}{s_s + \beta\nu_m^2}. \tag{42}$$

If the function H_{jk} is defined as

$$H_{jk} = \lim_{K,N\to\infty, K/N=v/\tau} \frac{1}{4K} \times \sum_{m=1}^{\frac{1}{2}(K-1)} \frac{\cos[(2\pi/K)(k-j)(m-1)]}{s_s + \beta\nu_m^2}. \tag{43}$$

Then, in the normal region,

$$\lim_{K,N\to\infty} \langle n_j n_k \rangle = (\tau\rho)^2 + H_{jk}, \tag{44}$$

while in the transition region,

$$\lim_{K,N\to\infty} \langle n_j n_k \rangle = \gamma \lim_{K\to\infty} \cos\left[\frac{2\pi}{K}(k-j)\right] + (\tau\rho)^2 + H_{jk}, \quad (45)$$

where γ is given by Eq. (35).

A more detailed distribution function is the conditional average, $\langle n_j \rangle_{n_k}$. This is the average number of particles in the jth cell when the number in the kth cell is fixed, and is given by [4,5]

$$\langle n_j \rangle_{n_k} = \tau\rho + \frac{1}{4}\frac{n_k - \tau\rho}{\tau\rho(1-\tau\rho)} \sum_{l=1}^{K-1} t_{jl} t_{kl} \langle y_l^2 \rangle. \quad (46)$$

In the normal region,

$$\lim_{K,N\to\infty} \langle n_j \rangle_{n_k} = \tau\rho = \frac{1}{4}\frac{n_k - \tau\rho}{\tau\rho(1-\tau\rho)} H_{jk}, \quad (47)$$

while in the transition region

$$\lim_{K,N\to\infty} \langle n_j \rangle_{n_k} = \tau\rho + \frac{n_k - \tau\rho}{4\tau\rho(1-\tau\rho)} \times \left\{ \gamma \lim_{K\to\infty} \cos\left[\frac{2\pi}{K}(k-j)\right] + H_{jk} \right\}. \quad (48)$$

Both $\langle n_j n_k \rangle$ and $\langle n_j \rangle_{n_k}$ were also computed in reference 5 for the model treated in that work with results completely equivalent to those given here. As was found previously, the important difference in the behavior of both these averages in the normal and transition regions is due to the existence of the term γ in the transition region. This term has the effect of extending the influence of a particle in one cell out to very great distances. For example, if there is one particle in the kth cell, then the average number in all surrounding cells out to distances of the order of the linear dimensions of the containing vessel is increased, due to the presence of the term γ. Conversely, if there are no particles in the kth cell, the average number in all surrounding cells is decreased due to the term γ.

There is another aspect of the long range correlation which concerns the fluctuations in the number of particles in a region which contains many cells of volume τ. The average number of particles in a volume $L\tau$ is given by

$$\langle N_L \rangle = \langle \sum_{j=1}^{L} n_j \rangle = L\tau\rho. \quad (49)$$

The average value for the square of the number of particles is

$$\langle N_L^2 \rangle = \tau\rho L + \sum_{j\neq k}\sum \langle n_j n_k \rangle. \quad (50)$$

The square of the relative fluctuations in N_L is then

$$\frac{\langle (N_L - \langle N_L \rangle)^2 \rangle}{\langle N_L \rangle^2} = \frac{\langle N_L^2 \rangle - \langle N_L \rangle^2}{\langle N_L \rangle^2} = \frac{\tau\rho L - (\tau\rho L)^2 + \sum_{j\neq k}\sum \langle n_j n_k \rangle}{(\tau\rho L)^2}. \quad (51)$$

If particles in adjacent cells did not interact, we would have

$$\sum_{j\neq k}\sum \langle n_j n_k \rangle = L(L-1)\langle n_j^2 \rangle = (\tau\rho)^2 L(L-1) \quad (52)$$

and

$$[\langle N_L^2 \rangle - \langle N_L \rangle^2] / \langle N_L \rangle^2 = (1-\tau\rho)/L\tau\rho. \quad (53)$$

The average number N_L is then a well-determined macroscopic quantity.

In the transition region, the square of the relative fluctuation in N_L is given by

$$\frac{\langle N_L^2 \rangle - \langle N_L \rangle^2}{\langle N_L \rangle^2} = \frac{1-\tau\rho}{L\tau\rho} + \frac{1}{(L\tau\rho)^2} \times \sum_{j\neq k}\sum \left\{ \gamma \lim_{K\to\infty} \cos\left[\frac{2\pi}{K}(k-j)\right] + H_{jk} \right\}. \quad (54)$$

H_{jk} goes to zero as the distance between the kth and jth cells becomes large. By taking the volume $L\tau$ sufficiently large, the second term on the right will become of order one, and the fluctuations in N_L about its average $\langle N_L \rangle$ of order $\langle N_L \rangle$ will no longer be negligible. In this case, $\langle N_L \rangle$ ceases to be a well determined macroscopic quantity, as one expects for a system when $(\partial P/\partial v)_T$ approaches zero.

V. NEGATIVE PRESSURE

In Sec. III, we mentioned the nonphysical behavior characterized by the pressure becoming negative for sufficiently low temperatures. As Pressman and Keller have noted, there is another distinct type of negative pressure occurring in the model, namely, for all temperatures at sufficiently large volumes. Whereas, the low-temperature failure of the model seems difficult to remove, this second behavior appears to be more easily rectifiable.

It has its origin in the fact that the region of integration for the SM, which according to Eq. (6) is the common volume defined by the two constraints, $\sum x_j = 2N-k$ and $\sum x_j^2 = K$ goes to zero for $N\to 0$ or $N\to K$. This is in contrast to the c.p.f. for the lattice gas, which goes to the value one for these limiting cases. This apparently small difference in the relative behaviors has a crucial effect at low densities. To demonstrate this, consider the case when $\epsilon = 0$, so there is no interaction between particles in different cells. Then

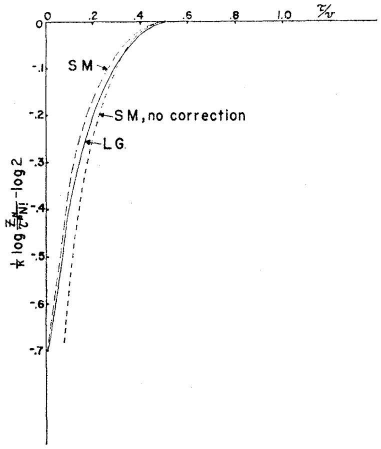

FIG. 2. Behavior of the quantity $K^{-1}\ln(Z_N/\tau^N N!)-\ln 2$ when $\epsilon=0$ as a function of τ/v for the lattice gas (LG), the spherical model (SM, no correction) and the spherical model (SM) with the modified constraint given by Eq. (59).

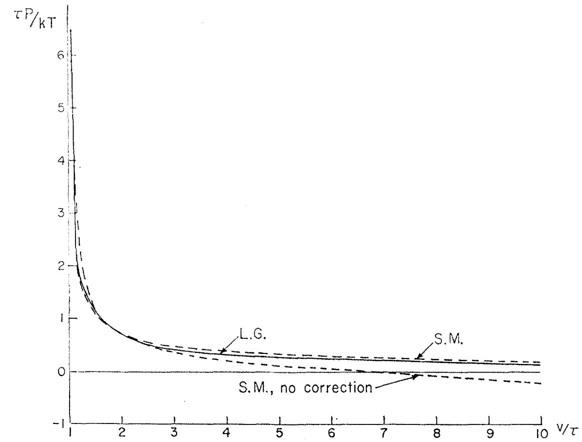

FIG. 4. Behavior of $\tau P/kT$ when $\epsilon=0$ as a function of v/τ for the lattice gas and the spherical model.

for the lattice gas we have the c.p.f.

$$\frac{Z_N}{N!}=\tau^N\frac{K!}{N!(K-N)!}, \tag{55}$$

while for the SM, we have, from Eqs. (23) and (25)

$$\frac{Z_N}{N!}=\tau^N\left[16\frac{N}{K}\left(1-\frac{N}{K}\right)\right]^{K/2}. \tag{56}$$

Figure 2 shows the quantity $(1/K)\ln(Z_N/\tau^N N!)-\ln 2$ plotted for both models. For the SM this quantity approaches minus infinity as N approaches zero or N approaches K. This has the effect on $\exp(-\psi/kT)=(Z_N/\tau^N N!)^{1/N}$ shown in Fig. 3. For the SM this quantity reaches a maximum for $\tau\rho\sim 0.2$ and then decreases for smaller values of the density. This implies that the pressure becomes zero at this density and negative for smaller values of the density. Figure 4 shows the pressure from the two models.

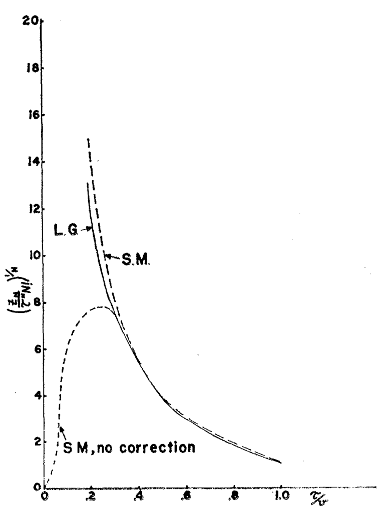

FIG. 3. Behavior of $(Z_N/\tau^N N!)^{1/N}$ when $\epsilon=0$ as a function of τ/v for the lattice gas and the spherical model with and without modification of the constraint.

To eliminate this behavior in a simple fashion, one needs to ensure for the SM a nonzero region of integration as N approaches zero or K. This may be done in a rather heuristic fashion by modifying the constraint $\sum x_j=2N-K$ so that it reads

$$\sum x_j=2N-K+\alpha(1-2N/K). \tag{57}$$

The form of the added term is chosen to preserve the model symmetry about the value $N/K=1/2$. For the parameter α positive, it ensures a nonvanishing integration region for $N=0$ or $N=K$. The parameter α may be chosen so that $(1/K)\ln(Z_N/\tau^N N!)\rightarrow 0$ for the SM as it does for the lattice gas. It is a simple exercise to show that this yields for α the value

$$\alpha=K(1-\sqrt{3}/2). \tag{58}$$

So that our constraint of total number of particles now reads

$$\sum_{j=1}^{K} x_j=\frac{\sqrt{3}}{2}(2N-K) \tag{59}$$

In Figs. 2, 3, and 4 the improvement affected by this modification is shown. We now have the pressure always positive in this "ideal gas" region. Moreover, this modification does not affect the qualitative behavior of the model when interactions are present, so that our previous results are not materially affected.

VI. CONCLUSIONS

The spherical model of a lattice gas leads to a phase transition in three dimensions characterized by constant condensation pressure.

The interpretation of the normal modes shows that the model contains the general aspect of the clustering of particles. The distribution of mean square amplitudes among the various modes depends on density and temperature in a way similar to what one expects for the distribution of clusters of various sizes in an imperfect gas.

The very large fluctuations and the long range correlation are characteristics to be expected for the condensation process, and are consistent with the fact that the pressure is constant.

APPENDIX. BEHAVIOR OF THE PRESSURE AT TRANSITION VOLUMES

This Appendix shows that $\partial p/\partial v$ is continuous and $\partial^2 p/\partial v^2$ is discontinuous at the transition volumes v_L and v_G. Since p is constant in the transition region, we have only to show that $\partial p/\partial v$ approaches zero while $\partial^2 p/\partial v^2$ goes to a nonzero value as the specific volume v tends to v_L or v_G from outside the transition region.

We start with Eq. (38) for the pressure in the normal region

$$\frac{P}{kT}=\frac{1}{2\tau}\ln\frac{2}{e}+\frac{4\tau}{v^2}s_s-\frac{1}{2\tau}G_3(s_s), \tag{A1}$$

where s_s is determined from the saddle point, Eq. (29), which we write in the equivalent form

$$\frac{8\tau}{v}\left(1-\frac{\tau}{v}\right)=\left(\frac{dG_3}{ds}\right)_{s_s}. \tag{A2}$$

Then successive differentiation of p with respect to v yields the equations

$$\frac{1}{kT}\frac{\partial P}{\partial v}=\frac{4}{v}\left(\frac{2\tau}{v}-1\right)\frac{\partial s_s}{\partial v}-\frac{8\tau}{v^3}s_s, \tag{A3}$$

$$\frac{1}{kT}\frac{\partial^2 P}{\partial v^2}=\frac{4}{v}\left(2\frac{\tau}{v}-1\right)\frac{\partial^2 s_s}{\partial v^2}-\frac{4}{v^2}\left(6\frac{\tau}{v}-1\right)\frac{\partial s_s}{\partial v}+24\frac{\tau}{v^4}s_s. \tag{A4}$$

The volume derivatives of s_s follow from Eq. (A2), dropping the subscript s,

$$\frac{\partial s}{\partial v}=\left[\frac{8\tau}{v^2}\left(2\frac{\tau}{v}-1\right)\right]\Big/\left(\frac{d^2G_3}{dS^2}\right). \tag{A5}$$

$$\frac{\partial^2 s}{\partial v^2}=-\left[16\frac{\tau}{v^3}\left(3\frac{\tau}{v}-1\right)\right]\Big/\left(\frac{d^2G_3}{dS^2}\right)-\left[\frac{8\tau}{v^2}\left(\frac{2\tau}{v}-1\right)\right]^2\frac{d^3G_3}{dS^3}\Big/\left(\frac{d^2G_3}{dS^2}\right)^3. \tag{A6}$$

The function $G_3(s)$ is related to $g_3(s)$ through Eq. (22),

$$G_3(s)=-\frac{2\tau}{v}g_3(s)+8\frac{\tau}{v}\left(1-\frac{\tau}{v}\right)s. \tag{A7}$$

In the neighborhood of the branch point, $s=0$, we may use for $g_3(s)$ the expansion given by Eq. (35) to obtain

$$\begin{aligned} G_3(s)&\simeq G_3(0)+I(0,T)s-\frac{2\tau}{v}\delta s^{\frac{3}{2}},\\ dG_3/dS&\simeq I(0,T)-\frac{3\tau}{v}\delta s^{\frac{1}{2}},\\ d^2G_3/dS^2&\simeq-\frac{3}{2}\frac{\tau}{v}\delta s^{-\frac{1}{2}},\\ d^3G_3/dS^3&\simeq\frac{3}{4}\frac{\tau}{v}\delta s^{-\frac{3}{2}}. \end{aligned} \tag{A8}$$

Putting these into Eqs. (A5) and (A6), we get the results

$$\begin{aligned} &\lim_{s_s\to 0}\frac{\partial s_s}{\partial v}=0,\\ &\lim_{s_s\to 0}\frac{\partial^2 s_s}{\partial v^2}=-\frac{2}{9}\frac{v^2}{\tau^2\delta^2}\left[\frac{8\tau}{v^2}\left(2\frac{\tau}{\sigma}-1\right)\right]^2. \end{aligned} \tag{A9}$$

Consequently,

$$\lim_{s_s\to 0}\frac{\partial P}{\partial v}=0, \tag{A10}$$

whereas

$$\lim_{s_s\to 0}\frac{\partial^2 P}{\partial v^2}=4\pi^2\beta^2\frac{\epsilon^3}{v^3}\left(2\frac{\tau}{v}-1\right)^3 \tag{A11}$$

measures the discontinuity in the second derivative of pressure with respect to volume at the transition volumes v_L and v_G.