PHYSICAL REVIEW A VOLUME 35, NUMBER 11 JUNE 1, 1987

Nonuniform classical fluid at high dimensionality

H. L. Frisch
Department of Chemistry, State University of New York at Albany, Albany, New York 12222

J. K. Percus
Courant Institute of Mathematical Sciences and Department of Physics, New York University, New York, New York 10012

(Received 24 November 1986)

We investigate the existence of nonuniform thermodynamic states of classical fluids with purely repulsive finite-range interaction, such as that of hard spheres. Both free energy and nonuniform profile are obtained in the strict limit of an infinitely large spatial dimension. We establish the density at which the uniform state undergoes a Kirkwood instability, and provide a basis for the surmise that this instability leads continuously to an ordered lattice.

I. INTRODUCTION

The effect of high spatial dimensionality on the qualitative properties of many-body statistical mechanics has been observed with increasing frequency.[1,2] For lattice gases, the mean spherical nature of unbounded coordination number is a result of long standing,[3] and more recent investigations[4,5] have pointed out the dramatic structural simplification of a hard-core continuum fluid in the high-dimensionality limit. The bulk thermodynamics format of these studies, however, precludes the vast array of phenomena associated with spatial heterogeneity, which constitutes the subject of the present paper. We will for simplicity restrict our attention to simple classical fluids with purely repulsive finite-range interactions.

In Sec. II we derive a simple expression for the free energy of a nonuniform repulsively interacting fluid in the strict infinite-dimensional limit. From this, we obtain the appropriate density profile equation, which is of the nonuniform Debye-Hückel type. It is used in Sec. III to study the stability of the uniform state, and in sufficient approximation in Secs. II and III to study the spatial pattern of the resulting symmetry breaking. In particular, the low-dimensional corrugated patterns, indicative of a lattice structure, are examined in Sec. V. We conclude with some remarks on the validity of the profiles uncovered as legitimate asymptotic results.

II. FREE ENERGY

We will make use of the Mayer diagrammatic expansion in a grand canonical ensemble. Adopting the convention $\mathbf{r}_j \sim j$, one knows[6] that the grand potential for a pairwise interacting system with a nonuniform density $n(1)$ is given by

$$\beta\Omega = -\int n(1)\,d1 + \sum_{N=2}^{\infty} \frac{N-1}{N!}\{\text{all distinct connected diagrams with no articulation points, links } f(i,j),\ N \text{ vertices } n(i),\text{ and integrated over } 1,2,\ldots,N\}\ . \tag{2.1}$$

By an articulation point, one means a vertex whose excision disconnects the diagram, β denotes reciprocal temperature, and $f(i,j)=\exp[-\beta\phi(i,j)]-1$ for internal interaction $\phi(i,j)$, which will be taken as nonnegative, translation invariant, and of finite range.

In estimating the contributions of various diagrams, one thing is obvious: Since $-1 \le f(i,j) \le 0$ for repulsive interactions, each factor $f(i,j)$ reduces the absolute value of a diagram, which is thereby bounded from above by diagrams with fewer links. Furthermore if $N>2$, an N-vertex diagram must have at least one loop; we identify such a loop. Then, if links are successively removed, so that any vertex outside this loop becomes singly connected to the loop, we remain with one loop whose vertices have dangling trees. See, for example, Fig. 1. In this fashion,[5] any N-vertex diagram I_N is reduced to one with a single p loop and N-p links in trees. But if n_M is the maximum value of the density in the domain of the system, then certainly

$$\left|\int n(1)f(1,2)\,d1\right| \le n_M \left|\int f(1,2)\,d1\right| = n_M \int |f(1)|\,d1\ , \tag{2.2}$$

where $f(r_1,r_2)=f(r_{12})$. Using (2.2), each tree is reduced to its root, and so we have for any N-vertex diagram with $N>2$,

$$|I_N| \le n_M^{N-p}\left|\int f(1)\,d1\right|^{N-p}\left|\int\cdots\int n(1)f(1,2)n(2)f(2,3)n(3)\cdots\times\cdots f(p,1)\,d1\cdots dp\right|$$
$$\le n_M^{N-1}\left|\int f(1)\,d1\right|^{N-p}\left|\int\cdots\int n(1)f(1,2)f(2,3)\cdots f(p,1)\,d1\cdots dp\right|\ ,$$

or

$$|I_N| \le n_M^{N-1}\int n(1)\,d1\ \left|\int f(1)\,d1\right|^{N-p}\left|\int\cdots\int f(2)f(2,3)\cdots f(p-1,p)f(p)\,d2\cdots dp\right|\ . \tag{2.3}$$

In order to define the $D\to\infty$ limit, we shall take $1/n$ in units of the generalized exclusion volume

$$v=\int -f(1)\,d1\ , \tag{2.4}$$

i.e., we write

$$|I_N|\le (n_M v)^{N-1}Q_P\ , \tag{2.5}$$

where

$$Q_p=\left|\int\cdots\int f(2)f(2,3)\cdots f(p-1,p)f(p)\,d2\cdots dp\right| \Big/ \left|\int f(1)\,d1\right|^{p-1} \tag{2.6}$$

and $p>2$. The estimation of Q_p is most readily done in Fourier transform. We set

$$\tilde f(k)=\int f(r)e^{ik\cdot r}d^Dr\ , \tag{2.7}$$

whence

$$Q_p=\frac{1}{(2\pi)^2}\left|\int [\tilde f(k)]^p d^Dk\right| \Big/ |\tilde f(0)|^{p-1}\ . \tag{2.8}$$

For a very weak but sufficient bound, we observe first that since $-f(r)\ge 0$, then $|\tilde f(k)|\le|\tilde f(0)|$. Hence, using Schwartz's inequality,

$$\begin{aligned}\left|\int [\tilde f(k)]^p d^Dk\right| &\le \left[\int [\tilde f(k)]^2 d^Dk\right]^{1/2}\left[\int [\tilde f(k)]^{2p-2} d^Dk\right]^{1/2}\\ &\le \left[\int [\tilde f(k)]^2 d^Dk\right]^{1/2}|\tilde f(0)|^{p-3}\left[\int [\tilde f(k)]^4 d^Dk\right]^{1/2}.\end{aligned}$$

But

$$\int [\tilde f(k)]^2 d^Dk=(2\pi)^D\int [f(r)]^2 d^Dr\le (2\pi)^D\int [-f(r)]d^Dr=(2\pi)^D|\tilde f(0)|\ .$$

We conclude from (2.8) that

$$Q_p\le Q_4^{1/2}\ . \tag{2.9}$$

One can now show at leisure that $Q_4\to 0$ as $D\to\infty$. For an upper bound, we can of course replace $f(r)$ by $f_0(r)=\epsilon(R-|r|)$, where $f(r)=0$ for $|r|>R$. Going to hyperspherical coordinates, we first compute

$$\int f_0(r-r')f_0(r')d^Dr'=S_{p-1}(1)\int f_0\{[r^2+(r')^2-2rr'\mu]^{1/2}\}f_0(r')(1-\mu^2)^{(D-3)/2}(r')^{D-1}d\mu\,dr'$$

$$=S_{D-1}(1)/2^{D-3}r^{D-2}\int\int_\Delta \epsilon(R-r'')\epsilon(R-r)\{2r^2[(r')^2+(r'')^2]-[(r')^2-(r'')^2]^2-r^4\}^{(D-3)/2}r'\,dr'\,dr''\ ,$$

where

$$S_D(1)=2\pi^{D/2}\Big/\left[\frac{D}{2}-1\right]! \tag{2.10}$$

is the surface area of a D-dimensional unit sphere and Δ signifies the triangle condition: $|r'-r''|\le r\le r'+r''$. For an upper bound, it suffices to integrate $[q'=(r')^2]$

$$\int_0^{R^2}\int_0^{R^2}[4r^2R^2-r^4-(q'-q'')^2]^{(D-3)/2}dq'\,dq''\ ,$$

and we readily find

$$\int f_0(r-r')f_0(r')d^Dr'\le\frac{\pi^{D/2}}{2^{D-1/2}[(D-2)/2]!}(4R^2-r^2)^{D/2}f(2R-r)\ . \tag{2.11}$$

Of course, we also have

$$|\tilde f(0)|\ge v_D(1)(R')^D f_m\ , \tag{2.12}$$

where f_m is the minimum of $|f(r)|$ in the interval $|r|<R'$ and

$$v_D(1)=\pi^{D/2}/(D/2)! \tag{2.13}$$

is the volume of a D-dimensional unit sphere. Finally, we have

$$\int\cdots\int f_0(1)f_0(2-1)f_0(3-2)f_0(3)\,d1\,d2\,d3=S_D(1)\int\left[\int f_0(r-r')f_0(r')d^Dr'\right]^2 r^{D-1}dr\ ,$$

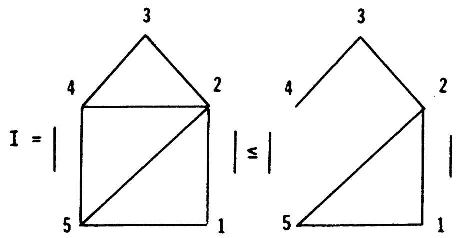

FIG. 1. Basic reduction for repulsive potential.

or via (2.11),

$$\int \cdots \int f_0(1)f_0(2-1)f_0(3-2)f_0(3)\,d1\,d2\,d3 \le 2^{D+2}\pi^{3D/2}R^{3D}D! \Big/ \left[\frac{D-1}{2}!\right]\left[\frac{3D}{2}\right]! \,, \tag{2.14}$$

which combined with (2.13) yields the estimate

$$f_m^3 Q_4 < D\,2^D \frac{D!\frac{D}{2}!}{(3D/2)!}\left[\frac{R}{R'}\right]^{3D} \sim \left[\frac{2\pi D^3}{3}\right]^{1/2}\left[\frac{16}{27}\right]^{D/2}\left[\frac{R}{R'}\right]^{3D} \tag{2.15}$$

an exponentially decreasing function of D as long as $R/R' < 4^{1/3}/3^{1/2}$.

We conclude from (2.5) and (2.15) that if the Mayer series (2.1) converges absolutely for any value of D, then as $D \to \infty$ (with $1/v$ as density unit), only the first two terms remain, so that

$$\beta\Omega = -\int n(r)\,d^D r + \tfrac{1}{2}\int\int n(r)f(r-r')n(r')\,d^D r\,d^D r' \,. \tag{2.16}$$

The "bulk" or internal Helmholtz free energy

$$F^B = F - \int n(r)u(r)d^D r \tag{2.17}$$

for external potential $u(r)$ is more useful for nonuniform systems, and is related to Ω by

$$F^B - \int n(r)\frac{\delta F^B}{\delta n(r)}d^D r = \Omega \,. \tag{2.18}$$

This relation is clearly consistent with the expression[5,7]

$$\beta F^B = \int [n(r)\ln n(r) - n(r)]d^D r - \tfrac{1}{2}\int\int n(r)f(r-r')n(r')\,d^D r\,d^D r' \tag{2.19}$$

and uniqueness is established by starting with the ideal-gas form

$$\beta\Omega_0 = -\int n(r)\,d^D r \,, \qquad \beta F^B = \int [n(r)\ln n(r) - n(r)]d^D r \,, \tag{2.20}$$

then turning up the interaction from 0.

It must be emphasized that (2.19) has been constructed [see (2.5)] by letting $D \to \infty$ at fixed n_M, and is thus a limiting model. It is this model that we will now focus on, and in particular examine its consequence as $n_M \to \infty$ in a D-dependent fashion. Abandoning control of joint limits raises the possibility that the model may be used out of its range of correspondence with reality, and indeed Kirkpatrick has pointed out[6] that some of the striking consequences of the model occur at a density at which the estimates (2.5) do not converge. With this caveat, we now proceed.

III. STABILITY OF UNIFORM STATE

The reaction of an equilibrium fluid to an external field is determined by the relation

$$\mu - u(r) = \delta F^B/\delta n(r) \,, \tag{3.1}$$

or explicitly in the present case

$$\beta[\mu - u(r)] = \ln n(r) - \int f(r-r')n(r')\,d^D r' \,, \tag{3.2}$$

recognized as a version of the nonlinear Debye-Hückel equation. When $u=0$, there will in general exist a uniform state, satisfying

$$\beta\mu = \ln n - \tilde{f}(0)n \,. \tag{3.3}$$

But this state can bifurcate under an arbitrarily small perturbation $\delta u(r)$. It will do so if $\delta u(r)=0$ for some perturbation of (3.2) about uniformity, i.e., if

$$0 = \frac{1}{n}\delta n(r) - \int f(r-r')\delta n(r')\,d^D r' = 0 \,. \tag{3.4}$$

Taking the Fourier transform,

$$\left[\frac{1}{n} - \tilde{f}(k)\right]\delta\tilde{n}(k) = 0 \,. \tag{3.5}$$

Thus uniformity will at least be metastable to excitations at some wave vector if

$$n \ge n_0 = \min_k[1/\tilde{f}(k)] \,, \tag{3.6}$$

suggesting a phase transition at n_0. This is the Kirkwood instability.[4]

Assessing the relevance of (3.6) is easy but not trivial. To start, we go to hyperspherical coordinates,[8] so that

$$\begin{aligned}\tilde{f}(k) &= S_{D-1}(1)\int_0^\infty \int_0^\pi f(r)e^{ikr\cos\theta}\sin^{D-2}\theta\, r^{D-1}\,d\theta\,dr \\ &= 2S_{D-1}(1)\int_0^\infty f(r)\int_0^{\pi/2}\cos(kr\cos\theta)\sin^{D-2}\theta\,d\theta\, r^{D-1}\,dr \,,\end{aligned} \tag{3.7}$$

or

$$\tilde{f}(k) = \left[\frac{2\pi}{k^2}\right]^{D/2}\int_0^\infty f(r)(kr)^{D/2}J_{D/2-1}(kr)\,dkr \,.$$

Let us now restrict our attention to a fluid of pure hard cores of diameter R, in which case (3.7) simplifies to

$$\tilde{f}(k)=-(2\pi)^{D/2}R^{D}J_{D/2}(kR)/(kR)^{D/2} \ . \tag{3.8}$$

We want to maximize (3.8), i.e., find the first minimum, the first stationary point, of $J_{D/2}(kR)/(kR)^{D/2}$. Since

$$(d/dkR)[J_{D/2}(kR)/(kR)^{D/2}]=-J_{D/2+1}(kR)/(kR)^{D/2} \ ,$$

k must satisfy

$$J_{D/2+1}(kR)=0 \ . \tag{3.9}$$

Now

$$J_\nu(\nu+z\nu^{1/3})=2^{1/3}A_i(-2^{1/3}z)\nu^{-1/3}+O(\nu^{-1}) \ , \tag{3.10}$$

where

$$A_i(-x)=\tfrac{1}{3}x^{1/2}[J_{1/3}(\tfrac{2}{3}x^{3/2})+J_{-1/3}(\tfrac{2}{3}x^{3/2})] \tag{3.11}$$

is the standard Airy function. If

$$A_i(-2^{1/3}z_0)=0 \ , \tag{3.12}$$

where $z_0=1.8558\ldots$ for the first zero, then inversion of $J_\nu(\nu+z\nu^{1/3})=0$ from (3.10) yields

$$z=z_0+O(\nu^{-2/3}) \tag{3.13}$$

or since $\nu=D/2+1$ in our case,

$$kR=\frac{D}{2}+z_0\left[\frac{D}{2}\right]^{1/3}+1+O(2/D) \ . \tag{3.14}$$

With (3.14), we can now evaluate

$$J_{D/2}(kR)=J_{D/2}\left\{\frac{D}{2}+\left[\frac{D}{2}\right]^{1/3}\left[z_0+\left[\frac{D}{2}\right]^{-1/3}+\cdots\right]\right\}$$

$$=2^{1/3}\left[A_i(-2^{1/3}z_0)-2^{1/3}\left[\frac{D}{2}\right]^{-1/3}A_i'(-2^{1/3}z_0)\right]\left[\frac{D}{2}\right]^{-1/3}+O(2/D) \ ,$$

or

$$J_{D/2}(kR)=-0.699(4/D)^{2/3}+O(2/D) \ . \tag{3.15}$$

Hence substituting into (3.6) and (3.8),

$$n_0=(D/4\pi)^{D/2}\frac{e}{0.699}e^{z_0(D/2)^{1/3}}(D/4)^{2/3}R^{-D} \ ,$$

which we may write as[4]

$$n_0=0.871(e/2)^{D/2}D^{1/6}e^{1.473D^{1/3}}/v \ldots \ . \tag{3.16}$$

Since this is only a bit greater per dimension, $(e/2)^{1/2}=1.166$, than the reciprocal exclusion volume, such a bifurcation appears to occur at a physical density. In fact, a more incisive comparison can be made. Referring to Rogers's elegant monograph[9] on the subject, one finds that n_0 of (3.16) lies in between the upper and lower bounds for maximum packing, consistent with, but of course not proving, its physical reality.

To what extent does this result depend upon the explicit hard-core nature of the Mayer function $f(r)$? Not very much, since the positivity of $\tilde{f}(k)$ at some k is guaranteed when $f(r)$ truncates to 0 at finite R, and the corresponding maximum value and hence minimum density is not hard to estimate. Let us briefly consider this point. By "integration by parts," we have

$$\tilde{f}(k)=\int_{r\le R}f(r)e^{ik\cdot r}d^Dr=\frac{1}{ik^2}\int_{r\le R}f(r)\nabla\cdot ke^{ik\cdot r}d^Dr$$

$$=\frac{1}{ik^2}\left[f(R)\int_{r=R}e^{ik\cdot r}k\cdot d^{D-1}S-\int e^{ik\cdot r}k\cdot\nabla f(r)d^Dr\right]$$

$$=\frac{1}{ik}f(R)\int_{r=R}e^{ik\cdot r}\hat{k}\cdot d^{D-1}S-\frac{1}{k^2}f'(R)\int_{r=R}e^{ik\cdot r}d^{D-1}S+\frac{1}{k^2}\int_{r\le R}e^{ik\cdot t}(\hat{k}\cdot\nabla)^2f(r)\,d^Dr \ .$$

It is clear that at large k, the $f(R)$ term dominates the expression, giving a trivially modified hard-core result, unless $f(R)=0$ in which case the similar $f'(R)$ term dominates, and so forth. Thus, the pure hard-core fluid is generic for finite-range repulsive interactions, and we confine our attention to this case in the bulk of the sequel.

IV. NONUNIFORM PROFILE: NEGATIVE RESULTS

Does the bifurcation (3.4) to a nonuniform state have equilibrium significance, i.e., does the resulting state have lower free energy at fixed particle number? This in fact is not the case at threshold. We simply observe that, with $n(r)=n_0+\delta n(r)$, (2.19) can be rewritten as

$$\beta F^B=\int\{n_0\ln n_0-n_0+\delta n(r)\ln(n_0)+\tfrac{1}{2}[\delta n(r)]^2/n_0\}d^Dr$$
$$-\tfrac{1}{2}\int\int[n_0+\delta n(r)]f(r-r')[n_0+\delta n(r')]d^Dr\,d^Dr'-\tfrac{1}{2}\int_0^1\int(1-\lambda)^2[\delta n(r)]^3/[n_0+\lambda\delta n(r)]^2d^Dr\,d\lambda\ . \quad (4.1)$$

Since $\int\delta n(r)\,d^Dr=0$, the linear terms in $\delta n(r)$ cancel, and if the threshold condition $\min_k[1/n_0-\tilde{f}(k)]=0$ holds, the bilinear terms are non-negative. Hence (4.1) reduces to

$$\beta F^B\geq\beta F_0^B-\tfrac{1}{2}\int_0^1(1-\lambda)^2\int[\delta n(r)]^3[n_0+\lambda\delta n(r)]^{-2}d^Dr\,d\lambda\ . \quad (4.2)$$

But

$$\int_{\delta n>0}(\delta n)^3/(n_0+\lambda\,\delta n)^2d^Dr+\int_{\delta n<0}(\delta n)^3/(n_0+\lambda\,\delta n)^2d^Dr<\int_{\delta n>0}(\delta n/\lambda^2)d^Dr+\int_{\delta n<0}(\delta n/\lambda^2)d^Dr=0\ . \quad (4.3)$$

It follows that unless $\delta n(r)=0$,

$$\beta F^B>\beta F_0^B\ .$$

Hence the transition cannot be discontinuous.

If some self-supported nonuniform state does exist at higher density, we should be able to find it directly from the profile equation (3.2). Let us search for possibilities. Since the equation of state (3.3) has only one solution for the density n, a true two-phase state cannot occur, although this argument can sometimes be circumvented by zero-density pseudouniform states.

We note at the outset that scaling in the $D\to\infty$ limit involves some subtlety, for at the present stage, we really have a model based upon the $D\to\infty$ limit, not a limiting model. For example, the state (3.16), of very high density in the natural unit $1/v$, does not exist in the $D\to\infty$ limit under a natural scaling. To see the consequences of this on the attainment of a nonuniform profile, we first rewrite (3.2) at zero field for hard cores as

$$\beta\mu'=\ln\rho(r)+\frac{1}{v}\int\epsilon[R^2-(r')^2]\,\rho(r-r')d^Dr'\ , \quad (4.4)$$

where $\rho(r)=vn(r)$, and suppose that the profile is s dimensional, $\rho(r)=\rho(x)$, $x=(x_1,\ldots,x_s)$. Then, integrating out the remaining D-s variables in (4.4),

$$\beta\mu'=\ln\rho(x)+\frac{1}{v}\int\epsilon[R^2-(x')^2][R^2-(x')^2]^{(D-s)/2}v_{D-s}(1)\rho(x-x')d^sx'$$
$$=\ln\bar{\rho}(x)+\frac{v_{D-s}(1)}{v_D(1)}\int\left[1-\frac{(x')^2}{D}\right]^{(D-s)/2}\bar{\rho}(x-x')d^sx'/D^{s/2}\ , \quad (4.5)$$

where $\bar{\rho}(x)=\rho(Rx/D^{1/2})$. Hence, blindly taking the $D\to\infty$ limit,

$$\beta\mu'=\ln\bar{\rho}(x)+(2\pi)^{-s/2}\int e^{-(x')^2/2}\bar{\rho}(x-x')d^sx'\ . \quad (4.6)$$

This has no finite nonuniform solution, for the gradient of (4.6) yields

$$\int\left[\frac{\delta(x-x')}{\bar{\rho}(x)}+(2\pi)^{-s/2}e^{-(x-x')^2/2}\right]\nabla\bar{\rho}(x')d^sx'=0\ ; \quad (4.7)$$

the kernel is a positive definite operator, implying that $\nabla\bar{\rho}(x)=0$.

Even without going to the $D=\infty$ limit, the possibilities of nonuniform states are greatly restricted. Can one have a hyperplane interface at all, even if one of the "phases" is never actually attained? Again consider (3.2), and apply the gradient

$$\frac{\nabla n(r)}{n(r)}-\int\mathbf{r}'[f'(r')/r']n(r-r')d^Dr'=0\ , \quad (4.8)$$

so that for z-directed profile,

$$\frac{n'(z)}{n(z)} = \int z'[f'(r')/r']n(z-z')d^Dr'$$
$$= \int_{z'\geq 0} z'[f'(r')/r'][n(z-z')-n(z+z')]d^Dr' . \tag{4.9}$$

In particular, if $f'>0$, the possibility of a monotonic profile is clearly precluded: One cannot have both $n'(z)>0$ and $n(z+z')<n(z-z')$ for $z'\geq 0$.

One of the "phases" might, however, be microscopic, e.g., a hyperspherical droplet or bubble in a uniform fluid, the separation maintained by surface tension. To check this, we again use (4.8), now assuming spherical symmetry:

$$\frac{n'(r)}{n(r)} = \int r'\mu'[f'(r')/r']n\{[r^2+(r')^2-2rr'\mu']^{1/2}\}d^Dr'$$
$$= \int_{\mu'\geq 0} r'\mu'[f'(r')/r'](n\{[r^2+(r')^2-2rr'\mu']^{1/2}\}-n\{[r^2+(r')^2+2rr'\mu']^{1/2}\})d^Dr' . \tag{4.10}$$

We conclude again that a monotonic profile, bubble of droplet, does not exist.

V. NONUNIFORM PROFILE: POSITIVE RESULTS

The above conclusions are not surprising, since we know that excitations (3.5) from uniform density occur at $k\neq 0$, implying a corrugated pattern, presumably leading to a lattice structure as the ultimate symmetry-breaking state. Let us start with the simplest broken symmetry, a one-dimensional pattern $n(x)$ of period l. Fourier expanding in a box of length l, we can write

$$n(x)=\frac{1}{l}\sum \tilde{n}(Kq)e^{-iKqx} , \tag{5.1}$$

where $q=2\pi/l$ and K is an integer. Equation (3.2) in the field-free case thus becomes

$$\beta\mu = \ln n(x) - \frac{1}{l}\sum \tilde{f}(kq)\tilde{n}(Kq)e^{-iKqx} , \tag{5.2}$$

where $\tilde{f}$ denotes the D-dimensional transform, $\tilde{n}$ that in one dimension.

Suppose now that $q\sim D/2R$, corresponding to the equation (3.5). Due to the factor $(kR)^{-D/2}$ in (3.8), only $k=0,\pm 1$ will contribute to (5.2). If $x=0$ is a surface of symmetry, $\tilde{n}(q)=\tilde{n}(-q)$, so that (5.2) reads

$$\beta\mu = \ln n(x) - \frac{1}{l}[\tilde{f}(0)-\tilde{n}(0)+2\tilde{f}(q)\tilde{n}(q)\cos(qx)] . \tag{5.3}$$

But $\tilde{f}(0)=-v=-R^D/v_D(1)$, $\tilde{n}(0)=nl$ where n is the mean density, and so

$$n(x)=e^{\beta\mu-nv}e^{[2\tilde{f}(q)\tilde{n}(q)/l]\cos(qx)} . \tag{5.4}$$

Taking zeroth and qth Fourier components, we thus have

$$\begin{aligned} n &= e^{\beta\mu-nv}I_0((2/l)\tilde{f}(q)\tilde{n}(q)) , \\ \tilde{n}(q) &= le^{\beta\mu-nv}I_1((2/l)\tilde{f}(q)\tilde{n}(q)) , \end{aligned} \tag{5.5}$$

the second of which, of course, requires $\tilde{f}(q)>0$.

If n is given, the quotient of the two equations of (5.5),

$$\tilde{n}(q)=nlI_1((2/l)\tilde{f}(q)\tilde{n}(q))/I_0((2/l)\tilde{f}(q)\tilde{n}(q)) , \tag{5.6}$$

thus determines $\tilde{n}(q)$. More conveniently, if $v(q)=\tilde{n}(q)/nl$, then

$$v(q)=I_1(2n\tilde{f}(q)v(q))/I_0(2n\tilde{f}(q)v(q)) . \tag{5.7}$$

Since

$$I_1(2n\tilde{f}(q)v(q))/v(q)I_0(2n\tilde{f}(q)v(q))$$

decreases monotonically from $n\tilde{f}(q)$ to 0 as $v(q)$ increases from 0 to ∞, (5.7) will indeed have a unique solution $v(q)=0(1)$ whatever

$$n\tilde{f}(q)>1 . \tag{5.8}$$

This solution is a bit strange, since it is stratified with a periodicity of $l\sim 4\pi R/D$, very much smaller than the minimum spacing R. It is clear, however, that it can be obtained, e.g., from a lattice of mean density n by projecting at an angle to x and averaging perpendicularly.

It is of course vital to know whether (5.4) is stable with respect to the uniform state of density n. Now on eliminating $\int f(r-r')n(r')d^Dr'$ from (3.2) and (2.19), it follows that

$$\beta F^B = \tfrac{1}{2}\int n(r)[\beta\mu+\ln n(r)]d^Dr = \int n(r)\,d^Dr . \tag{5.9}$$

Hence dividing by the cross-sectional area A perpendicular to x and eliminating μ via the first of (5.5),

$$\beta F^B = \int [\tfrac{1}{2}nv+\ln n-1-\ln I_0((2/l)\tilde{f}(q)\tilde{n}(q)) + \frac{1}{l}\tilde{f}(q)\tilde{n}(q)\cos(qx)]n(x)dx . \tag{5.10}$$

In particular, if we integrate over a slab of thickness l and divide by l,

$$\beta F^B/V = n(\tfrac{1}{2}nv+\ln n-1) + n\left[\frac{1}{n\tilde{f}(q)}\left[\frac{\tilde{f}(q)\tilde{n}(q)}{l}\right]^2 - \ln I_0(2(\tilde{f}(q)\tilde{n}(q)/l))\right] , \tag{5.11}$$

where V is the system volume. Suppose that $n\tilde{f}(q)>1$. Then the bracketed expression in (5.11) is zero at the uniform state $\tilde{n}(q)=0$, decreases thereafter since $\ln I_0(z)=\frac{1}{4}z^2+\cdots$, and reaches its minimum precisely at the condition (5.6). In other words, the free energy is indeed lower than that of the uniform fluid.

A similar analysis can be carried out for periodic solution in s-dimensional space. Let us imagine going right to the limit of a body-centered hypercubical lattice in D dimensions. The characteristic wave number of the instability is still $q \sim D/2R$, but this corresponds to a unit Cartesian wave number of $D^{1/2}/2R$, a consequent periodic box of side $4\pi R/D^{1/2}$ and mean interparticle spacing of $4\pi R$. We surmise that the Kirkwood instability in fact leads continuously to an ordered lattice.

VI. CONCLUDING REMARKS

We have presented a largely heuristic analysis of repulsively interacting classical fluids in high dimensionality. The precise role of the dimensionality must be pointed out. In certain cases, e.g., (4.6), we have in fact created a sequence of systems in which—via (2.16) as well as (4.5)—the $D \to \infty$ limit can literally be carried out. These, however, are the less interesting cases. The more interesting ones are those in which, while the $D \to \infty$ limit has been taken in deriving the free energy and profile equations, the dimensionality of the physical space has remained less than ∞. Thus we have really analyzed a model system associated with the $D \to \infty$ limit. In order for our conclusions as to phase transitions, nonuniform phases, and the like to be other than heuristic, and certainly in order to estimate an upper critical dimension, it will be necessary to perform a consistent asymptotic large D expansion, which is indeed our next task. Here, of course, it is important that questions be framed so as to permit such a description, and it is not *a priori* clear how this is to be done, e.g., when the full anticipated D-dimensional lattice structure of the Kirkwood instability is to be studied.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation and by the Donors of the Petroleum Fund of the American Chemical Society.

[1]H. L. Frisch, N. Rivier, D. Wyler, Phys. Rev. Lett. **54**, 2061 (1985).
[2]T. R. Kirkpatrick, J. Chem. Phys. **85**, 3515 (1986).
[3]H. E. Stanley, Phys. Rev. **176**, 718 (1968).
[4]W. Klein and H. L. Frisch, J. Chem. Phys. **84**, 2 (1986).
[5]J. K. Percus, in *Studies in Statistical Mechanics,* edited by J. L. Lebowitz (North-Holland, Amsterdam, in press).
[6]T. R. Kirkpatrick (private communication).
[7]See, e.g., G. Stell, in *Equilibrium Theory of Classical Fluids,* edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).
[8]See, e.g., A. Erdelýi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol. 2, Chap. XI.
[9]C. A. Rogers, *Packings and Covergings* (Cambridge University Press, Cambridge, 1964), Chaps. 4 and 7.