Phase transitions in the Gaussian core system

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Some aspects of phase transition behavior have been studied for a classical system of particles which interact in pairs via repelling Gaussian potentials. In a specific low-temperature, low-density limit, this model acts as though it were composed of rigid spheres. Study of lattice sums suggests that at $T = 0$, a fcc crystal stable at low density transforms under compression to a bcc crystal. It is shown that sufficient compression at any fixed $T > 0$ always produces a fluid phase. Under suitable temperature and density conditions, the model can exhibit positive, negative, or vanishing volumes of melting.

I. INTRODUCTION

It is widely believed that the repulsive portions of intermolecular forces play a crucial role in fluid–solid phase changes.[1-4] Molecular arrangements present in liquids at their freezing points are determined primarily by nonoverlap conditions between neighbors, while crystal structures formed by solidification demonstrate geometrically efficient ways of packing the atoms or molecules in space.[5]

Statistical-mechanical studies of freezing have traditionally relied on model systems with very simple repulsive forces. Frequently occurring examples are the rigid sphere model and inverse-power pair potentials. These elementary cases have led to valuable insights into the freezing behavior of monatomic substances.

This paper is devoted to study of another simple model. Specifically, the postulated interaction potential Φ consists of a pairwise sum of additive Gaussian components. Using suitable reduced units, we thus write the N-molecule interaction as follows:

$$\Phi(\mathbf{r}_1 .. \mathbf{r}_N) = \sum_{i<j} \varphi(r_{ij}) , \qquad \varphi(r) = \exp(-r^2) . \tag{1.1}$$

The "Gaussian core" model embodied in Eq. (1.1) deserves attention for at least three reasons. First, the relative "softness" of the interactions suggests that it may display behavior similar to that of real substances which form plastic crystals (low melting entropy,[6] high solid-phase mobility[7]). Secondly, this model is one for which terms in an asymptotic high-temperature series for the free energy may be evaluated explicitly. Thirdly, it should be relatively easy to generate a precise data base for the model by digital computer simulation.

We leave each of these attractive features for later consideration. The present paper instead concentrates on some elementary properties of the Gaussian core model. The conclusions of this study indicate sufficient richness of behavior to command attention even beyond that of the above three aspects.

Section II shows that the Gaussian core model reduces to the venerable rigid sphere model in an appropriate low-temperature low-density limit. This reduction encompasses both equilibrium and kinetic properties (in the linear transport regime).

Section III examines the zero-temperature behavior of the Gaussian core system at nonzero density. By evaluating lattice sums, we seem to have established that the stable crystal structure undergoes at least one first-order transformation (f.c.c. to b.c.c.) as the system is compressed at zero absolute temperature.

An argument is presented in Sec. IV indicating that whenever the temperature is positive, application of sufficient pressure to the system will always cause melting. This observation implies that a maximum temperature exists at which crystallinity persists, and at this maximum the melting process entails no volume change.

II. RIGID SPHERE LIMIT

The classical partition function corresponding to Φ in Eq. (1.1) is the following:

$$Z = (\lambda^{3N} N!)^{-1} \int_V d\mathbf{r}_1 \ldots \int_V d\mathbf{r}_N \exp(-\beta\Phi) , \tag{2.1}$$

where λ is the mean thermal deBroglie wavelength, V is the volume, and β stands as usual for $(k_B T)^{-1}$. The integrand in Eq. (2.1) is a product of pair Boltzmann factors

$$b(r_{ij}) = \exp[-\beta \exp(-r_{ij}^2)] . \tag{2.2}$$

It is clear that b is a monotonically increasing function of distance.

Define the temperature-dependent distance R by

$$R(\beta) = (\ln\beta)^{1/2} ; \tag{2.3}$$

at this distance b has risen to $1/e$ of its asymptotic value. Now consider

$$f(x) = \lim_{\beta \to \infty} b(xR). \tag{2.4}$$

By inserting Eq. (2.3) into Eq. (2.2) one finds

$$f(x) = \lim_{\beta \to \infty} \exp(-\beta^{1-x^2})$$
$$= U(|x| - 1) , \tag{2.5}$$

where U is the unit step function:

$$U(y) = 0 \qquad (y < 0)$$
$$= 1/e \quad (y = 0) \tag{2.6}$$
$$= 1 \qquad (y > 0) .$$

Hence on the distance scale established by R at least, b acts more and more like the corresponding pair

Boltzmann factor for the rigid sphere interaction, as T approaches 0.

The discontinuous limiting behavior of b does not arise merely because the unit distance R diverges. Since one has

$$\left.\frac{db}{dr}\right|_{r=R} = \frac{2}{e}(\ln\beta)^{1/2} , \qquad (2.7)$$

the rise of b from 0 to 1 (essentially) is confined to an increasingly narrow range in r, even in unscaled units. Thus we also have

$$\lim_{\beta\to\infty} b(x+R) = U(x) . \qquad (2.8)$$

Since each integrand factor $b(r_{ij})$ in the partition function develops the same discontinuity at the low-temperature limit, the collection of N particles should behave as a system of rigid spheres in that limit (provided the density is low enough that all particle pairs can stay beyond distance R).

We now make this assertion more precise. The excess Helmholtz free energy for the Gaussian core model, $F_G^{(ex)}$, is related to the configuration integral in Eq. (2.1) as follows ($\rho = N/V$):

$$\exp\left[-\beta F_G^{(ex)}(\beta,\rho)\right] = V^{-N}\int_V d\mathbf{r}_1\ldots\int_V d\mathbf{r}_N \exp(-\beta\Phi) . \qquad (2.9)$$

An exactly analogous relation defines the hard-sphere-model excess free energy $F_{HS}^{(ex)}(\beta,\rho)$ for N spheres with diameters a in volume V. Then the preceding considerations lead to the conclusion that

$$\lim_{\beta\to\infty}\frac{F_G^{(ex)}[\beta,\rho_0 a^3/R^3(\beta)]}{F_{HS}^{(ex)}[\beta,\rho_0]} = 1, \qquad (2.10)$$

provided of course that

$$\rho_0 a^3 < \sqrt{2} , \qquad (2.11)$$

so that the geometric close packing density is avoided.

It is also clear that the low-temperature behavior of the b's will cause molecular distribution functions for the Gaussian core model to approach rigid-sphere values. Specifically, the sth order correlation function for the Gaussian case is defined by

$$g_G^{(s)}(\mathbf{r}_1\ldots\mathbf{r}_s, \beta, \rho) = \frac{V^s\int_V d\mathbf{r}_{s+1}\ldots\int_V d\mathbf{r}_N \exp(-\beta\Phi)}{\int_V d\mathbf{r}_1\ldots\int_V d\mathbf{r}_N \exp(-\beta\Phi)} \qquad (2.12)$$

and a similar expression applies for the β-independent hard-sphere function $g_{HS}^{(s)}(\mathbf{r}_1\ldots\mathbf{r}_s, \rho)$. Then

$$\lim_{\beta\to\infty}\frac{g_G^{(s)}[(R/a)\mathbf{r}_1\ldots(R/a)\mathbf{r}_s, \beta, \rho_0 a^3/R^3]}{g_{HS}^{(s)}[\mathbf{r}_1\ldots\mathbf{r}_s, \rho_0]} = 1 \qquad (2.13)$$

if Eq. (2.11) is satisfied and if

$$|\mathbf{r}_j - \mathbf{r}_i| > a \quad (1 \le i, j, \le s) . \qquad (2.14)$$

Just as we have demonstrated asymptotic reduction to hard-sphere behavior for all equilibrium properties, the same can be shown for kinetic and transport properties at least close to equilibrium. This follows by considering first the steepness of the Gaussian core for low-energy collisions, then examining the turning-point spread for such collisions.

Note that the inverse-power potential function

$$\varphi_0(r) = (\sigma/r)^n \qquad (2.15)$$

has the following logarithmic rate of change:

$$\varphi_0'/\varphi_0 = -n/r . \qquad (2.16)$$

The corresponding quantity for the Gaussian interaction is

$$\varphi'/\varphi = -2r . \qquad (2.17)$$

The position-dependent "effective exponent" for the Gaussian, to be denoted by $n^*(r)$, can thus be specified by setting

$$-n^*(r)/r = -2r , \quad n^*(r) = 2r^2 . \qquad (2.18)$$

Locally the Gaussian appears to act as a steeper and steeper wall as r increases, thus setting the stage for reduction to rigid-sphere dynamics if the preponderance of incident energies is low enough.

We now turn attention to the collision mechanics for a pair of Gaussian particles. In the center of mass coordinate system, the radial coordinate $r(t)$ is determined by the differential equation

$$dr/dt = \pm 2\{[E - \exp(-r^2)]/m - L^2/m^2 r^2\}^{1/2} , \qquad (2.19)$$

where E is the energy of relative motion, L is the angular momentum, and m is the mass of each particle.[8]

If E is small, the minimum value of r for most collisions will be essentially determined by the centrifugal barrier term $L^2/m^2 r^2$, i.e., the particles pass each other at sufficient distance to experience negligible mutual deflections. However, if L is also small (so the particles are initially well aimed toward each other), the minimum-r turning point r_m will be jointly determined by the centrifugal barrier and the direct central interaction. Equation (2.18) assures that the switchover will be a sudden one. Suppose, for one of these collisions, that

$$L^2/m^2 r_m^2 = \eta \exp(-r_m^2)/m , \qquad (2.20)$$

so that η measures the relative contribution of the two terms at the turning point. Since dr/dt vanishes at r_m,

$$E = (1+\eta)\exp(-r_m^2), \quad r_m(E,\eta) = \left[\ln\left(\frac{1+\eta}{E}\right)\right]^{1/2} . \qquad (2.21)$$

Since E is very small, the value of r_m will be dominated by the term $(-\ln E)^{1/2}$; the η part would provide only a negligible fractional change for any η of order unity. Consequently for those encounters producing significant enough deflections to be classed as "collisions," the distances of closest approach cluster strongly about $(-\ln E)^{1/2}$. In view of the specific functional form of this result, a modest spread in E values would cause little change in the clustering of turning points. In particular this is the observation already made about $b(r)$ for the Maxwell distribution of velocities, where $R(\beta)$ in Eq. (2.3) merely incorporates a suitable average collision energy. The implication of the more detailed collision analysis is that even with a modestly perturbed Maxwellian distribution, collisions can continue to behave as though rigid particles were involved.

An important conclusion following from the asymptotic reduction to rigid-sphere behavior is that in the low-density, low-temperature regime, the system of Gaussian particles undergoes the same fluid–solid transition as does the rigid-sphere model to a close-packed crystal. Computer simulations for the hard-sphere model indicate the following parameters at that transition[9]:

$$(\rho/\rho_{cp})_{\text{fluid}} = 0.667 \pm 0.003 \ ,$$

$$(\rho/\rho_{cp})_{\text{solid}} = 0.736 \pm 0.003 \ ,$$

$$\beta p/\rho_{cp} = 8.27 \pm 0.13 \ ,$$

$$\Delta S/Nk = 1.16 \pm 0.10 \ . \tag{2.22}$$

In these expressions ρ_{cp} stands for the maximum packing density. Although the cell cluster theory suggests that the hexagonal close-packed lattice has greater stability than the face-centered cubic lattice for hard spheres, the difference is predicted to be very small.[10] Molecular dynamics studies have been unable as yet to detect a stability difference,[11] whose existence therefore remains an open question. By implication, then, the stable crystal structure for the Gaussian core model is similarly uncertain in the limit used in Eqs. (2.10) and (2.13).

III. LATTICE SUMS

The structure of the Gaussian core system at $T = 0$ will be the next object for study. It is natural to expect that this structure, corresponding to the particle arrangement with minimum total interaction Φ, will be crystalline. Consequently we have evaluated lattice sums for several simple lattices, over a wide range of particle densities, in an attempt to identify the absolutely stable arrangement. We are concerned here only with the conventional large system limit (N, $V \to \infty$, ρ fixed), so that the results will be unaffected by the presence of boundaries.

For any crystal in which all particle sites are equivalent, the relevant lattice sum may be written as follows:

$$\frac{\Phi}{N} = \frac{1}{2} \sum_{\nu=1}^{\infty} Z_\nu \exp(-\xi_\nu^2 l^2) \ . \tag{3.1}$$

The terms in this sum collect contributions from successive shells of neighbors, indexed by ν. The nearest neighbor distance has been denoted by l; the νth neighbor shell comprises Z_ν particles at distance $\xi_\nu l$. It is useful to compare lattice sums with Φ_0/N, the mean interaction energy per particle for a random particle distribution at the given density:

TABLE I. Lattice-sum parameters.

Lattice	c [Eq. (3.3)]	Max. ν	Max. ξ_ν^2	Total neighbors
s.c.	1	92	108	4728
b.c.c.	$3^{3/2}/4$	68	200/3	2974
f.c.c.	$2^{1/2}$	60	65	3102
h.c.p.	$2^{1/2}$	130	185/3	2882
dia.	$3^{3/2}/8$	80	328/3	3108

TABLE II. Lattice sums (Φ/N) for the Gaussian core model.

ρ	S.c.	B.c.c.	F.c.c.
0.1	0.0294885602	0.0178224647	0.0173386422[a]
0.2	0.1791163214	0.1526057824[a]	0.1528149849
0.3	0.3968345053	0.3734162339[a]	0.3742473692
0.5	0.9088059189	0.8987023648[a]	0.8993063911
0.7	1.453802333	1.450207325[a]	1.450443624
1.0	2.285028123	2.284296878[a]	2.284342296
2.0	5.068333242	5.068328175[a]	5.068328351
3.0	7.852492056	7.852491996[a]	7.852491997
5.0	13.42081999	13.42081999[a]	13.42081999
7.0	18.98914799	18.98914799[a]	18.98914799

ρ	Hcp.	Dia.	Random
0.1	0.0173387416	0.0621164883	0.2784163998
0.2	0.1528284648	0.2424360989	0.5568327997
0.3	0.3743070889	0.4578664986	0.8352491995
0.5	0.8994156605	0.9446984950	1.392081999
0.7	1.450519692	1.471692930	1.948914799
1.0	2.284368105	2.290956417	2.784163998
2.0	5.068328641	5.068503672	5.568327997
3.0	7.852492000	7.852498865	8.352491995
5.0	13.42081999	13.42082001	13.92081999
7.0	18.98914799	18.98914799	19.48914799

[a]Denotes apparent stable structure.

$$\frac{1}{2} \rho \int \exp(-r^2) \, d\mathbf{r} = \frac{1}{2} \pi^{3/2} \rho \equiv \frac{\Phi_0}{N} \ . \tag{3.2}$$

Not all lattice sums tested would have to give lower results than this, but certainly the stable configuration must.

No finite procedure exists for deciding with absolute certainty what the stable $T = 0$ structure is. But it is plausible to expect that structure to be found among the simple and highly symmetrical lattices. Consequently that is where we have searched. We do not rule out the possibility that our tentative conclusions could be preempted by results of further search, though at least at low densities this seems unlikely.

The specific lattices examined were simple cubic, body-centered cubic, face-centered cubic, hexagonal close-packed, and diamond. For each, the nearest neighbor distance is related simply to ρ:

$$l^3 = c/\rho \ , \tag{3.3}$$

with the various c values listed in Table I. The lattice sums were evaluated in all cases by inclusion of spheres of more than 2800 neighbors (Table I lists specific numbers), supplemented by integral estimates of more remote contributions when necessary.

Table II displays some representative results for the lattice sums, from a much more exhaustive study. Even before doing the calculations, one could anticipate that the face-centered cubic structure would prevail at $T = 0$ for low density, and that is borne out by the table. The most important feature of the low-density case is the nearest-neighbor distance, and this distance is maximized by the f.c.c. and h.c.p. lattices. However, where these lattices first differ in coordination shell structure, h.c.p. has two neighbors

TABLE III. Coexistence parameters for $T = 0$ structural transition.

	F.c.c.		B.c.c.
ρ	0.17941		0.17977
Φ/N	0.115465107		0.116073318
p		0.05529	
$\Delta\rho$		0.00036	
$\Delta(\Phi/N)$		0.000608211	

at a distance where f.c.c. has none, so the latter will have the lower energy.

Evidently the f.c.c. structure gives way to b.c.c. at intermediate density. No obvious explanation suggests itself for this tendency to lower coordination as density rises. The s.c., h.c.p., and dia. lattices are apparently unstable at all densities.

The thermodynamic transition between the different crystal structures must be first order, since different symmetry groups are involved.[12] The only condition for coexistence of distinct crystal structures required at $T = 0$ is equality of pressure p in the two phases, where in this limit

$$p = -\partial(\Phi/N)/\partial(1/\rho) \ . \tag{3.4}$$

Coexisting states can be located most conveniently by plotting Φ/N for the different structures versus $1/\rho$, and then applying Maxwell's double tangent construction to the resulting curves.[13] Table III provides transition parameters obtained in this way for the f.c.c. to b.c.c. transition.

The stability of the crystal structures against certain simple types of modifications is easy to check. One such possibility is the change caused by removal of particles to cause formation of a few widely separated vacancies, followed by compression to the initial density. But if

$$\rho \, \partial(\Phi/N)/\partial\rho > \Phi/N \ , \tag{3.5}$$

this process causes the energy to rise, and that was always found to be the case for the lattice sums examined.

Another conceivable instability is that for which the lattice spacing increases as j particles are caused to sit atop one another at each lattice site. In order that this restructuring produce energy increase, it is necessary that

$$(\Phi/N)_\rho < \tfrac{1}{2}(j-1) + j(\Phi/N)_{\rho/j} \ . \tag{3.6}$$

Once again we find that the lattice sums numerically satisfy the criterion for stability.

The validity of Table II, for $\rho = 1$, has been checked independently by "molecular dynamics" computer studies.[14] Systems of 432 particles in a cubical cell (subject to periodic boundary conditions) were cooled slowly toward, and heated from, absolute zero. These systems were observed spontaneously to freeze into the body-centered cubic crystal structure in several trials. No alternative structure with lower final energy has ever arisen.

IV. COMPRESSION MELTING

Entries in Table II suggest that energy differences between lattices might disappear as density rises toward infinity. Furthermore it seems that the common lattice value lies about one-half unit below that for the uniform particle distribution. We will now confirm that these observations are not coincidental, but have a rational basis and lead to important conclusions about phase behavior for the Gaussian core system.

Suppose that the particles, with positions $r_1 \ldots r_N$, form any regular array all of whose sites are equivalent. Then for this structure we have

$$\frac{\Phi}{N} = \frac{1}{2}\sum_{j=2}^{N} \exp(-r_{1j}^2) \ . \tag{4.1}$$

Introduce nearest-neighbor (Voronoi) polyhedra $P_1 \ldots P_N$ for the particles.[15] All of these polyhedra are equivalent, and each has volume $V/N = 1/\rho$. Formally we can write

$$\frac{\Phi}{N} = \tfrac{1}{2}\rho\sum_{j=2}^{N} \int_{P_j} \exp(-r_{1j}^2)\, d\mathbf{r} \ , \tag{4.2}$$

where each integral spans only one polyhedron.

The random-distribution potential Φ_0/N may be expressed in analogous fashion:

$$\frac{\Phi_0}{N} = \tfrac{1}{2}\rho\sum_{j=1}^{N} \int_{P_j} \exp(-|\mathbf{r} - \mathbf{r}_1|^2)\, d\mathbf{r} \ . \tag{4.3}$$

Therefore we have

$$\frac{\Phi_0 - \Phi}{N} = \tfrac{1}{2} + \tfrac{1}{2}\rho\sum_{j=1}^{N} \int_{P_j} [\exp(-|\mathbf{r} - \mathbf{r}_1|^2) - \exp(-|\mathbf{r}_j - \mathbf{r}_1|^2)]\, d\mathbf{r} \ . \tag{4.4}$$

As the system is compressed isotropically, the polyhedra P shrink with linear dimensions proportional to $\rho^{-1/3}$. In the high density limit we wish to show that the sum of integral terms in Eq. (4.4), including the multiplier ρ, vanishes. Basically the summation represents the error term in a three-dimensional generalization of the "rectangle rule" for numerical quadrature and it must be established that this error vanishes more strongly than ρ^{-1}. Unfortunately the theory of numerical approximation for multiple integrals is quite incomplete,[16] and does not seem to offer the required demonstration.

For each integrand in Eq. (4.4) we can invoke Taylor's expansion:

$$\exp(-|\mathbf{r} - \mathbf{r}_1|^2) - \exp(-|\mathbf{r}_j - \mathbf{r}_1|^2)$$
$$= \{(\mathbf{r} - \mathbf{r}_j) \cdot \nabla_j + \tfrac{1}{2}(\mathbf{r} - \mathbf{r}_j)(\mathbf{r} - \mathbf{r}_j) : \nabla_j\nabla_j + \ldots\}$$
$$\times \exp(-|\mathbf{r}_j - \mathbf{r}_1|^2) \ . \tag{4.5}$$

The Voronoi polyhedra for lattices listed in Table II have symmetries such that insertion of expansion (4.5) into Eq. (4.4) will cause linear and cubic terms to integrate to zero. Of those terms from Eq. (4.5) which survive the integration, it will suffice to keep only the quadratic and quartic terms; simple scaling arguments show that higher-order terms will lead to lower orders in ρ (as ρ diverges) than for those terms retained.

Thus we examine the following reduced form for the

sum term R in Eq. (4.4):

$$R = \tfrac{1}{2}\rho\,(R_2 + R_4)\ ,$$

$$R_2 = \frac{1}{2}\sum_{j=1}^{N}\left[\int_{P_j}(\mathbf{r}-\mathbf{r}_j)(\mathbf{r}-\mathbf{r}_j)d\mathbf{r}\right] : \nabla_j\nabla_j\exp(-r_{1j}^2)\ ,$$

$$R_4 = \frac{1}{24}\sum_{j=1}^{N}\left[\int_{P_j}(\mathbf{r}-\mathbf{r}_j)(\mathbf{r}-\mathbf{r}_j)(\mathbf{r}-\mathbf{r}_j)(\mathbf{r}-\mathbf{r}_j)\,d\mathbf{r}\right]$$

$$:: \nabla_j\nabla_j\nabla_j\nabla_j\exp(-r_{1j}^2)\ . \tag{4.6}$$

Since each P_j has linear dimensions proportional to $\rho^{-1/3}$, the separate integrals in R_4 will be proportional to $\rho^{-7/3}$. The summation in R_4 can do no more than generate another factor ρ, considering the density of lattice points over the range of $\exp(-r_{1j}^2)$. Consequently

$$R_4 = O(\rho^{-4/3})\ , \tag{4.7}$$

and no corresponding contribution to R survives as ρ approaches infinity.

All of the integrals appearing in R_2 are identical. For the lattices under consideration (those in Table II), the P_j have sufficiently high degrees of symmetry that the integrals must be proportional to the unit dyad $\mathbf{1}$. Considering once again how the linear dimensions of the P_j vary with ρ, we can write

$$K\rho^{-5/3}\mathbf{1} \tag{4.8}$$

for each integral, where K is a suitable positive constant. Thus

$$R_2 = \tfrac{1}{4}K\rho^{-5/3}\sum_{j=1}^{N}\nabla_j^2\exp(-r_{1j}^2)\ . \tag{4.9}$$

The last sum may be written as a corresponding integral plus an error term E_2:

$$R_2 = \tfrac{1}{4}K\rho^{-5/3}\left[\rho\int\nabla_j^2\exp(-r_{1j}^2)\,d\mathbf{r}_j + E_2\right]\ . \tag{4.10}$$

Of course the integral vanishes. E_2 may be readily estimated by repetition of the Taylor expansion method already used; the conclusion is that E_2 is proportional to $\rho^{1/3}$ at most. Consequently

$$R_2 = O(\rho^{-4/3})\ , \tag{4.11}$$

so that

$$R = O(\rho^{-1/3})\ . \tag{4.12}$$

This finally permits one to conclude that

$$\lim_{\rho\to\infty}(\Phi_0 - \Phi)/N = \tfrac{1}{2} \tag{4.13}$$

for the lattices considered in Table II.

The geometric significance of result (4.13) is that when a particle is incorporated in a regular lattice, it is necessarily surrounded by a "correlation hole" of volume $1/\rho$ from which other particles are excluded. Such correlation (and the resulting potential energy reduction) obviously is not present in the random distribution.

Although the corresponding generalized analysis is more elaborate, it is actually possible to prove that

Eq. (4.13) is valid for any three-dimensional periodic array. It should also be stressed that a result of type (4.13) applies to any potential which, like the Gaussian $\varphi(r)$, is differentiable at least four times, vanishes strongly enough at infinity to be integrable, and is $+1$ at the origin.

Equation (4.13) has important consequences for the phase behavior of the Gaussian core model. It shows that the energetic advantage to the placing of particles in a regular lattice is bounded, compared to the random arrangement. That would be sufficient to ensure crystallinity at $T=0$, as suggested in the preceding section. But when $T>0$, the requirement that particles remain confined to a regular lattice as the spacing in that lattice goes to zero creates a diverging negative entropy that could only be offset by an unbounded energy in the same limit. Since this is not the case, sufficient compression at any $T>0$ will inevitably produce a noncrystalline thermodynamic state. Put in other terms, a crystal at nonzero temperature can always be made to melt by isothermal compression.

V. DISCUSSION

Because pair interactions in the Gaussian core model are bounded, at any given ρ they can only suffice to maintain crystalline order below some finite melting temperature $T_m(\rho)$. The results of Sec. II have verified the intuitively obvious result

$$\lim_{\rho\to 0} T_m(\rho) = 0\ , \tag{5.1}$$

while Sec. IV leads to the less obvious conclusion that

$$\lim_{\rho\to\infty} T_m(\rho) = 0\ . \tag{5.2}$$

Between these limits there must exist a density which maximizes $T_m(\rho)$. It is reasonable to suppose that this density is unique. We denote it by ρ_c.

Without detailed numerical study of the Gaussian core model (as can be provided by molecular dynamics[14]) it is not possible to know the values of ρ_c or $T_m(\rho_c)$, or to know which crystal structure achieves this maximum melting temperature. Nevertheless we can anticipate that whatever values and crystal structure are involved, the general phase behavior near the maximum melting point should conform to that shown in Fig. 1.

The melting temperature $T_m(\rho)$ is represented in Fig. 1 by the curve BCD, which achieves its maximum at point C. Along the low-density portion CD of this curve, the melting solid produces fluid of lower density, i.e., the volume of melting is positive. However, along the high density curve BC, the fluid is more dense at coexistence than the crystal (negative melting volume). In this high-density melting regime the Gaussian model thus behaves like the real substances Si, Ge, Bi, H_2O, and a variety of III–V compounds[17] which contract upon melting. However, the reason that it happens in the Gaussian core model is not obviously relevant to these other materials.

At point C in Fig. 1 the crystal and its melt have the same density, and of course the same pressure. How-
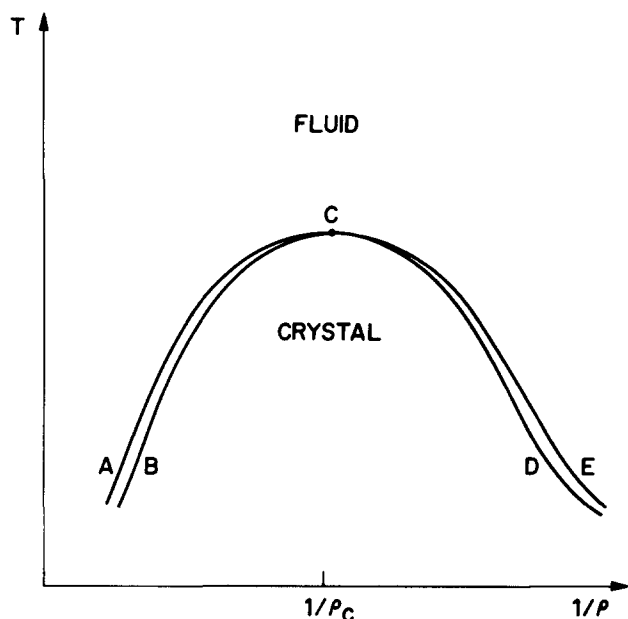
FIG. 1. Phase behavior near the point (C) of maximum melt-
ing temperature for the Gaussian core model. Fluid and crys-
tal coexist in the narrow regions between curves BCD and ACE.

ever, the melting transition at C can still be thermo-
dynamically first order, with nonvanishing latent heat,
and sudden disappearance of crystalline long-range
order.

That equal-density phases should be in coexistence at
C, suggests that relatively minor structural changes
(particle displacements) are needed to transform one
into the other. As a result the entropy of melting at C
may be small, and in particular considerably smaller
than the rigid-sphere value displayed in Eqs. (2.22).
If only rather small structural changes are indeed re-
quired at C, then spontaneous fluctuations in each phase
should frequently form domains or clusters characteris-
tic of the other phase. Possibly these fluctuations are
large enough to create significant anomalies both in
thermodynamic properties and in molecular distribu-
tion functions in the neighborhood of C.

It is even conceivable that structural fluctuations
might be sufficiently strong to eliminate any distinction
between the two phases at C. Then melting at C would
be a continuous transition with no latent heat ($\Delta S = 0$),
and with long-range crystalline order vanishing con-
tinuously as C is approached from within the crystal
region in Fig. 1. This behavior conflicts with the
classic Landau theory of second-order phase
change.[12,18,19] Nevertheless, strong fluctuations could
undermine the analyticity assumptions (of free energy
in order parameters) that underlie Landau theory, just
as diverging fluctuations at liquid–vapor critical points
render inapplicable the naive theory of classical criti-
cal exponents.[20] The unanswered questions about the
precise nature of point C add extra importance to the
study of the Gaussian core system by computer simula-
tion.

The Gaussian core model has been introduced in this
paper largely on account of its pleasant mathematical

properties. However, it must be stressed that at least
some portions of the model's T, ρ phase plane can
probably represent real materials with useful fidelity.
The softness of interaction between close particle pairs
[illustrated for example by effective exponent n^* in Eq.
(2.18) when r is small] can be realized by polyatomic
molecules which, when pressed together, can mutually
deform and rotate to fit "bumps" into "depression."
As already mentioned in the Introduction, plastic crys-
tals typically involve globular polyatomic molecules
(such as camphene and cyclohexane[6]). It seems reason-
able to suppose that detailed studies of phonon spectra,
of defects, and of the self-diffusion process in crystal
phases of the Gaussian core model will help to under-
stand the peculiar properties of real plastic crystals.

The suggestion that the present model might help to
understand polyatomic materials has an interesting ex-
tension to polymer solutions. When suspended in a
"good" solvent, a randomly coiling linear polymer will
be rather extended. If two such extended coils diffuse
close together (compared to their radii of gyration), the
steric hindrances between chains would cause loss of
configurational entropy. On the average this would give
rise to a repulsive force between the chains. For suit-
ably chosen polymer and solvent pairs, the potential of
mean force could be close to a Gaussian function of
distance between the respective polymer coil centroids.

This potential of mean force plays a central role in
the McMillian–Mayer theory[21] for osmotic properties
of the polymer solution. The osmotic pressure of the
solution might then be modelled by the pressure com-
puted for our Gaussian core system. In particular it
would be interesting to see if the phase behavior illus-
trated in Fig. 1 could be produced experimentally in
the osmotic behavior of polymer solutions.

Finally, notice should be given to the observation of
crystalline arrays of charged colloidal particles which,
like the Gaussian core model crystals, owe their stabil-
ity entirely to repulsive forces.[22] The relevance of the
present type of model is reinforced by the fact that
transitions between face-centered and body-centered
cubic arrays have been observed for aqueous suspen-
sions of polystyrene spheres.[23]

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