

# Do variational formulations for inhomogeneous density functions lead to unique solutions?

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In principle, the equilibrium density in an inhomogeneous system is that density field which extremalizes the free energy and all the system's equilibrium properties can be deduced from this. A simple, but qualitatively realistic model free energy is presented which shows that approximate free energy functionals can easily possess a large number of extremalizing solutions. The usual interpretation when multiple solutions are found is that the correct solution is the one associated with the lowest value of the free energy. This rule is not very reassuring when, as the model exhibits for some range of parameter values, a continuum of solutions can be found. A more careful analysis of the variational problem shows that a variational formulation only provides a complete characterization of an equilibrium system when the variational problem possesses a unique solution. A multiplicity of solutions actually corresponds to the existence of a multiplicity of Hamiltonians which could give rise to the postulated free energy functional. There is no variational basis for comparing different Hamiltonians, however, and hence choosing from among a multiplicity of solutions on the basis of the value of the free energy is an additional extrathermodynamic rule.

## I. INTRODUCTION

The spatial variation of the density in an equilibrium fluid at a phase boundary or at a wall may be viewed as a system's response to a single particle external field  $U(\vec{r})$ . A wall corresponds to an abrupt spatial variation of  $U(\vec{r})$ , but even a slow spatial variation of  $U(\vec{r})$  leads to a rapid variation of the number density  $\rho(\vec{r})$  in regions where the local compressibility is large, as one finds in interphase regions. In this view, the characterization of the spatial variation of  $\rho(\vec{r})$  is thus the characterization of the functional  $\rho(\vec{r}, [U])$ . The present paper develops an interpretation for variationally determined  $\rho(\vec{r}, [U])$  functionals.

The variational approach is only one of several approaches to the construction of  $\rho(\vec{r}, [U])$ . Experimentally, when the number of particles  $N$ , the temperature  $T$ , and the volume  $V$  are specified, a unique  $\rho(\vec{r})$  is found for every  $U(\vec{r})$ . Numerical simulations using the Hamiltonian for a classical system of particles of mass  $m$  interacting through pair-wise additive forces [with potential  $\phi(\vec{r})$ ] in a field  $U(\vec{r})$  (which fixes the volume  $V$ ),

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i < j} \phi(\vec{r}_i - \vec{r}_j) + \sum_{i=1}^N U(\vec{r}_i), \quad (1)$$

also find a unique  $\rho(\vec{r})$  for every  $U(\vec{r})$  field. Likewise, the canonical ensemble prescription for the average density,<sup>1,2</sup>

$$\rho(\vec{r}) = \frac{1}{N! h^{3N}} \int \cdots \int d\vec{r}_1 \cdots d\vec{r}_N d\vec{p}_1 \cdots d\vec{p}_N \times e^{\beta(A-H)} \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i), \quad (2)$$

with  $A = A(T, V, N)$  the Helmholtz free energy fixed by the normalization condition

$$e^{-\beta A} = \frac{1}{N! h^{3N}} \int \cdots \int d\vec{r}_1 \cdots d\vec{r}_N d\vec{p}_1 \cdots d\vec{p}_N e^{-\beta H}, \quad (3)$$

associates a unique  $\rho(\vec{r})$  with each  $U(\vec{r})$ . While these routes do show that  $\rho(\vec{r})$  is a well defined functional of  $U(\vec{r})$  and they lead to essentially exact solutions to the  $\rho(\vec{r}, [U])$  problem, they are not easy routes to follow. This is particularly so when one is interested in studying a variety of interaction models, i.e., a family of  $\phi(\vec{r})$  potentials.

The basis for developing *approximate* routes to  $\rho(\vec{r}, [U])$  is the converse of the observation that  $U(\vec{r})$  leads to a unique  $\rho(\vec{r})$ : If a realizable density  $\rho(\vec{r})$  is prescribed, there is a unique external field  $U(\vec{r})$  which will give rise to this  $\rho(\vec{r})$ .<sup>3,4</sup> This means that any *exact* relation between  $\rho(\vec{r})$  and  $U(\vec{r})$  can only possess a unique solution  $\rho(\vec{r}, [U])$  for each  $U(\vec{r})$  field. It is a natural extrapolation that an equation which is an approximation to an exact relation will have a unique solution which approximates the exact  $\rho(\vec{r}, [U])$ . The earliest examples of analytic theories for  $\rho(\vec{r}, [U])$  are the analysis of van der Waals<sup>5</sup> of the liquid-vapor density profile and the identification of Kirkwood and Monroe<sup>6</sup> of oscillating density functions with the solid phase. These early approaches have evolved into the general method of determining  $\rho(\vec{r})$  as a solution to an integral equation obtained by using physically motivated approximations to the higher order distribution functions in exact integral equations relating  $\rho(\vec{r})$  and  $U(\vec{r})$ , an approach which has received extensive numerical attention.<sup>7</sup> The approximations used to construct practical integral equations, however, lead to a shift in the *number* of solutions which the integral equations possess.<sup>8</sup> This very nonphysical behavior can be understood as a consequence of the fact that not only does the correct  $\rho(\vec{r})$  satisfy an exact integral equation, but such an equation also correctly predicts the slopes in all directions in function space, i.e., that there are generalized tangency relations associated with the solution of the exact equation and even the smallest error in an approximation can destroy these. A similar instability in the number of solutions has been found in

the corresponding integral equation routes to radial distribution functions in fluids.<sup>9</sup>

It has been generally assumed that the problems which arise from the approximate integral equations possessing a variable number of solutions can be avoided by taking a *variational* approach. In this approach, one models (approximates) the free energy of a system as a functional of  $\rho(\vec{r})$ . The actual  $\rho(\vec{r})$  is then taken to be that which minimizes the model free energy. The extended interpretation is that knowing the free energy as a functional of  $\rho(\vec{r})$  completely determines *all* the properties of a system. The Hamiltonian which would generate this free energy *exactly* could be determined by evaluating the functional derivatives of this free energy with respect to  $\rho(\vec{r})$ . Hence, the generalized tangency relations are satisfied by definition<sup>8</sup> and this route should yield a unique  $\rho(\vec{r})$ . The reported numerical experience is usually described in such terms.<sup>10</sup>

In the following analysis, it is shown that the shift from taking  $U(\vec{r})$  as an independent field to taking  $\rho(\vec{r})$  as an independent field is not so simple. Strictly speaking, the variational program contains an extrathermodynamic assumption and practical executions of this program are just as likely to produce multiple solutions as the direct integral equation approach. A concrete example is then given to illustrate how easily multiple solutions arise and hence how difficult it is to know the physical significance of the solutions.

## II. THE STRUCTURE OF VARIATIONAL FORMULATIONS

### A. The standard formulation

Variational approaches start with a model for the free energy which is regarded as a functional of the density. As an example, consider a cylindrical system with the cylinder's axis coincident with the  $x$  axis. If properties only vary in the  $x$  direction (i.e., the diameter of the cylinder is large enough to neglect boundary terms at the edge of the cylinder), then  $\rho(\vec{r}) = \rho(x)$ . A typical example of an approximate free energy functional (energy per unit area perpendicular to the  $x$  axis in this case) is

$$F[\rho(x)] = k_B T \int dx [\rho(x) \ln \rho(x) - \rho(x)] - \frac{1}{2} \int \int dx_1 dx_2 \rho(x_1) K(x_1 - x_2) \rho(x_2) + \int dx \rho(x) U(x). \quad (4)$$

The first term represents an ideal configurational entropy, the second term an interaction between particles at  $x_1$  and  $x_2$  (after averaging over the coordinates perpendicular to the  $x$  axis), and the last term represents a single particle interaction with the external field  $U(x)$ .

For notational simplicity, we write  $F[\rho(\vec{r})]$  although  $F$  obviously depends upon the temperature  $T$ . If the particles are confined to  $0 < x < L$ , then  $F$  also depends upon  $L$  (i.e., upon the volume), but, as such confinement arises from  $U(x)$  becoming very large for  $x < 0$  and  $x > L$ , the parameter  $L$  is formally contained in  $U(x)$ . Hence, if the extremaliza-

tion of  $F[\rho(\vec{r})]$  in Eq. (4) is made with a prescribed  $U(x)$ , the integrals in Eq. (4) can be taken over  $-\infty < x < \infty$ .

One pictures Eq. (4) as representing the Helmholtz free energy  $A$  which is a minimum at prescribed  $T$ ,  $V$ , and  $N$ . Thus, the physically correct  $\rho(x)$  is that which minimizes  $F[\rho(x)]$ , subject to the constraint

$$N = \int dx \rho(x). \quad (5)$$

Using the Lagrange multiplier  $\mu$  to accommodate this constraint leads to the Euler-Lagrange equation for  $\rho(x)$ ,

$$\mu = k_B T \ln \rho(x) - \int dx' K(x - x') \rho(x') + U(x), \quad (6)$$

an integral equation for  $\rho = \rho(x, [\mu - U])$ , with  $\mu$  identified as the chemical potential. Hence, there are two equivalent routes to determining  $\rho(x)$ : One may search in a space of  $\rho(x)$  functions for that  $\rho(x)$  which extremalizes  $F[\rho(x)]$  in Eq. (4) or one may solve the integral equation Eq. (6) for  $\rho(x)$  with  $\mu$  chosen so that Eq. (5) is satisfied.

### B. Functionals which fix the properties of a system

In general, it is  $A = A(T, N, [U(\vec{r})])$ , the Helmholtz free energy function/functional, which fixes the equilibrium properties of a system.  $A(T, N, [U(\vec{r})])$  fixes thermodynamic properties like

$$\mu = \frac{\partial A}{\partial N} \quad (7)$$

and molecular distribution functions such as<sup>2</sup>

$$\rho(\vec{r}) = \frac{\delta A}{\delta U(\vec{r})}, \quad (8)$$

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1) \rho(\vec{r}_2) - \rho(\vec{r}_1) \delta(\vec{r}_1 - \vec{r}_2) - k_B T \frac{\delta^2 A}{\delta U(\vec{r}_1) \delta U(\vec{r}_2)}. \quad (9)$$

From  $\rho^{(N)}(\vec{r}_1, \dots, \vec{r}_N)$ , one could deduce the Hamiltonian of the system.

The choice of independent variables is not arbitrary, however. While knowing  $A$  as a functional of  $T, V, N$  does determine all thermodynamic properties, for example, knowing  $A = f(T, V, \mu)$  does not fix  $N$ . To see this, suppose that the free energy as a function of  $T, V, N$  were actually of the form  $A = g[T, V, N + \nu(T, V)]$ . The use of Eq. (7) to deduce  $\mu$  gives  $\mu = \partial g[T, V, N + \nu(T, V)] / \partial N$  which shows that it is  $N + \nu(T, V)$  which is determined by  $T, V, \mu$ :  $N + \nu(T, V) = h(T, V, \mu)$ , whatever  $\nu(T, V)$  is. Subsequent elimination of  $N + \nu(T, V)$  from  $g[T, V, N + \nu(T, V)]$  gives  $f(T, V, \mu) = g[T, V, h(T, V, \mu)]$ , a result in which  $\nu(T, V)$  does not appear. Any shift in the number of particles  $\nu(T, V)$  is thus consistent with a prescribed  $A = f(T, V, \mu)$ .  $N$  is not determined by  $A = f(T, V, \mu)$ .

If  $T, V, \mu$  are chosen to be the independent variables, the standard thermodynamic approach is to describe the system with the Legendre transformed free energy function,

$$\Omega(T, V, \mu) = A[T, V, N(T, V, \mu)] - \mu N(T, V, \mu), \quad (10)$$

the grand potential, with  $N(T, V, \mu)$  determined by inverting

Eq. (7). Since

$$N = -(\partial\Omega/\partial\mu), \quad (11)$$

the transformation in Eq. (10) can be reversed. Thus  $\Omega(T, V, \mu)$  provides the same information that  $A(T, V, N)$  does.

The functional analog of this argument from classical thermodynamics is that while knowing  $A[U]$  does completely describe the equilibrium properties of a system, a knowledge of  $A[\rho]$  does not. Given  $A[\rho]$ , one cannot determine what  $U(\vec{r})$  is actually present. But if  $\rho(\vec{r})$  is to be taken as the independent variable, a complete characterization of all equilibrium properties is provided by the functional Legendre transformed free energy,<sup>11</sup>

$$\mathcal{F}[\rho] = A[U[\rho]] - \int d\vec{r} \rho(\vec{r}) U(\vec{r}, [\rho]). \quad (12)$$

Since

$$U(\vec{r}) = -\frac{\delta\mathcal{F}[\rho]}{\delta\rho(\vec{r})}, \quad (13)$$

the transformation in Eq. (12) can be reversed. Thus  $\mathcal{F}[\rho]$  provides the same information that  $A[U]$  does. The analog of Eq. (9) is that the second functional derivative of  $\mathcal{F}[\rho]$  is related to the Ornstein-Zernike direct correlation function,<sup>2</sup>

$$c(\vec{r}_1, \vec{r}_2) = \frac{\delta(\vec{r}_1 - \vec{r}_2)}{\rho(\vec{r}_1)} - \beta \frac{\delta^2\mathcal{F}[\rho]}{\delta\rho(\vec{r}_1)\delta\rho(\vec{r}_2)}, \quad (14)$$

a function which is generally simpler in a dense fluid<sup>12</sup> than  $\rho^{(2)}(\vec{r}_1, \vec{r}_2)$ .

Equation (13) shows that  $\mathcal{F}[\rho]$  is not extremalized by the correct  $\rho(\vec{r})$ .  $\mathcal{F}[\rho]$  is not the functional approximated in Eq. (4). Equation (12) prescribes an  $\mathcal{F}[\rho]$  for every  $\rho(\vec{r})$  field which can be realized in the laboratory. By contrast,  $F[\rho]$  is defined [for each prescribed  $U(\vec{r})$ ] for a family of hypothetical density fields  $\rho(\vec{r})$  of which only one (extremalizing) field is necessarily realizable in the laboratory.

The  $\mathcal{F}$  corresponding to the explicit model  $F$  in Eq. (4) can be identified by rearranging Eq. (6) into

$$\begin{aligned} U(x) = & -\frac{\delta}{\delta\rho(x)} \\ & \times \{k_B T \int dx [\rho(x) \ln \rho(x) - \rho(x)] - \frac{1}{2} \\ & \times \int \int dx dy \rho(x) K(x-y) \rho(y) - \mu \int dx \rho(x)\}. \end{aligned} \quad (15)$$

Comparison with Eq. (13) shows that  $\mathcal{F}[\rho]$  is, to within an additive density independent function, the term in brackets in Eq. (15),

$$\begin{aligned} \mathcal{F}[\rho] = & k_B T \int dx [\rho(x) \ln \rho(x) - \rho(x)] - \frac{1}{2} \\ & \times \int \int dx dy \rho(x) K(x-y) \rho(y) - \mu \int dx \rho(x). \end{aligned} \quad (16)$$

Subtracting out Eq. (4) gives

$$F[\rho] = \mathcal{F}[\rho] + \int dx \rho(x) [U(x) + \mu]. \quad (17)$$

Here,  $U(x)$  is an externally fixed field, not a functional of  $\rho(x)$ , and hence  $F[\rho]$  can be evaluated at density fields which would only be realizable in an external field different from  $U(x)$ , if at all. The functional derivative of Eq. (17) evaluated at  $\rho(\vec{r}, [U])$  does reproduce Eq. (6). Using Eq. (12), one can deduce the numerical value of the extremum of  $F[\rho]$ ,

$$F[\rho]_{\text{extremum}} = A[U[\rho]] + \mu N, \quad (18)$$

to within an additive constant. Thus, one can identify the value of the extremum of  $F[\rho]$  as the Helmholtz free energy to within the additive constant  $\mu N$ .

### III. THE ROLE OF THE INTEGRAL EQUATION

$A[U]$  provides a complete description of an equilibrium system. This is true even if the expression for  $A[U]$  is approximate, for "approximate" simply means that the Hamiltonian which would generate  $A[U]$  exactly differs from the Hamiltonian of interest. In this sense that every  $A[U]$  is exact, the generalized tangency conditions are also always satisfied.

If, on the other hand, one starts with  $A[\rho] = F[\rho] - \mu N$  [i.e., Eq. (18)], one does not start with a complete description of the system. To develop a complete description, one must supplement  $A[\rho]$  with a knowledge of either

$$\rho = \rho(\vec{r}, [U]) \quad (19)$$

or

$$U = U(\vec{r}, [\rho]). \quad (20)$$

If Eq. (19) is given, one can deduce  $A[U] = F[\rho[U]] + \mu N$  which *does* provide a complete description. If Eq. (20) is given, one can complete the functional Legendre transformation indicated in Eq. (12) to  $\mathcal{F}[\rho]$ , which also provides a complete description.

When Eqs. (19) or (20) provide a unique relation between  $\rho(\vec{r})$  and  $U(\vec{r})$ , the extension to  $A[U]$  or  $\mathcal{F}[\rho]$  leads to a characterization of a unique system. When they provide no relation or a multiple-valued relation, however, no or many systems are described. Since each  $A[U]$  or  $\mathcal{F}[\rho]$  completely describes a system, the multiplicity of free energy functionals results from the fact that a multiplicity of Hamiltonians can be associated with the model  $F[\rho]$  functional. Associated with each realization—i.e., with each Hamiltonian corresponding to each solution of Eqs. (19) or (20)—is a corresponding  $A[U]$  or  $\mathcal{F}[\rho]$ . The generalized tangency relations are satisfied for each realization.

It is tempting to argue that if there are multiple solutions to Eq. (6), and hence a multiplicity of extremalizing values for  $F[\rho]$  in Eq. (4), then the correct one is that which produces the lowest value of  $F[\rho]$ . This is an extrathermodynamic rule, however. Each solution corresponds to a particular Hamiltonian. One can choose which  $\rho(x)$  is the best by choosing that for which the corresponding Hamiltonian is the closest in some appropriate sense to the real Hamiltonian, but the value of  $F[\rho]$  has no clear relation to this measure.

As the following analysis of a representative equation shows, while particular searches may discover only a few

solutions, there are in fact very many solutions to realistic problems. Hence, sorting through their significance on the basis of a one-dimensional measure is fraught with difficulty. The variational formulation is just as susceptible to ambiguous results as the conventional integral equation approach.

#### IV. A SIMPLE EXAMPLE

##### A. A toy model for Eq. (4)

In view of Eqs. (14) and (17), we see that the kernel in the model free energy functional Eq. (4) should be identified<sup>12</sup> with the direct correlation function integrated over directions perpendicular to the symmetry axis,

$$K(x-y) = k_B T \bar{c}(x,y). \quad (21)$$

By assuming that  $\bar{c}(x,y)$  is independent of the density over the density range of interest, one also assures that the required translational invariance obtains for  $K$ .

Diffraction experiments can be employed to determine direct correlation functions in dense monatomic fluids such as liquid argon.<sup>13</sup> Figure 1 schematically indicates the shape of this radially symmetric function  $c(r)$ . If  $c(r)$  has this symmetry, the integral required for  $K$  has the form

$$K(x-y) = 2\pi k_B T \int_{|x-y|}^{\infty} r c(r) dr. \quad (22)$$

Figure 2 shows qualitatively the shape expected. Our "toy model" is generated by the following crude, but mathematically simple approximation to  $K$ ,

$$K(u) = -Ak_B T [1 + B \cos(u/r_0)] \quad (|u| \leq \pi r_0), \quad (23)$$

$$= 0 \quad (\pi r_0 < |u|).$$

$A$ ,  $B$ , and  $r_0$  are suitable constants. Equation (6) now adopts the form

$$\ln \rho(x) = \ln z - A \int_{x-\pi r_0}^{x+\pi r_0} \{1 + B \cos$$

$$\times [(x-y)/r_0]\} \rho(y) dy, \quad (24)$$

under the assumption that walls represented by  $U(x)$  have receded to  $\pm \infty$  and where we have introduced the fugacity

$$z = \exp(\mu/k_B T). \quad (25)$$

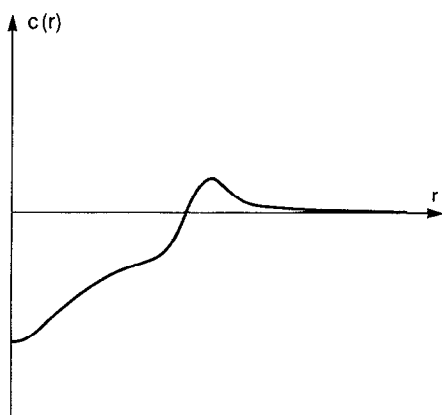


FIG. 1. A typical direct correlation function in a liquid (after Ref. 12).

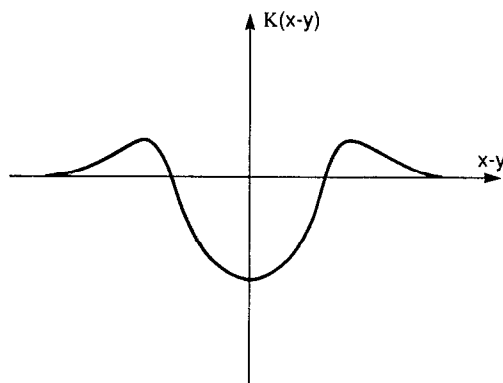


FIG. 2. The expected form of the kernel in Eqs. (4) and (6) [cf. Eq. (21)].

If we make the following scale changes:

$$x \rightarrow r_0 x, \quad z \rightarrow z/2\pi r_0 A, \quad (26)$$

$$\rho(x) \rightarrow \rho(r_0 x)/2\pi r_0 A,$$

the toy model integral equation simplifies to

$$\ln \rho(x) = \ln z + \int_{-\infty}^{+\infty} \hat{K}(x-y) \rho(y) dy;$$

$$\hat{K}(u) = \frac{K(r_0 u)}{2\pi A k_B T} = - (2\pi)^{-1} (1 + B \cos u) \quad (|u| \leq \pi),$$

$$= 0 \quad (\pi < |u|). \quad (27)$$

Figure 3 illustrates one such simplified  $\hat{K}$ , bearing a superficial resemblance to the curve in Fig. 2. The shape indicated in Fig. 2 suggests that  $B > 0$  on physical grounds, at least for simple monatomic substances. We are at, however, liberty to seek solutions to Eq. (27) for all  $z > 0$  and any real  $B$ .

##### B. Some exact solutions

It is clear that Eq. (27) always has the uniform-density solution  $\rho(x) = \rho_0$ , where [in the dimensionless units introduced in Eq. (26)]

$$z(\rho_0) = \rho_0 \exp \rho_0$$

$$= \sum_{n=0}^{\infty} \rho_0^{n+1}/n!. \quad (28)$$

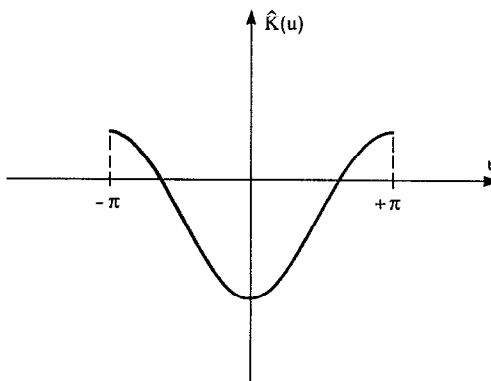


FIG. 3. The toy analytic model assumed for  $\hat{K}(u)$  in Eq. (23).

Elementary thermodynamics shows<sup>12</sup> that the pressure  $p$  (in units of  $1/2\pi r_0 A$ ) in this uniform fluid exhibits only a second virial coefficient correction to the ideal gas pressure,

$$p/k_B T = \rho_0 + \frac{1}{2} \rho_0^2. \quad (29)$$

The Lagrange method for series reversion<sup>14</sup> reveals that the inverse of Eq. (28) has the series,

$$\rho_0(z) = \sum_{n=1}^{\infty} (-n)^{n-1} z^n / n!, \quad (30)$$

whose radius of convergence is  $1/e$ .

Periodic solutions to Eq. (27) can also be obtained, having the form

$$\rho(x) = \exp[a + b \cos(x - x_0)]. \quad (31)$$

Here  $x_0$  is arbitrary, reflecting the translation invariance of the kernel. Substituting Eq. (31) into Eq. (27) yields a pair of simultaneous equations for  $a$  and  $b$ ,

$$\begin{aligned} a &= \ln z - \exp(a) I_0(b), \\ b &= -B \exp(a) I_1(b), \end{aligned} \quad (32)$$

wherein the  $I_j$  are the modified Bessel functions.<sup>15</sup> It is useful to observe that the spatially averaged density corresponding to Eq. (31) is

$$\langle \rho(x) \rangle = \exp(a) I_0(b), \quad (33)$$

so that Eqs. (32) can be rewritten

$$a = \ln z - \langle \rho \rangle, \quad (34)$$

$$b = -B \langle \rho \rangle I_1(b) / I_0(b). \quad (35)$$

For a given  $B$  and  $\langle \rho \rangle$ , the last three equations offer a convenient procedure for finding  $a$ ,  $b$ , and the appropriate  $z$ . Figure 4 illustrates a simple graphical solution of Eq. (35) for  $b$ ; using the determined  $b$  value in Eq. (33) yields  $a$ ; finally, Eq. (34) produces the proper  $z$  value.

As Fig. 4 indicates,  $I_1(b)/I_0(b)$  is an odd continuous function of  $b$  which rises monotonically between finite limits. Its intersections with the straightline  $-b/B \langle \rho \rangle$  determine the available solutions. One always has  $b = 0$  as a solution, but this is just the uniform density case already discussed. The slope of  $I_1/I_0$  at the origin is  $1/2$ , so a pair of nontrivial solutions  $\pm b \neq 0$  also exists provided

$$B \langle \rho \rangle < -2. \quad (36)$$

Since  $\langle \rho \rangle$  is non-negative,  $B$  must be negative in order to produce

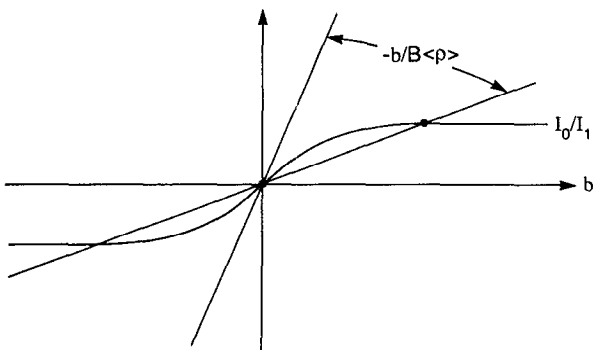


FIG. 4. The graphical solution to Eq. (35) for  $b$ .

produce these nonconstant periodic densities. Although the simple direct correlation function depicted in Fig. 2 suggests  $B > 0$ , a value of  $B$  satisfying Eq. (36) is not necessarily non-physical. Formally, we know<sup>11</sup> that there is a short ranged pair potential which will produce any short range direct correlation function. Thus, Eq. (36) may be found in some more complex systems. Even for simple systems, Eq. (36) is probably not unrealistic: The conflict with Fig. 2 probably arises from the approximation that  $K(x)$  is density independent. Despite the fact that the integral Eq. (6) is a toy model and hence the connection between Eq. (36) and a molecular level description is not that direct, the variation of the number of solutions with density is just that seen in more elaborate, molecular based equations: The single solution present at low  $\langle \rho \rangle$  bifurcates into a uniform and an oscillatory solution as  $\langle \rho \rangle$  increases.<sup>8</sup> In any case, the periodic densities Eq. (31) present when Eq. (36) is satisfied qualitatively, resemble those expected for a crystalline phase with low-index planes of particles perpendicular to the  $x$  axis.

### C. Additional solutions arising via bifurcation

Further analysis is facilitated by considering the linear eigenvalue spectrum associated with  $\hat{K}$

$$\int_{-\infty}^{+\infty} \hat{K}(x-y) \exp(iky) dy = \lambda(k) \exp(ikx), \quad (37)$$

where

$$\lambda(k) = -\frac{\sin(\pi k)}{\pi k} \left[ 1 + \frac{Bk^2}{1-k^2} \right] (|k| \neq 1), \quad (38)$$

and

$$\lambda(\pm 1) = \lim_{k \rightarrow 1} \lambda(k) = -B/2. \quad (39)$$

We can now carry out a stability analysis of the functional  $F[\rho(x)]$ , with respect to sinusoidal perturbations of the uniform density; i.e., we consider

$$\rho(x) = \rho_0 [1 + \epsilon \cos(kx)], \quad (40)$$

where  $\epsilon$  is a small parameter. Upon inserting this density into  $F[\rho(x)]$ , Eq. (4), with use of the toy model kernel Eq. (27), we obtain the following free-energy density

$$\begin{aligned} F[\rho(x)] / (Lk_B T) &= F[\rho_0] / (Lk_B T) + (\rho_0/8/\pi A) \\ &\quad \times [1 - \rho_0 \lambda(k)] \epsilon^2 + O(\epsilon^4). \end{aligned} \quad (41)$$

Through quadratic order in  $\epsilon$ , the magnitude of  $\lambda(k)$  controls whether the sinusoidal density wave produces a rise or a reduction in free energy.

If  $1 - \rho_0 \lambda(k)$  is negative, the sinusoidal perturbation succeeds in lowering the free energy, suggesting (but not guaranteeing) that a nontrivial solution with period  $2\pi/k$  should exist. Indeed, this is exactly what we have found in the previous Sec. IV B for the closed-form densities Eq. (31) with  $k = 1$ . The criterion Eq. (36) is precisely equivalent to  $1 - \rho_0 \lambda(a) < 0$ .

Figure 5 shows a plot of  $\lambda(k)$  vs  $k$  for  $B = 3$ . It is typical to the extent that it displays decaying oscillations about zero. The dominant maximum occurs at  $k_m = 2.4360$ , for which

$$\lambda(k_m) = 0.333\ 922. \quad (42)$$

As the uniform density  $\rho_0$  increases from 0,  $k_m$  is the first wave-

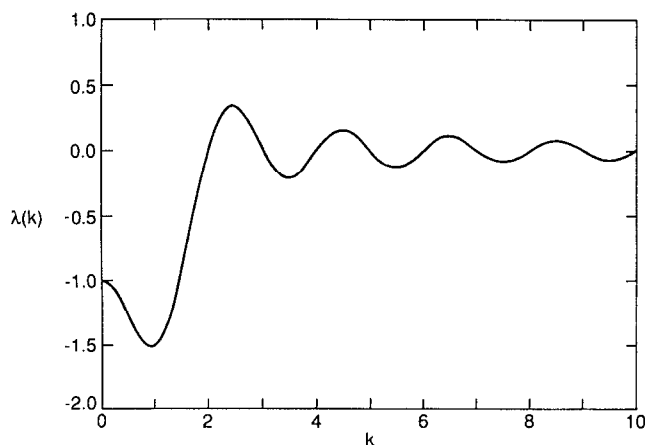


FIG. 5. The plot of  $\lambda(k)$  vs  $k$  for  $B = 3.0$ .

length to become unstable; This occurs when

$$\rho_0 = 1/\lambda(k_m) = 2.99471 \quad (B = 3). \quad (43)$$

Further increase in the average density would cause a finite range of  $k$ 's surrounding  $k_m$  to experience instability. Reference to Fig. 5 shows that as the density continues to increase, a succession of  $k$  intervals farther and farther from the origin manifest instability.

Numerical study of the toy model integral Eq. (27) indicates that whenever a nonvanishing  $k$  interval exists over which

$$1 - \rho_0(z)\lambda(k) < 0, \quad (44)$$

nontrivial periodic solutions exist with any one of these  $k$ 's as wave vector. Furthermore, each of these solutions can be translated arbitrarily along the  $x$  direction to give a doubly-infinite family of solutions. Figure 6 illustrates this solution multiplicity for the case

$$B = -1.69021, \quad z = 3.5, \quad \rho_0(z) = 1.13029. \quad (45)$$

Here, the range of instability is found to be

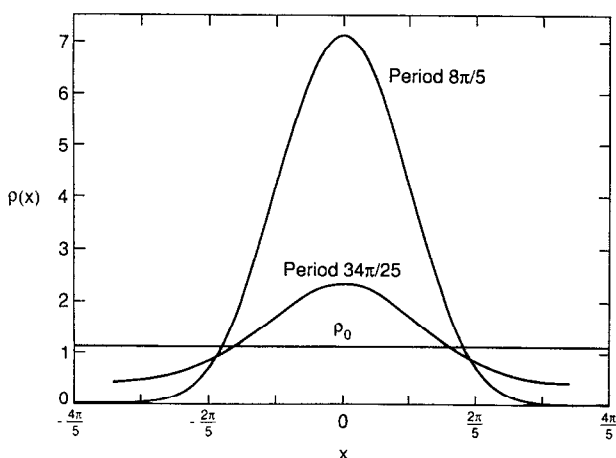


FIG. 6. The uniform and two nonuniform solutions to the toy model integral equation for  $\rho(x)$ . All solutions have  $B = -1.69021$  and  $z = 3.5$ .

$$1.02946 < k < 1.47787. \quad (46)$$

The Fig. 6 presents two solutions with distinct periods in this range, obtained by iteration of Eq. (27) until convergence. The uniform density  $\rho_0(z)$  is included for comparison.

We have not yet investigated the possibility of nonperiodic solutions to Eq. (27). It does appear that for some special  $B, z$  pairs that a nonuniform periodic solution yields the same pressure as the uniform solution  $\rho_0(z)$ , Eq. (29). This amounts to thermodynamic coexistence of a crystal and a fluid, suggesting that an interface profile solution (say crystalline as  $x \rightarrow -\infty$ , fluid as  $x \rightarrow +\infty$ ) could be constructed. It is also possible that unphysical chaotic solutions exist. Further analysis of this toy model seems warranted.

## V. DISCUSSION

It has been recognized since the early numerical work of Kirkwood and Monroe<sup>6</sup> that the nonlinear integral equations used for the determination of the singlet density  $\rho(\vec{r})$  often possess multiple solutions. The usual experience is that only a uniform  $\rho_0$  solution is present at low densities, but that additional oscillatory solutions appear as the average density increases. This behavior suggests the physical interpretation that the appearance of oscillatory solutions at high density corresponds to the appearance of solid phases and that the oscillatory solutions are approximations to the density variation in a solid phase.

There are several objections which often apply to this interpretation.<sup>8</sup> It is known that the one-dimensional versions of these integral equations exhibit the same qualitative behavior while, of course, no solid phases are possible. The integral equations which are solved are based on descriptions of liquids, so their solutions are radially symmetric, i.e., the oscillatory solutions oscillate in a radial direction, not a behavior which can be realized in any real solid. The oscillatory solutions often appear via bifurcation off the uniform solutions, an event associated with a similarly unphysical singularity in the wavelength dependent mechanical susceptibility.

For integral equations derivable from a free energy functional of the density via a variational principle, however, these objections have not appeared to be relevant. Since a free energy functional of the density  $\rho(\vec{r})$  in principle, determines the Hamiltonian of the system, the extremalizing  $\rho(\vec{r})$  and its associated free energy may be viewed as exact evaluations corresponding to an approximate Hamiltonian. As an exact solution, the generalized tangency conditions<sup>8</sup> characteristic of the real systems are necessarily satisfied. The argument that it is the approximation procedure itself that alters the number of solutions would not seem to apply.

It is still true, however, that a nonlinear integral equation is associated with a variational formulation. The relation between the model free energy functional in Eq. (4) and the associated Euler-Lagrange Eq. (6) is typical. Further, as the free energy functionals typically possess multiple extremalizing density fields at high average densities, the corresponding integral equations must similarly possess multiple solutions. What is shown in Sec. III, however, is that when a variational free energy possesses multiple solutions it does not in fact provide a complete physical

description of the system. A family of solutions to an integral equation does not correspond to a family of (possibly metastable) physically realizable states associated with a fixed (but approximate) Hamiltonian, but rather corresponds to a family of Hamiltonians which would give rise to the various solutions. Multiple solutions do not correspond to a multiplicity of states of a fixed system, but to a multiplicity of systems. A numerical value for the free energy is, of course, associated with each solution, but a direct comparison of free energy values for different solutions is of quite uncertain meaning since the distinct solutions correspond to physically distinct Hamiltonians.

The model integral equation analyzed in Sec. IV shows all the characteristics of the integral equations which have been analyzed numerically. At low density there is a unique spatially uniform solution. As the density is increased, however, nonuniform solutions bifurcate off the uniform solution. Beyond the first bifurcation point, a continuum of bifurcations gives rise to a continuum of solutions.

The continuum of solutions can be reduced to a discrete set of solutions (as is typically done) by restricting the solution space (by presupposing a particularly simple structure for a solution). This is an extrathermodynamic assumption about the structure of the solutions, however. In the absence of such an assumption, there is little guidance for selecting a physically relevant solution from among the continuum of solutions the integral equation possesses. Every solution has an associated free energy value, but using this as a selection measure is physically remote from what is really sought: The best solution is that for which the corresponding approximate Hamiltonian is physically closest to the real Hamiltonian.

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