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Optimal and nearly optimal distribution functions for ^{4}He

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The properties of the Euler-Lagrange equation obtained by minimizing the hypernetted-chain energy of a boson fluid are studied. We consider the asymptotic form of the resulting two-body distribution function, $g(r)$, and show that $g(r)-1$ is proportional to r^{-4} for short-ranged potentials. The stability condition for $g(r)$ is expressed as an eigenvalue problem, and the relation to the adiabatic compressibility is established. Previous numerical results for liquid ^{4}He are shown to describe an energy minimum. The existence of low-lying eigenvalues for all l and the nature of the related nonspherically symmetric eigenfunctions suggest the existence of additional "crystalline" solutions of the Euler-Lagrange equations.

I. INTRODUCTION

Treatments of the many-body problem of infinite matter invariably involve compromise between the desire to invoke only general principles and the need to produce numbers which may be compared with experiment. Consider first the exact wave function. Feynman's elegant arguments provide a very useful relationship between the compressibility and the liquid-structure function at small momenta.[1] Detailed calculations at this level, involving the equally elegant Monte Carlo solution of the Schrödinger equation for a finite number of particles,[2] provide useful numbers but are short on analytic results. At a second level, one may consider variational calculations using correlated pair (i.e., Jastrow) wave functions. For this problem, Krotscheck has made some interesting analytic arguments,[3] Monte Carlo calculations provide numerical results,[4] but neither approach provides both. Our discussion will be at a still lower level, that of a correlated-pair wave function within the hypernetted-chain (HNC) approximation. Within this framework, we are able to obtain both useful analytic properties and respectable numerical results. In fact, the interplay between numerical and analytical methods has had a substantial effect in directing our work. Our studies indicate that this level may be particularly rich because the important numerical and analytic features of the many-body problem which must appear separately at higher levels of discussion are seen to be rendered rather faithfully within the HNC framework.

We have previously constructed Euler-Lagrange equations to find the two-body distribution function, $g(r)$, which minimizes the energy of boson matter as calculated in the HNC approximation and have offered a numerically convenient method for its solution.[5–7] Solutions of the Euler-Lagrange equation are the same as solutions obtained with the pair-phonon analysis[8,9] in the HNC approximation.[10,11] In the present work we have used the Euler-Lagrange equation formalism to investigate the behavior of the energy functional in the neighborhood of stationary points and hence to address some interesting and closely related problems arising in this region. In Sec. II we shall demonstrate by a specific example an inadequacy of the Jackson-Feenberg energy functional. Specifically, the expectation value of the kinetic energy operator is not necessarily positive, and the binding energy of boson matter may be made arbitrarily large, provided only that the volume integral of the two-body potential is finite. This pathology is similar to but less serious than difficulties previously noted for the Pandharipande-Bethe energy functional.[7,12] As a consequence, it becomes important to verify that solutions to the Euler-Lagrange equation are truly local energy minima.

In Sec. III we shall construct formal tests for the stability of these solutions in terms of the positivity of the eigenvalues of the linearized kernel which was previously introduced to facilitate numerical solution of the Euler-Lagrange equation. This provides considerable support for the numerical strategy previously adopted. We shall illustrate this point by demonstrating the stability of the numerical solutions found earlier for ^{4}He.

In Sec. IV we shall consider a number of points related to the asymptotic behavior of $g(r)$ and the related liquid-structure function, $S(k)$, obtained from the Euler-Lagrange equation. We stress that our analysis is based solely on the Euler-Lagrange equation and makes no reliance on arguments like Feynman's. For potentials falling to zero faster than r^{-10}, we shall demonstrate that if $S(k) \propto k^{\nu}$ for small k, then ν is necessarily 1. This demonstrates the long-range nature of the optimum $g(r)$ [i.e., that $g(r)-1$ is proportional to r^{-4} for large r]. Short-ranged solutions can exist only if $S(0) \neq 0$. In this case we shall show that if the corresponding eigenvalue spectrum is positive, then the compressibility must be negative. As a consequence, short-ranged solutions to the Euler-Lagrange equation can exist but, if they do, they are of little physical interest. The asymptotic behavior of $g(r)$ is also determined for potentials of longer range.

Finally, in Sec. V we shall return to the question of stability and consider the eigenvalues for nonspherically symmetric eigenfunctions of the linearized kernel. Both the spectrum of eigenvalues and the qualitative features of the eigenfunctions are of interest. We shall also discuss the role that these nonspherically symmetric functions might play in generating crystalline states of boson matter.

II. AN INSTRUCTIVE EXAMPLE

We have previously shown that attempts to solve the Euler-Lagrange (EL) equation using the Pandharipande-Bethe form of the kinetic energy are not successful.[7] Specifically in this form the expectation value of the kinetic energy operator is not guaranteed to be positive. Starting from reasonable initial guesses for $g(r)$ we were led smoothly to physically useless $g(r)$ yielding an arbitrarily large and negative value for the kinetic energy. This was not the case when the Jackson-Feenberg (JF) form of the kinetic energy operator[10] was used. We wish to note, by means of an example, that the JF kinetic energy is not entirely free of problems. To show this, let us write the HNC energy of boson matter, using the JF kinetic energy functional, as

$$E_{\mathrm{JF}} = -\tfrac{1}{8}\rho \int g \nabla^2 \ln g \, d^3r + \frac{1}{8\rho} \int \frac{d^3k}{(2\pi)^3} \frac{k^2(S-1)^3}{S} + \tfrac{1}{2}\rho \int g V \, d^3r \qquad (1)$$

in units where $\hbar^2/m$ is equal to 1. Of course this functional is only approximate because the HNC equation has been used to eliminate the correlation function in favor of $g(r)$. Here, the first two terms may be identified with the kinetic energy, while the last term is the potential energy. The liquid-structure function, $S(k)$, is simply $1+\rho\,\mathcal{F}(g-1)$, where $\mathcal{F}(f)$ denotes the Fourier transform of f. Let us evaluate E_{JF} using the following short-ranged choice for $g(r)$:

$$g(r) - 1 = a e^{-br^2}$$

and

$$S(k) - 1 = \rho a \left(\frac{\pi}{b}\right)^{3/2} e^{-k^2/4b} , \qquad (2)$$

where a and b are constants to be determined. Casting the integrals in Eq. (1) in dimensionless form, one finds

$$E_{\mathrm{JF}} = 8\pi\rho \frac{a^2}{b^{1/2}} \int x^4 e^{-2x^2} \left[\frac{1-\rho a^2(\pi/b)^{3/2} e^{-2x^2}}{(1+ae^{-x^2})\,[1+\rho a(\pi/b)^{3/2} e^{-x^2}]} \right] dx + \tfrac{1}{2}\rho \int d^3r\,(1+ae^{-br^2})\,V(r) \ . \qquad (3)$$

Let us consider potentials with a finite volume integral such that the potential energy term in Eq. (3) is less than $\frac{1}{2}\rho(1+a)$ times the volume integral of the potential. (Here, a is assumed positive.) The numerator term in the kinetic-energy integral varies from $1-\rho a^2(\pi/b)^{3/2}$ for small x to $+1$ for large x. We consider the case $a \gg 1$ and $b^{3/2} \ll \rho$. In this case the term in large parentheses can be made negative (and approximately -1) until well beyond the peak in $x^4 e^{-2x^2}$ so that the kinetic energy is negative and proportional to a^2. Thus, E_{JF} may be made arbitrarily negative by choosing a to be suitably large. The feature of the trial g which causes this instability is its large overshoot of 1. The particular form used above was chosen for simplicity so that g and S would both have simple analytic forms and the unboundedness from below of the energy functional could be easily demonstrated. More physically appealing g's could do the same trick.

The above example demonstrates the worst kind of runaway: small changes in the distribution function cause linear decreases in the energy. A solution of the EL equation is an improvement because it at least guarantees a stationary point of the energy functional. However, smooth variations of g still may lead, albeit quadratically, into a region of runaway. If in addition the solution corresponds to a local minimum, infinitesimal variations of the distribution function can only increase the energy and it will take at least a finite variation in g to reach a region where runaway can occur. We shall insist that solutions be local minima before granting them physical significance. This will not guarantee the validity of the HNC approximation, but it certainly rules out those distribution functions which most openly take advantage of weakness in the HNC approximation.

Note that the problem with the Pandharipande-Bethe energy functional is worse than with the present Jackson-Feenberg functional, since solutions of the corresponding EL equation have not been found. Finally, distribution functions may give apparent local minima when constrained by some parametric form. In the complete function space these generally do not correspond to extremals or even saddle points; hence, distribution functions obtained this way depend crucially on the constraint imposed by the parametrization. A true solution to the Euler-Lagrange equation has no such external constraint.

III. STABILITY CONDITIONS AND THE COMPRESSIBILITY

We have previously constructed the EL equation designed to find choices of $g(r)$ which yield extrema for the energy of Eq. (1).[5,6] This assumes the form

$$-\nabla^2 g^{1/2} + (V + W) g^{1/2} = 0 \ , \tag{4}$$

where W is defined in terms of its Fourier transform

$$W(k) = \mathfrak{F}\left\{ \frac{-k^2(2S+1)(S-1)^2}{4\rho S^2} \right\} \ . \tag{5}$$

We now wish to find ways to verify that a solution to Eqs. (4) and (5) corresponds to a local minimum of $E_{\rm JF}$. This is most easily accomplished by adding to the solution $g^{1/2}$ an almost arbitrary[13] function, $\delta g^{1/2}$, and finding the conditions such that contributions to $E_{\rm JF}$ of order $(\delta g^{1/2})^2$ are positive for all choices of $\delta g^{1/2}$. Since $g^{1/2}$ is a solution of Eqs. (4) and (5), we expect linear contributions to $E_{\rm JF}$ to vanish automatically. We start by rewriting Eq. (1) as

$$E_{\rm JF} = \tfrac{1}{2}\rho \int g^{1/2} \left[-\nabla^2 + V + \mathfrak{F}\left\{ \frac{-k^2(S-1)^2}{4\rho S} \right\} \right] g^{1/2}\, d\tau \tag{6}$$

and expanding through second order in $\delta g^{1/2}$. This yields

$$E_{\rm JF}(g^{1/2} + \delta g^{1/2}) = E_{\rm JF} + \rho \int \delta g^{1/2} \left[-\nabla^2 + V + \mathfrak{F}\left\{ \frac{-k^2(S-1)^2}{4\rho S} \right\} \right] g^{1/2}\, d\tau + \tfrac{1}{2}\rho \int g\, \mathfrak{F}\left\{ \frac{-k^2(S^2-1)}{4S^2}\, \mathfrak{F}(\delta g) \right| d\tau + \delta E_2 \ , \tag{7}$$

$$\delta E_2 = \tfrac{1}{2}\rho \int \delta g^{1/2} \left[-\nabla^2 + V + \mathfrak{F}\left\{ \frac{-k^2(S-1)^2}{4\rho S} \right\} \right] \delta g^{1/2}\, d\tau \ , \tag{8}$$

where we note that

$$\delta g = 2 g^{1/2} \delta g^{1/2} + (\delta g^{1/2})^2 \ . \tag{9}$$

Changing orders of integration we find that

$$E_{\rm JF}(g^{1/2} + \delta g^{1/2}) = E_{\rm JF} + \delta E_2 + \tfrac{1}{2}\rho \int \delta g^{1/2} \mathfrak{F}\left\{ \frac{-k^2(S-1)^2(S+1)}{4\rho S^2} \right\} \delta g^{1/2}\, d\tau + \rho \int \delta g^{1/2} (-\nabla^2 + V + W) g^{1/2}\, d\tau \ . \tag{10}$$

Using Eq. (4), the last term in Eq. (10) vanishes and we find

$$E_{\rm JF}(g^{1/2} + \delta g^{1/2}) = E_{\rm JF}(g^{1/2}) + \tfrac{1}{2}\rho \int \delta g^{1/2} K \delta g^{1/2}\, d\tau \ , \tag{11}$$

where the kernel, K, is defined by

$$Ky = (-\nabla^2 + V + W) y - g^{1/2} \int W' * (g^{1/2} y)\, d\tau \tag{12}$$

and

$$W'(k) = \mathfrak{F}\left\{ \frac{k^2(S^3-1)}{S^3} \right\} \ . \tag{13}$$

Here, the symbol $*$ denotes a convolution integral. Note that the linear terms in $\delta g^{1/2}$ have vanished from Eq. (11) as expected. The condition that $E_{\rm JF}(g^{1/2})$ be a minimum is equivalent to the condition that the second term in Eq. (11) be positive for all choices of $\delta g^{1/2}$. This will be the case if all eigenvalues, λ_n, of K defined by

$$K y_n = \lambda_n y_n \ , \tag{14}$$

are positive.[14]

Equation (14) is a linear integrodifferential eigenvalue equation. Lest the reader find this unduly formidable, we hasten to emphasize that Eqs. (12)–(14) form a practical test and fit neatly into the iterative scheme previously advocated for the numerical solution of the EL equation.[5] Specifically, given an nth-order approximation, $g_n^{1/2}$, we find the inhomogeneous equation

$$K(g_{n+1}^{1/2} - g_n^{1/2}) = (\nabla^2 - V - W) g_n^{1/2} \ , \tag{15}$$

where K is again given by Eqs. (11) and (13). Approximating the integral in Eq. (15) by a sum over a suitable mesh of points and replacing ∇^2 by finite differences, Eq. (15) becomes a set of inhomogeneous linear equations. The iterations of this Newton-Raphson scheme converge rapidly. Similar numerical approximations convert Eq. (14) to a matrix eigenvalue equation. The positivity of all eigenvalues of this matrix then ensures that $g^{1/2}$ will represent an energy minimum. This test is thus elementary (i.e., linear) and easily performed.

As a numerical example, we shall consider liquid ^{4}He using the Lennard-Jones potential of Ref. 15. In

Table I we show the lowest eigenvalue of Eq. (14) at each density for spherically symmetric $\delta g^{1/2}$. The energies in this density range have been reported previously in Ref. 7. All calculations were performed in a box of radius at least 48 Å. Although this is roughly 20 times the range of the force, smaller box sizes have noticeable effects on both eigenfunctions and consistency of solution. For all densities greater than the calculated equilibrium density (about 0.017 Å^{-3}), the lowest eigenvalue is positive and the calculated energy corresponds to a local minimum. We shall postpone a more detailed discussion of these eigenfunctions and their eigenvalues to Sec. V.

The kernel of Eqs. (12) and (13) plays yet another role. The density derivative of the optimum distribution function is readily determined from the inhomogeneous equation

$$K\frac{dg^{1/2}}{d\rho}=g^{1/2}\mathfrak{F}\left(\frac{k^2(S-1)^2(S+2)}{4\rho^2S^3}\right) . \tag{16}$$

This density derivative is particularly useful in evaluating the compressibility[7]

$$C=E+\rho\frac{dE}{d\rho}-\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}\left(\frac{k^2(S-1)^2(S+2)}{4S^3}\frac{dS}{d\rho}\right) . \tag{17}$$

Equation (17) may be recast in terms of K by first multiplying Eq. (16) by $dg^{1/2}/d\rho$ and integrating to obtain

$$\int\frac{dg^{1/2}}{d\rho}K\frac{dg^{1/2}}{d\rho}d\tau =\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}\left[\frac{k^2(S-1)^2(S+2)}{4\rho^2S^3}\mathfrak{F}\left(\frac{dg}{d\rho}\right)\right] . \tag{18}$$

Recalling the definition of $S(k)$ we note

$$\frac{dS}{d\rho}=\frac{S-1}{\rho}+\rho\mathfrak{F}\left(\frac{dg}{d\rho}\right) \tag{19}$$

so that the integral of Eq. (18) is seen to play a role in the compressibility expression of Eq. (17). With the aid of the EL equation we may rewrite Eq. (1) as

$$E=\int\frac{d^3k}{(2\pi)^3}\left(\frac{k^3(S+1)(S-1)^3}{8\rho S^2}\right)+\frac{k^2}{8S^2}\bigg|_{k\to 0} , \tag{20}$$

$$\rho\frac{dE}{d\rho}=E-\frac{1}{2}\int\frac{d^3k}{(2\pi)^3}\left(\frac{k^2(S-1)^3}{4\rho S^2}\right) . \tag{21}$$

Inserting Eqs. (18)–(21) into Eq. (17), we find

$$C=\int\frac{d^3k}{(2\pi)^3}\left(\frac{k^2(S-1)^4(S+1)}{4\rho S^3}\right) -\rho^3\int\frac{dg^{1/2}}{d\rho}K\frac{dg^{1/2}}{d\rho}d\tau+\frac{k^2}{4S^2}\bigg|_{k\to 0} . \tag{22}$$

Equation (22) is not particularly useful numerically. However, a result of some importance may be derived from it. Consider the case when $S(0)\neq 0$. Working from Eq. (16) and the trivial equation

$$Kg^{1/2}=g^{1/2}\mathfrak{F}\left(\frac{-k^2(S^3-1)(S-1)}{\rho S^3}\right) , \tag{23}$$

one quickly arrives at the expression

$$K\frac{dg^{1/2}}{d\rho}+\frac{1}{2\rho}Kg^{1/2}=\frac{1}{\rho}gW . \tag{24}$$

Assuming that K^{-1} exists (i.e., that no eigenvalues are zero), one obtains an alternate form for Eq. (18)

$$\int\frac{dg^{1/2}}{d\rho}K\frac{dg^{1/2}}{d\rho}d\tau=\frac{1}{\rho^2}\int(g^{1/2}W)K^{-1}(g^{1/2}W)\,d\tau -\frac{1}{\rho}\int g^{1/2}K\frac{dg^{1/2}}{d\rho}d\tau -\frac{1}{4\rho^2}\int g^{1/2}Kg^{1/2}d\tau . \tag{25}$$

Using Eqs. (16) and (23), we obtain

$$\int\frac{dg^{1/2}}{d\rho}K\frac{dg^{1/2}}{d\rho}d\tau=\int(g^{1/2}W)K^{-1}(g^{1/2}W)\,d\tau +\int\frac{d^3k}{(2\pi)^3}\left(\frac{k^2(S-1)^4(S+1)}{4\rho^4S^3}\right) . \tag{26}$$

Comparison with Eq. (22) yields a very simple expression for the compressibility valid when $S(0)\neq 0$

$$C=-\rho\int(g^{1/2}W)K^{-1}(g^{1/2}W)\,d\tau . \tag{27}$$

Equation (27) allows us to make a reasonably strong statement when $S(0)\neq 0$. If any of the eigenvalues of K are negative, the solution under consideration does not represent an energy minimum and is not of interest. If all eigenvalues of K are positive, the solution represents an energy minimum

TABLE I. Lowest $l=0$ eigenvalue as a function of density. Note that 1 $\text{Å}^{-2}=12.12$ °K.

ρ (Å^{-3})	λ (Å^{-2})
0.0165	2.51
0.018	2.46
0.021	2.32
0.024	2.16
0.027	2.00
0.030	1.83

but, according to Eq. (27), the compressibility is negative. The solution is thus unstable with respect to small perturbations of the density. (We can make no statement in the case when one or more of the eigenvalues of K is precisely zero.) Thus, while the EL equation may have solutions with $S(0) \neq 0$, they are of no physical interest. We shall show in Sec. IV that (for potentials going to zero faster than r^{-10}) if there are solutions with $S(0) \neq 0$, they are necessarily of short range so that $g(r)-1$ approaches zero faster than any power of r for large r. Thus, we are well on the way towards showing that Eqs. (4) and (5) possess no short-range solutions of physical interest.

IV. ASYMPTOTIC PROPERTIES OF THE DISTRIBUTION FUNCTION

We wish to study the structure of the EL equation for large r in order to determine constraints on $g(r)$ for large r and, simultaneously, $S(k)$ for small k. To facilitate these considerations we shall employ some properties of asymptotic Fourier transforms.[16] In particular, if $\mathfrak{F}(Z)$ is proportional to k^{ν} for small k, $Z(r)$ is proportional to $r^{-\nu-3}$ for large r unless ν is an even integer greater than or equal to zero. In this case, $Z(r)$ vanishes faster than any power of r (for large r), and nonleading contributions to $\mathfrak{F}(Z(r))$ determine the asymptotic form of $Z(r)$.

Let us rearrange the EL equation slightly as

$$\left[-\frac{1}{2}(\nabla^2 g)\frac{1-g}{g^{1/2}}+\frac{1}{4}\frac{(\nabla g)^2}{g^{3/2}}\right]+g^{1/2}\omega(r)+Vg^{1/2}=0 \ , \tag{28}$$

where

$$\omega(r)=\mathfrak{F}\left[\frac{k^2(S^2-1)}{4\rho S^2}\right] \ . \tag{29}$$

The point of this rearrangement is that if $g=1+\delta g$, the first term in Eq. (28) is of order $(\delta g)^2/r^2$.

One immediate result of this equation follows if we divide by $g^{1/2}$ and integrate over all space. This gives

$$\int V\,d\tau=\frac{1}{4}\int\frac{\nabla g\cdot\nabla g\,d\tau}{g^2}-\int\omega\,d\tau \ . \tag{30}$$

Since the two terms on the right are non-negative, the volume integral of the potential must be nonnegative for the EL equation to have a solution. Furthermore, if the volume integral of the potential is zero, then from Eq. (30), g must be one. The EL equation then implies that the potential is zero. In summary, the only system with a nonpositive volume integral of the potential which has a solution to the EL equation is the noninteracting boson gas. Hence the EL equation correctly signals the well-known collapse of matter for systems with potentials whose volume integral is negative.[17]

We shall next consider the interesting case in which $S(0)=0$. The case $S(0)\neq 0$ was essentially dismissed in Sec. III. For the moment, we shall consider the case of particular interest to nuclear physics in which $V(r)$ vanishes faster than any power of r for large r. The large r behavior of Eq. (28) is thus governed by the first two terms. In the following we assume that $S(k)$ is proportional to k^{ν} with $\nu>0$ in the small k limit. [This is consistent with the interesting case $S(0)=0$.] If ν is not equal to 2, δg vanishes at least as rapidly as $r^{-\nu-3}$ and the first term in Eq. (28) vanishes at least as rapidly as $r^{-2\nu-8}$. Since $\omega(k)$ is proportional to $k^{2-2\nu}$, if ν is not equal to 1 or 2, the second term in Eq. (28) is proportional to $r^{-5+2\nu}$. There is no $\nu>0$ such that these exponents are equal, and thus the leading terms cannot cancel. As a consequence, the EL equation can possess solutions of the form $S(k)\propto k^{\nu}$ only if $\nu=1$ or 2. The case $\nu=2$ will now be eliminated.

If $\nu=2$, the asymptotic behavior of δg is determined by nonleading terms in $S(k)$. If $S(k)\propto k^2(1+\beta k^{\mu})$, with $\mu>0$ and not an even integer, g is proportional to $r^{-5-\mu}$. The first term in Eq. (28) is proportional to $r^{-12-2\mu}$. The leading terms in $\omega(k)$ show that the second term is proportional to $1/r$. There is no $\mu>0$ which will satisfy the EL equation to leading order, and the case $\nu=2$ is excluded.

Finally, if $\nu=1$, the first term in Eq. (28) is proportional to r^{-10}. The second term is determined by nonleading terms and is proportional to $r^{-3-\mu}$. In this case an acceptable solution may be found with $\mu=7$. The coefficients of these terms with equal exponents can be made to vanish by a suitable choice of β. Thus, solutions of the EL equation of the form $S(k)\propto k^{\nu}$ with $\nu>0$ must have $\nu=1$. Additional odd powers of k may be added to $S(k)$ without changing the present results. The leading even term in $S(k)$ must be k^8. In this case $g-1$ is proportional to r^{-4} for large r. It is satisfying to note that this is the asymptotic behavior expected for the true (as opposed to the present HNC) distribution function.

By arguments completely parallel to those above, we can show that, if $S(0)$ is nonzero, no solution to the EL equation exists unless $S(k)$ is an even function of k and, hence, $g-1$ is of short range. Note that, as elsewhere in this section, this represents a necessary condition for solutions. We have not proved the existence of these solutions. We recall from Sec. III that solutions with $S(0)\neq 0$ either have negative compressibility or do not represent local energy minima. We now see they are also short ranged. Thus, we believe that the EL equation does not have physically interesting short-ranged solutions.

We have nonetheless constructed specific analytic potentials which have analytic short-ranged solutions of the EL equation. Further discussion of these

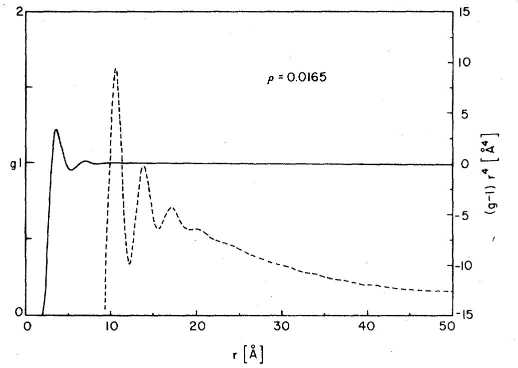

FIG. 1. Solid line shows the distribution function $g(r)$; the broken line shows $r^4(g-1)$. The density is 0.0165 Å^{-3}.

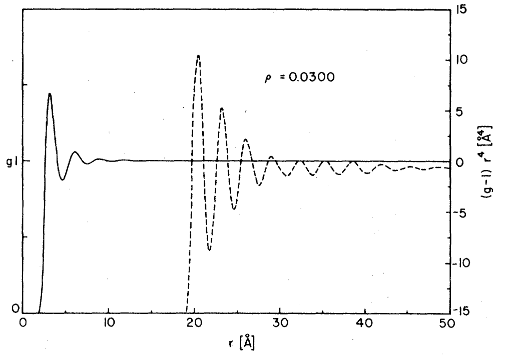

FIG. 3. Curves of Fig. 1 are shown at a density of 0.030 Å^{-3}.

cases is not warranted in view of the above remarks. It is amusing to note that solutions with $S(0)\neq 0$ are the only ones of physical interest in the HNC calculations of classical statistical mechanics; the long-ranged solutions with $S(k)$ proportional to k correspond to systems with infinite isothermal compressibility.

The present arguments must be modified slightly when $V(r)$ falls off less rapidly than r^{-10} for large r. In this case the leading terms, which must be made to cancel if a solution is to exist, come from the second and third terms in Eq. (28). Let us restrict our attention to potentials with asymptotic behavior r^{-n} where n is a positive integer. If $S(k)$ is proportional to k, the asymptotic behavior of $\omega g^{1/2}$ is determined by nonleading terms and solutions can exist for $n=4$, 6, 8, and 10. In this case the leading even term in $S(k)$ is k^{n-2}. For $S(k)$ proportional to k^{ν} with $\nu>0$ and $\nu\neq 1$, leading terms in $\omega g^{1/2}$ come from leading terms in $S(k)$. Thus, the sign of this term is uniquely determined as well as the exponent. Long-ranged solutions with $\nu=2$, $\frac{3}{2}$, and $\frac{1}{2}$ can thus be found for $n=1$ (repulsive), $n=2$ (attractive), and $n=4$ (attractive), respectively. The first case $\nu=2$, $n=1$ (repulsive) corresponds to the expected result for the Coulomb gas. Long-ranged solutions of the type considered here are thus excluded for attractive $1/r$ potentials and for potentials with $n=3$, 5, 7, and 9.

These arguments do not exclude short-ranged solutions with $S(0)\neq 0$. Neither have we excluded long-ranged solutions with $S(k)$ proportional to $k^{\nu}(\ln k)^{\mu}$ with $\nu>0$. These solutions should be studied for completeness. By a similar study of the leading terms in Eq. (28) at large r, it is possible to rule out the possibility that $S(k)$, or any of its derivatives, has a discontinuity along the real k axis. As a consequence, we can conclude that the oscillations in $g-1$, which are characteristic of solutions of the EL equation for the Lennard-Jones potential, must damp out exponentially revealing the simple power-law behavior discussed above. However, the distances at which this asymptotic behavior sets in are remarkably large. This is illustrated in Figs. 1–3. At low densities (e.g., 0.0165 Å^{-3}), the compressibility is small and the oscillations die quickly while the asymptotic behavior is achieved very slowly. At much higher densities (e.g., 0.030 Å^{-3}) the ringing persists to much large distances although the zero point of the oscillations attains its asymptotic value more rapidly.

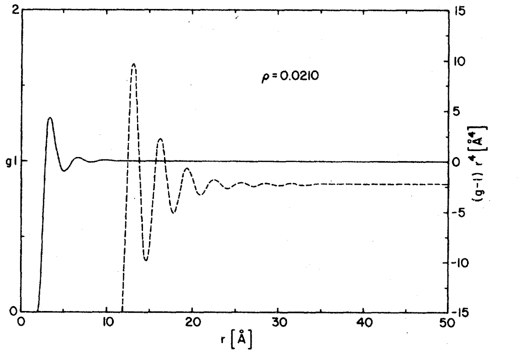

FIG. 2. Curves of Fig. 1 are shown at a density of 0.021 Å^{-3}.

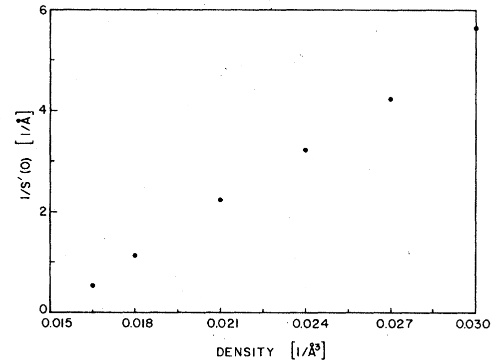

FIG. 4. Inverse of the slope of the liquid-structure function $S(k)$ at $k=0$ is shown as a function of density.

The full asymptotic form is reached most quickly for intermediate densities. From these and similar calculations we may extract the slope of S at $k=0$ as

$$S'(0) = -\rho\pi^2 \lim_{r\to\infty} [r^4(g-1)] \ .$$

The slope of S at $k=0$ is shown in Fig. 4 as a function of density. The plot suggests that $S'(0)$ becomes infinite at a density of approximately 0.015 Å^{-3} where the calculated compressibility goes to zero.

V. NONSPHERICALLY SYMMETRIC EIGENFUNCTIONS

Let us return to the stability conditions discussed in Sec. III. As shown in Eq. (11), a solution of the EL equation will represent an energy minimum if all eigenvalues of Eq. (14) are positive. In Table I we showed that all spherically symmetric eigenvalues for the liquid ^{4}He system are positive for densities greater than 0.0165 Å^{-3}. For the sake of thoroughness, however, we should verify the positivity of all eigenvalues of this kernel for all angular momenta. In the absence of the final (nonlocal) term in Eq. (12) one would anticipate that no surprises lurk in the higher l values. This is not the case. To see this simply let us consider Eqs. (12)–(14) in the limit of large l. If l is sufficiently large, the centrifugal barrier will force y to zero at short distances where the local terms, $V+W$, are of importance and where g is significantly different from 1. In this limit, one may write the Fourier transform of the eigenvalue equation as

$$k^2\mathcal{F}(y_n^l) - \frac{k^2(S^3-1)}{S^3}\mathcal{F}(y_n^l) \simeq \lambda_n^l\,\mathcal{F}(y_n^l) \ , \qquad (31)$$

It is clear from Eq. (31) that, in this approximation, the eigenfunctions $y_n^l(r)$ look like spherical Bessel functions $j_l(k_n r)$ with λ_n given as $k_n^2/S^3(k_n)$. In principle, these eigenvalues form a continuum. In practice, placing the system in a large box to facilitate numerical solution will sample the continuum spectrum at those values of k for which $y^l(kr)$ vanishes at the walls.

In Fig. 5 we show $k^2/S^3(k)$ for liquid ^{4}He for densities from 0.0165 to 0.024 Å^{-3}. A number of interesting features emerge. Since $S(k)$ vanishes linearly with k, the eigenvalue grows like $1/k$ for small k. For large k, $S(k)$ approaches 1 so that the eigenvalue grows like k^2. Thus, these continuum eigenvalues are at least doubly degenerate. (Although this rigorous degeneracy will be broken when the system is placed in a box, evidence for this twofold degeneracy is found in our numerical studies of the eigenvalue spectrum for all l.) The continuum spectrum begins at the minimum value of $k^2/S^3(k)$ independent of l with an eigenfunction which is characteristic of the momentum for which the minimum is found. These observations are supported by the numerical solution of Eqs. (12)–(14) for l up to $l=12$ as indicated in Fig. 6.

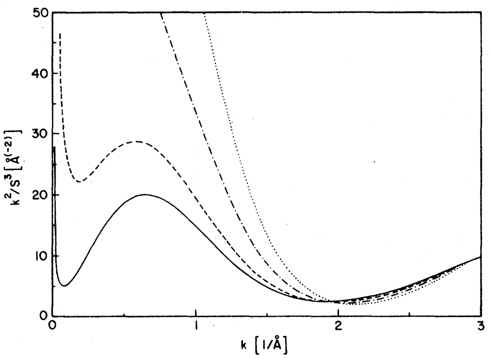

FIG. 5. Function $k^2/S^3(k)$ is shown as a function of k. The solid, dashed, dash-dot, and dotted curves correspond to the densities 0.0165, 0.018, 0.021, and 0.024 Å^{-3}, respectively.

Before discussing the possibility of a discrete spectrum of eigenvalues lying below this continuum, we note that the present arguments help explain the calculated instability in liquid ^{4}He at a density of approximately 0.015 Å^{-3}. In Fig. 5 we see that for $\rho = 0.018$ Å^{-3} a high second minimum has developed in $k^2/S^3(k)$ as the slope of S at $k=0$ begins to grow. When the density is reduced to $\rho = 0.0165$ Å^{-3}, this new minimum has dropped appreciably and, in a box of radius 48 Å, is responsible for the seventeenth $l=0$ eigenvalue. This eigenvalue is very close to the value of $k^2/S^3(k)$ at the new minimum. The corresponding eigenfunction, shown in Fig. 7, has gross structure associated with the small k characteristic of the new minimum modulated by admixtures of essentially degenerate eigenfunctions with the large k characteristic of the old minimum. This new minimum grows deeper rapidly as the density decreases and soon passes the conventional

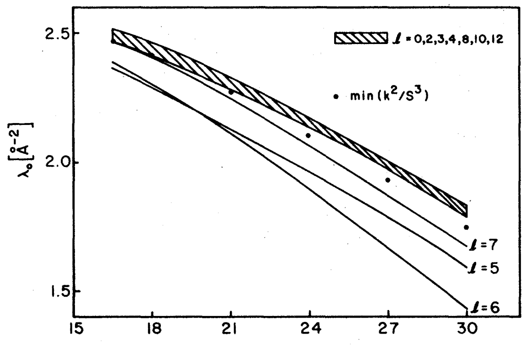

FIG. 6. Lowest eigenvalue, λ_0, for each value of l up to $l=12$ are shown along with the estimated $\min(k^2/S^3)$ as a function of density.

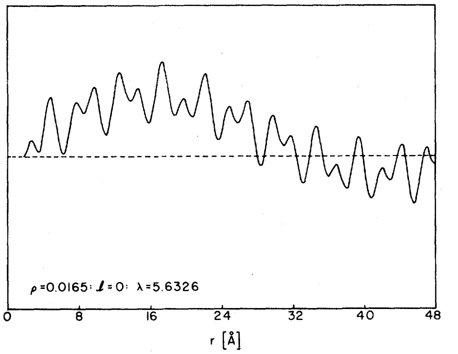

FIG. 7. First $l=0$ eigenvector with an appreciable component with the k corresponding to the new minimum in k^2/S^3 at a density of 0.0165 Å^{-3}. The associated eigenvalue is λ.

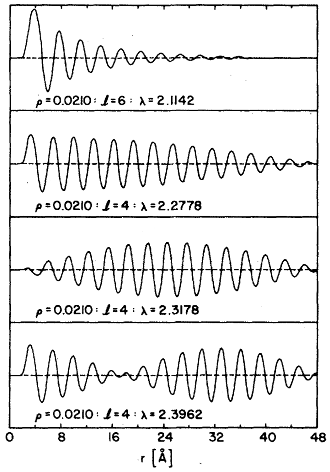

FIG. 8. Top curve shows the eigenvector associated with the discrete $l=6$ eigenvalue at a density of 0.021 Å^{-3}. The bottom three curves show the behavior of the three lowest $l=4$ states using a box size of 48 Å. Each curve is labeled by its eigenvalue, λ.

minimum. Numerical calculations in this region have not been attempted since a step in k of appreciably less than 0.003 Å^{-3} must be used making the calculations prohibitively time consuming. It is tempting to associate the instability noted in Sec. III and in Ref. 7 (which is due to the presence of a negative $l=0$ eigenvalue) with the fact the $S'(0)$ approaches infinity, as shown in Fig. 4, so that the lower bound on the continuum eigenvalue spectrum approaches zero. This expectation is seen to be consistent with the familiar Feynman argument[1] which suggests that

$$S(k) \lesssim \hbar k/2mc \ ,$$

where $S(k)$ is the *true* structure function and c is the velocity of sound by recognizing that c and the compressibility should both vanish at this instability.

Since the approximate eigenfunctions of Eq. (31) are plane waves, it is possible to rewrite the eigenvalue Eqs. (12)–(14) in the form of a Lippmann-Schwinger equation with a suitable nonlocal potential with the obvious change that the energy of the state k is $k^2/S^3(k)$ instead of k^2. For solutions with energy greater than the minimum value of $k^2/S^3(k)$ we expect eigenfunctions which, asymptotically, are linear combinations of the two "plane waves" having the same energy. In a large box, the low-lying states all have wave numbers roughly equal to k_0. Thus, the actual low-lying eigenfunctions for large l should look like $j_l(k_0 r)$ times a slowly varying envelope. (For liquid ^{4}He, k_0 is approximately 2 Å^{-1}.) If we approximate $k^2/S^3(k)$ in the vicinity of the minimum by a parabola and place the system in a spherical box, the envelope will look like the standard solutions for a particle in a box. In the lower part of Fig. 8 we show that this simple expectation is verified numerically, in this case for $l=4$.

Formally recasting Eqs. (12)–(14) as a modified Lippmann-Schwinger equation also makes it plausible that, for suitable $V+W$, there may be a discrete spectrum of eigenvalues with λ less than the minimum of $k^2/S^3(k)$ and with eigenfunctions which decay with an exponentially damped envelope. For ^{4}He we have studied the eigenvalue spectrum for l up to $l=12$. For densities greater than 0.021 Å^{-3} we have found three such states with $l=5$, 6, and 7, respectively. Except for the lowest densities, the $l=6$ state represents the lowest eigenvalue found for any l at each density as shown in Fig. 6. The related eigenfunctions have the expected exponentially damped envelope. An example is shown at the top of Fig. 8. These eigenvalues are also insensitive to box size, since the box size exceeds the range of the envelope. [There is still a contribution to the lowest continuum eigenvalues from box size in a box of 50 Å which may be seen in Fig. 8 as the difference between the calculated lowest eigenvalues and the minimum value of $k^2/S^3(k)$.] Numerically, we would expect $l=6$ to be the most likely channel in which to find a discrete eigenvalue since the first maximum of $j_6(k_0 r)$ happens to coincide with the first maximum in $g(r)$ for all densities considered. At each density considered, this nonspherically symmetric state represents the softest possible deformation which can be made of the stable spherical solution to the Euler-Lagrange equation.

Earlier in this section we explained the appearance and form of a low-lying eigenvalue near the spinodal point of liquid helium. We now wish to present evidence associating the discrete eigenvalues and their associated eigenfunctions with clustering very similar to what one would find in a close-packed solid lattice. The $l=6$ eigenvector is the only definitely discrete one which contributes to an fcc lattice, while the $l=5$, 6, and 7 eigenvectors could all contribute to an hcp structure (which lacks inversion symmetry). The following discussion is based on an fcc lattice because in this case there is unambiguous identification of the eigenfunction's radial and angular factors.

For each l value, the eigenvalue and radial eigenfunction is independent of m, and the choice of the angular function could be any combination of the Y_{lm}'s. The additional requirement of invariance under cubic point group operations restricts the angular function to one particular combination of the Y_{lm} for $l < 12$. In particular, there is only one angular function permissible for $l = 6$. Since the radial form of the eigenvector is uniquely determined from the kernel, there is exactly one $l = 6$ discrete eigenfunction invariant under the cubic point group operations. This eigenfunction enhances the probability of finding a particle in some places and lowers the probability in others. Table II shows what this function does at the nearest-neighbor sites in an fcc lattice whose spacing is determined solely by the density. The overall sign is the product of the signs of the angular and radial factors. This angular function has extrema in the directions of the first, second, fourth, and sixth nearest neighbors and, as shown in the table, the product of these is positive at each of these sites, even though the angular function is negative in two of the directions. Further, the extrema in the radial part of the function occur at roughly the neighbor distances.

The $l = 6$ eigenvector is also significant because it is the lowest value of l which can describe the directions of the twelve nearest neighbors. The lowest $l = 12$ eigenfunction may be discrete as well. (There are signs, but not definite ones, of a damped envelope in the numerical results). This could describe the 24 third nearest neighbors in an fcc lattice rather well since its first extremum is very close to the third-nearest-neighbor distance shown in the table.

A corresponding analysis for an hcp structure (the real structure for solid helium) would be less clear cut, since the eigenfunctions with different l values could come in with different and rather arbitrary weights. In spite of their very different properties under rotations and reflections, the two structures have the same packing fraction and the same number of nearest neighbors. It is unlikely at this level of sophistication that one will see significant differences between the structures.

While building up small amounts of this short-range order costs a little bit of energy, it is not necessarily the case that crystallization would be expensive. For example, extrapolation of the lowest $l = 6$ eigenvalue as a function of density indicates that it will pass through zero at about $\rho = 0.048$ Å^{-3}. [The numerical calculations become very difficult beyond the largest density used here because there is nontrivial long-range structure in $g(r)$ and a prohibitively large box must be used.] If this eigenvalue did go through zero, there would no longer be a local minimum in the energy surface and some anisotropic state would always be at a lower energy. Even at lower densities, however, it is quite plausible that a noninfinitesimal change in the distribution function could lower the energy.

So far we have not considered the possibility of secondary, and possibly nonspherically symmetric, solutions to the EL equation. In this connection we note that Eqs. (4) and (5) were derived making no assumptions regarding spherical symmetry of the solution. Also Jastrow functions (or extended Jastrow functions) have been used previously to describe crystals.[18,19] Even if we were willing to confront the formidable problem of solving Eq. (15) for nonspherically symmetric distribution functions, it would be hard to decide on a suitable initial guess for g. The present spherically symmetric solutions would not be acceptable since they represent genuine energy minima as we have taken pains to demonstrate. One way to move away from our stable solutions is through a sharply constrained study of the energy,

TABLE II. Location of the peaks in the lowest $l = 6$ eigenfunction is compared with the nearest-neighbor distance for a fcc lattice. The sign of the radial eigenfunction and the sign of the product of the radial eigenfunction with the crystal averaged $l = 6$ eigenfunction are also shown. The density is 0.027 Å^{-3}.

Nearest neighbor	No. nearest neighbors	Neighbor distance (Å)	Peak location (Å)	Sign of $r\delta g_6^{1/2}$	Sign of $r\delta g_6^{1/2}$ times angular function
1	12	3.7	3.5	+	+
2	6	5.3	5.5	−	+
3	24	6.5	· · ·	· · ·	· · ·
4	12	7.5	7.1	+	+
5	24	8.4	· · ·	· · ·	· · ·
6	8	9.2	8.7	−	+

Eq. (6), as a function of g. Motivated by the notion that the easiest way to find the next valley is to go over the lowest hill, Eq. (11) suggests a trial $g^{1/2}$ made by adding a multiple of that eigenfunction of Eq. (14) having the lowest eigenvalue to the previous solution of the EL equation. In the present case, this would correspond to the discrete $l=6$ eigenfunction. The energy surface could then be explored as a function of the mixing parameter to reveal a possible secondary minimum which would be a suitable starting point for a second solution of the EL equation.

Of course, the short-ranged discrete eigenfunctions considered here do not yield long-range order. They may, however, be successful in describing those properties of the crystal (e.g., the binding energy of a non-ionic crystal) which do not depend sensitively on distant neighbors. There are certainly simpler ways to describe crystals than with the use of Jastrow wave functions. The point here is that it appears likely that "crystalline" states will emerge from a calculation which is demonstrably successful at describing properties of the liquid. It is thus tempting to speculate that further study of this problem will yield some insight into liquid-solid phase transitions and may yield more reliable criteria for the existence of a solid phase than those conventionally employed. Work continues on this problem.

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[14] This assumes that $\delta g^{1/2}$ can be expanded in the eigenfunctions of K. Since the y_n are orthogonal to $g^{1/2}$, the restriction that $\int \delta g \, d\tau = 0$ is necessary to guarantee the uniform convergence of this expansion. Here, $S(0)$ is assumed to be zero.

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