Numerical Calculation of the Density Autocorrelation Function for Liquid Argon

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Numerical calculations of the dynamic scattering function $S(\vec{k}, \omega)$, the intermediate scattering function, and the van Hove distribution function $G(\vec{r}, t)$, based on an approximate expression for $S(\vec{k}, \omega)$ proposed in an earlier paper, are presented. The liquid structure factor $S(\vec{k})$ and first two even moments of $S(\vec{k}, \omega)$, which are needed as input, are obtained by means of the Percus-Yevick equation with a Lennard-Jones potential, making the calculation entirely self-contained. The calculation is applied to the liquid-argon case studied through molecular dynamics by Rahman; comparisons with these results and those of experiment show good qualitative agreement. A brief description of the numerical procedure is included.

I. INTRODUCTION

This paper reports on the results of a numerical calculation of the van Hove¹ distribution function $G(\vec{r}, t)$, and its Fourier transforms in space and time, as obtained from an approximate equation proposed in a recent article,² which shall be referred to here as I. In this section, we describe the ingredients of the approximation. A brief review of the numerical techniques employed is given in Sec. II. The results are presented in Sec. III.

For a classical N -particle system contained in a volume V , we define the van Hove function as

$$G(\vec{r}, t) = (nN)^{-1} \int d\vec{r}' \times \langle \sum_{i,j} \delta(\vec{r}' - \vec{r}_i(0)) \delta(\vec{r} + \vec{r}' - \vec{r}_j(t)) \rangle - 1, \quad (1)$$

where $\vec{r}_j(t)$ is the position of the j th particle at time t , n is the mean density N/V , and the angular brackets denote an equilibrium canonical ensemble average over the state at time $t=0$. Initially, then, $G(\vec{r}, t)$ has the value

$$G(\vec{r}, 0) = G(\vec{r}) + n^{-1} \delta(\vec{r}), \quad (2)$$

where

$$G(\vec{r}) \equiv g(\vec{r}) - 1 \quad (3)$$

is the total correlation function of equilibrium fluids and $g(\vec{r})$ is the pair correlation function. The space Fourier transform of $G(\vec{r}, t)$ is

$$G_{\vec{k}}(t) = \int d\vec{r} G(\vec{r}, t) e^{i\vec{k} \cdot \vec{r}}, \quad (4)$$

and the initial value of the intermediate scattering function $nG_{\vec{k}}(t)$ is

$$nG_{\vec{k}}(0) = 1 + nG_{\vec{k}} = S(\vec{k}); \quad (5)$$

that is, just the structure factor $S(\vec{k})$ of equilibrium fluids.

It was shown in I that the Laplace transform

$$\mathcal{G}_{\vec{k}}(z) = \int_0^\infty dt G_{\vec{k}}(t) e^{-zt} \quad (6)$$

of $G_{\vec{k}}(t)$ could be resolved as the ratio of two infinite-order determinants containing a set of $\vec{k}$ -dependent parameters ν_n , $n=0, 1, 2, \dots$, which are calculated from the initial state of the system. The proposed approximation to this formal solution was based on the assumption that a modeled function $\mathcal{G}_{\vec{k}}^2(z)$ could be found such that the corresponding ν_n° of this latter solution become progressively more similar, with increasing n , to the actual ν_n . In this case, an approximate solution for $\mathcal{G}_{\vec{k}}(z)$ could be constructed using $\mathcal{G}_{\vec{k}}^2(z)$ and the first few of the ν_n , ν_n° . In particular, with just the $n=0, 1$ parameters used explicitly, this approach gave³

$$\frac{\mathcal{G}_{\vec{k}}(z)}{G_{\vec{k}}(0)} = \frac{[\nu_0^\circ \nu_1 + (\nu_1 - \nu_1^\circ) z^2] \mathcal{G}_{\vec{k}}^\circ(z) - (\nu_1 - \nu_1^\circ) z G_{\vec{k}}(0)}{[\nu_0^\circ \nu_1 - \nu_0 \nu_1^\circ + (\nu_1 - \nu_1^\circ) z^2] z \mathcal{G}_{\vec{k}}^\circ(z) + [\nu_0 \nu_1^\circ - (\nu_1 - \nu_1^\circ) z^2] G_{\vec{k}}(0)}, \quad (7)$$

and it is with this approximation that we shall be concerned in the present paper. It will be more convenient to work with the time Fourier transform of $G_{\vec{k}}(t)$, rather than the Laplace transform. Thus, we obtain from (7) the corresponding dynamic scattering function

$$S(\vec{k}, \omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt nG_{\vec{k}}(t) e^{-i\omega t} \quad (8)$$

$$= (n/\pi) \lim_{\epsilon \rightarrow 0} \text{Re} \mathcal{G}_{\vec{k}}(\epsilon + i\omega). \quad (9)$$

This is, after some algebra,

$$S(\vec{k}, \omega) = \pi^{-1} S(\vec{k}) \nu_0^\circ \nu_0 \nu_1^\circ \nu_1 G_{\vec{k}}(0) \gamma_{\vec{k}}^2(\omega) \{ [\nu_0 \nu_1^\circ + (\nu_1 - \nu_1^\circ) \omega^2] \times G_{\vec{k}}(0) + [\nu_0^\circ \nu_1 - \nu_0 \nu_1^\circ - (\nu_1 - \nu_1^\circ) \omega^2] \omega \gamma_{\vec{k}}^2(\omega) \}^2 + \{ [\nu_0^\circ \nu_1 - \nu_0 \nu_1^\circ - (\nu_1 - \nu_1^\circ) \omega^2] \omega \gamma_{\vec{k}}^2(\omega) \}^2 \}^{-1}, \quad (10)$$

where we have put

$$\lim_{\epsilon \rightarrow 0} G_{\vec{k}}^{\circ}(\epsilon + i\omega) = \gamma_{\vec{k}}'(\omega) - i\gamma_{\vec{k}}''(\omega) . \quad (11)$$

The coefficients ν_n are related to the moments m_n of $S(\vec{k}, \omega)$,

$$m_n = S(\vec{k})^{-1} \int_{-\infty}^{\infty} d\omega \omega^n S(\vec{k}, \omega) , \quad (12)$$

and in particular we have²

$$\nu_0 = m_2 = k^2 / \beta m n G_{\vec{k}}(0) , \quad (13)$$

$$\begin{aligned} \nu_1 &= (m_4 - m_2^2) / m_2 \\ &= 3k^2 / \beta m - k^2 / \beta m n G_{\vec{k}}(0) \\ &\quad + (n/m) \int d\vec{r} g(r) [1 - \cos(\vec{k} \cdot \vec{r})] (\hat{k} \cdot \nabla)^2 \phi(r) . \end{aligned} \quad (14)$$

Here β is $(k_B T)^{-1}$, where T is the temperature of the system, $\hat{k}$ is a unit vector in the direction of $\vec{k}$, and $\phi(r)$ is the intermolecular potential.

For the modeled solution $G_{\vec{k}}^{\circ}(t)$ we choose a Gaussian function,

$$G_{\vec{k}}^{\circ}(t) = G_{\vec{k}}(0) \exp[-k^2 t^2 / 2\beta m n G_{\vec{k}}(0)] . \quad (15)$$

This differs from the ideal gas form discussed in I by the presence of the equilibrium structure factor $nG_{\vec{k}}(0)$ in the denominator of the exponent and has the advantage of yielding the correct second moment m_2 , with a consequent simplification of Eq. (10). With the choice (15), then, the modeled coefficients are

$$\nu_0^{\circ} = \nu_0 , \quad (16)$$

$$\nu_1^{\circ} = 2\nu_0 . \quad (17)$$

If we now define the k -dependent frequencies $\omega_0(k)$ and $\omega_1(k)$ by

$$\omega_0(k) = k[\beta m S(\vec{k})]^{-1/2} , \quad (18)$$

$$\omega_1(k) = k\{[3 + I(\vec{k})] / \beta m\}^{1/2} , \quad (19)$$

where

$$I(\vec{k}) \equiv (n/k^2) \int d\vec{r} g(r) [1 - \cos(\vec{k} \cdot \vec{r})] (\hat{k} \cdot \nabla)^2 \phi(r) , \quad (20)$$

so that

$$\nu_0 = \omega_0^2 , \quad (21)$$

$$\nu_1 = \omega_1^2 - \omega_0^2 , \quad (22)$$

then Eq. (10) can be simplified to read

$$\begin{aligned} S(\vec{k}, \omega) &= 2S(\vec{k})[\pi\omega_0(k)]^{-1} [2 + \Delta(k)] F_R(x) \{ [2 + \Delta(k)x^2 \\ &\quad + \Delta(k)(1 - x^2)x F_I(x)]^2 + [\Delta(k)(1 - x^2)x F_R(x)]^2 \}^{-1} , \end{aligned} \quad (23)$$

where

$$x = \omega / \omega_0(k) , \quad (24)$$

$$F_R(x) = (\frac{1}{2}\pi)^{1/2} e^{-x^2/2} , \quad (25)$$

$$F_I(x) = e^{-x^2/2} \int_0^x dy e^{y^2/2} , \quad (26)$$

$$\Delta(k) = [\omega_1(k) / \omega_0(k)]^2 - 3 . \quad (27)$$

Here we have used the mathematical result that, from the Laplace transform of (15),

$$\begin{aligned} G_{\vec{k}}^{\circ}(z) &= [G_{\vec{k}}(0) / \omega_0(k)] (\frac{1}{2}\pi)^{1/2} \exp[\frac{1}{2}[z / \omega_0(k)]^2] \\ &\quad \times \{1 - \operatorname{erf}[z / \sqrt{2}\omega_0(k)]\} , \end{aligned} \quad (28)$$

we get, in the notation of (24)–(26),

$$\lim_{\epsilon \rightarrow 0} G_{\vec{k}}^{\circ}(\epsilon + i\omega) = [G_{\vec{k}}(0) / \omega_0(k)] [F_R(x) - iF_I(x)] , \quad (29)$$

since

$$\lim_{\epsilon \rightarrow 0} \operatorname{erf}(\epsilon + iy) = (2i/\sqrt{\pi}) \int_0^y ds e^{-s^2} . \quad (30)$$

Equation (23), with the ancillary definitions (24)–(27), is the approximate dynamic scattering function studied in this paper. In Sec. II, we review briefly some of the numerical techniques needed to proceed from this expression to the intermediate scattering function $nG_{\vec{k}}(t)$ and finally to the space and time correlation function $G(\vec{r}, t)$. (Section II may be skipped with little loss in continuity.) The results of these calculations are presented in Sec. III for the particular case of liquid argon at density 1.374 g/cm³ and temperature 94.4 °K, where some comparisons can be made with experiment and the molecular dynamics study of Rahman.⁴

Before terminating this section, we note that it is of course possible to choose other functions for $G_{\vec{k}}^{\circ}(t)$. In particular, the “self” part of $G_{\vec{k}}(t)$ might be chosen for this role. The sequence of approximations discussed in I, wherein all ν_n are assumed equal to ν_n° for n greater than some integer i , then yields for its first two members, $i=0$ and 1, the convolution approximation of Vineyard⁵ and Kerr’s⁶ generalization of this, respectively. A numerical study of the next member of the sequence, corresponding to Eq. (7), is in progress.^{7,8}

II. NUMERICAL PROCEDURE

Since studies of the dynamic scattering functions $S(\vec{k}, \omega)$ are rarely carried through to the calculation of the space- and time-dependent density autocorrelation function $G(\vec{r}, t)$, it was thought worthwhile to include in this section some of the details of the numerical procedure followed here to accomplish this end.

It is convenient for the numerical calculations to express all quantities in reduced units. The units of distance and energy, σ and ϵ , are obtained in the usual way from the intermolecular potential, which in this work is the Lennard-Jones potential

$$\phi(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6] . \quad (31)$$

The unit of time τ is chosen so that

FIG. 1. Real and imaginary parts of $\omega_0(k)G_k^\circ(i\omega/S(k))$ for the Gaussian "ansatz" to the scattering function.

$$\epsilon = m(\sigma/\tau)^2, \quad (32)$$

where m is the mass of a molecule. Reduced units will be identified by an asterisk; in particular,

$$\begin{aligned} n^* &= n\sigma^3, \\ T^* &= k_B T/\epsilon, \\ \omega^* &= \omega\tau. \end{aligned} \quad (33)$$

As preliminary input for the evaluation of $S(\vec{k}, \omega)$ from Eq. (23), we need to know the pair distribution function $g(r)$ of the equilibrium liquid. In order to keep the calculation completely self-contained, avoiding any appeal to experimental data, we have obtained this quantity through the Percus-Yevick⁹ equation, following procedures described elsewhere.¹⁰ This function is needed for the evaluation of $\omega_0(k)$ and $\omega_1(k)$.

The imaginary part $F_I(x)$ of $G_k^\circ(i\omega)$, defined in Eq. (26), is essentially Dawson's integral¹¹ and was evaluated by a direct summation of its absolutely convergent power series expansion, except for values of x greater than 15, where an asymptotic form was used. Both $F_R(x)$ and $F_I(x)$ are shown in Fig. 1.

The principal feature of these calculations, however, is the numerical computation of sine and cosine Fourier transforms. Thus, given $S(\vec{k}, \omega)$, we need to evaluate a cosine transform to obtain $G_k^\circ(t)$:

$$\frac{G_k^\circ(t)}{G_k^\circ(0)} = 2 \int_0^\infty d\omega \frac{S(\vec{k}, \omega)}{S(\vec{k})} \cos \omega t. \quad (34)$$

Actually, because of the nature of $F_R[\omega/\omega_0(k)]$ appearing in (23), which rapidly vanishes with increasing ω for small values of k , this integral was evaluated in the form

$$G_k^\circ(y)/G_k^\circ(0) = 2 \int_0^\infty dx W_k(x) \cos xy, \quad (35)$$

where

$$W_k(x) = \omega_0(k)S(\vec{k}, \omega)/S(\vec{k}), \quad (36)$$

$$y = \omega_0(k)t, \quad (37)$$

and x is defined in Eq. (24). For the numerical evaluation, the infinite-range integral in (35) was replaced by a finite sum,¹²

$$\frac{G_k^\circ(y)}{G_k^\circ(0)} = 2\Delta x \sum_{i=1}^{N'-1} W_k(x_i) \cos x_i y, \quad (38)$$

with

$$\begin{aligned} x_i &= (i - \frac{1}{2})\Delta x, & i &= 1, 2, \dots, N'-1, \\ y_i &= (i - \frac{1}{2})\Delta y, & i &= 1, 2, \dots, N'-1, \\ \Delta x \Delta y &= \pi/(N' - \frac{1}{2}). \end{aligned} \quad (39)$$

Conditions (39) are designed to ensure orthogonality of the cosine basis set in the discrete transforms.

For the results reported in Sec. III, we used an interval $\Delta y = 0.1$ with $N' = 300$. Note that Δx is then automatically determined. The evaluation of $G_k^\circ(t)/G_k^\circ(0)$ at desired values of t was then performed by second-order interpolation into the computed $G_k^\circ(y)/G_k^\circ(0)$ for the various values of k .

Finally, for a particular value of t , we need to evaluate

$$G(\vec{r}, t) = (2\pi^2 r)^{-1} \int_0^\infty dk k G_k^\circ(t) \sin kr \quad (40)$$

to arrive at the van Hove function. The numerical algorithm used for the sine transform replaces this integral with¹²

$$G(r_j, t) = \frac{\Delta k}{2\pi^2 r_j} \sum_{i=1}^{N''-1} k_i G_{k_i}^\circ(t) \sin k_i r_j, \quad (41)$$

where

$$\begin{aligned} r_i &= i\Delta r, & i &= 1, 2, \dots, N''-1 \\ k_i &= i\Delta k, & i &= 1, 2, \dots, N''-1 \\ \Delta r \Delta k &= \pi/N''. \end{aligned} \quad (42)$$

Conditions (42) again ensure orthogonality of the discrete sine transforms. For this transform, we used the interval $\Delta r^* = 0.025$ with $N'' = 282$. Note that this again determines the reciprocal interval Δk^* . The same algorithm and numerical parameters were used in the solution of the Percus-Yevick equation and the computation of $S(\vec{k})$.

Given the above procedures, the values of t chosen for the interpolations are essentially arbitrary. We chose to evaluate $G_k^\circ(t)$ at 50 equally spaced intervals, with the spacing $\Delta t^* = 0.04648$. (For the case of liquid argon discussed in Sec. III, this corresponds to an interval in time of 10^{-13} sec.) The entire calculation, programmed in FORTRAN, took about 8 min on an IBM 360/75, not including the solution of the Percus-Yevick equation.

III. COMPUTED RESULTS

We have numerically evaluated $S(\vec{k}, \omega)$, in the

FIG. 2. Liquid structure factor $S(\vec{k}) = 1 + nG_{\vec{k}}$ for liquid argon at 94.4 °K and 1.374 g/cm³ calculated from the Percus-Yevick equation with a (truncated) Lennard-Jones potential.

approximation described in Sec. I, and its Fourier transforms $G_{\vec{k}}(t)$ and $G(\vec{r}, t)$ for a liquid with a Lennard-Jones (6-12) potential truncated at $r/\sigma = 2.25$ at the reduced density and temperature $n^* = 0.814$ and $T^* = 0.787$. Using the argon parameters $\sigma = 3.4$ Å and $\epsilon/k_B = 120$ °K, this corresponds to liquid argon at density 1.374 g/cm³ and temperature 94.4 °K, a case studied through molecular dynamics by Rahman.⁴ The corresponding unit of time, from Eq. (32), is $\tau = 2.151 \times 10^{-12}$ sec.

The equilibrium pair distribution function $g(r)$ needed to calculate $S(\vec{k})$, $\omega_0(k)$, and $\omega_1(k)$ was obtained through an iterative solution of the Percus-Yevick equation, thus making the calculation computationally self-contained. The resulting liquid structure factor $S(\vec{k})$ is shown in Fig. 2. The first four peaks of $S(\vec{k})$ occur at $k\sigma = 6.9$, 12.7, 18.7, and 24.5. These are in good agreement with the values 6.8, 12.5, 18.5, and 24.8 given by Rahman.

FIG. 3. "Dispersion laws" ω_0 and ω_1 obtained from the first two even moments of $S(\vec{k}, \omega)$, compared with the computed dispersion law ω_c , from Eq. (23); $\Delta(k)$ is a measure of the deviation of $S(\vec{k}, \omega)$ from a Gaussian form in ω .

The quantities $\omega_0(k)$ and $\omega_1(k)$, called by Schofield¹³ the low-frequency and high-frequency dispersion laws, are displayed in Fig. 3. They are of similar general form, showing maxima where $S(\vec{k})$ is a minimum and vice versa. For large k they settle down to a linear ideal gas behavior. Also shown in Fig. 2 is $\Delta(k)$, defined in Eq. (27), which is in effect a measure of the departure of $S(\vec{k}, \omega)$ from the Gaussian $S^0(\vec{k}, \omega)$, judged on the basis of the first two even moments. As is evident, the initial Gaussian ansatz becomes increasingly good for increasing values of k and is poorest in the vicinity of the origin and the first peak of $S(k)$, a not unexpected behavior that has been qualitatively discussed by de Gennes.¹⁴

The dynamic scattering function $S(\vec{k}, \omega)$ obtained using these computed quantities in Eq. (23) is shown in Fig. 4 as a function of k for selected values of ω and in Fig. 5 as a function of ω for selected values of k . We see, for example, that the initial peak at $k\sigma = 6.8$ decreases and broadens with increasing ω , becoming a minimum at about $\omega\tau = 15.9$, then rises to a second peak at about $\omega\tau = 18.9$. This second peak, associated with collective motion in the system,¹⁵ occurs for values of $k\sigma$ less than 8.5, after which it smooths into a broad shoulder of the central peak, but reappears again briefly for $11.3 \lesssim k\sigma \lesssim 13.1$. For large values of k , $S(\vec{k}, \omega)$ has only the Gaussian central peak of the ideal gas.

The values of ω at which the collective peak occurs for given k can be readily collected from the tabulated values of $S(\vec{k}, \omega)$. This dispersion law, labeled $\omega_c(k)$, is shown in Fig. 3. It is qualitatively similar to $\omega_0(k)$ and $\omega_1(k)$, though larger

FIG. 4. Computed scattering function $S(\vec{k}, \omega)$ for liquid argon at 94.4 °K and 1.374 g/cm³ for several values of $\omega\tau$.

FIG. 5. Computed scattering function $S(\vec{k}, \omega)$ for liquid argon at 94.4°K and 1.374 g/cm³ for several values of $k\sigma$.

than either, with the principal difference that it is broken and terminates definitely at $k\sigma \approx 13.1$. It is furthermore qualitatively similar to corresponding dispersion laws obtained experimentally for liquid argon¹⁶ and liquid lead.¹³ For very small values of k , where $F_R(x)$ rapidly vanishes with ω , the peak in $S(\vec{k}, \omega)$ occurs for $\omega = x\omega_0(k)$, where x is such that [see Eq. (23)]

$$2 + \Delta(k)x^2 + \Delta(k)(1 - x^2)x F_I(x) = 0 \quad (43)$$

or

$$F_I(x) = \frac{x^2 + 2/\Delta(k)}{x(x^2 - 1)} \quad (44)$$

For these small values of k , we can write

$$\omega_0(k) = k[\beta m S(0)]^{-1/2} + O(k^3), \quad (45)$$

so that the dispersion law for small k is

$$\omega_c(k) = x_0[\beta m S(0)]^{-1/2}k + O(k^3), \quad (46)$$

where x_0 is the solution of (44) for $k=0$. Comparing

FIG. 6. Computed intermediate scattering function $nG_{\vec{k}}(t)$, normalized to unity at $t=0$ for liquid argon at several values of the time in 10^{-12} sec.

(46) with the hydrodynamic dispersion law holding for small k ,

$$\omega_c(k) = ck, \quad (47)$$

where c is the speed of sound in the liquid, we get that in the present approximation

$$c = x_0[\beta m S(0)]^{-1/2}. \quad (48)$$

With the solution $x_0 = 2.27$ found graphically by plotting both sides of (44) [with $\Delta(0) = 12.9$] and the previously computed $S(0) = 0.127$, we obtain a value

$$c = 8.9 \times 10^4 \text{ cm/sec}$$

for the speed of sound in liquid argon. Rahman⁴ does not compute this quantity, but this result compares well with the experimental value 8.2×10^4 cm/sec for liquid argon at 90.3°K.¹⁷

A Fourier cosine transform over ω of $S(\vec{k}, \omega)$ produces the intermediate scattering function $nG_{\vec{k}}(t)$, shown (in normalized form) as a function of k in Fig. 6 for various values of the time and function of t in Fig. 7 for selected values of k . It is evident from Fig. 6 that $G_{\vec{k}}(t)$ decays more slowly with time in the region of the peaks of $S(\vec{k})$ and more so among these for smaller values of k . This is brought out more clearly in Fig. 7, where $G_{\vec{k}}(t)/G_{\vec{k}}(0)$ is shown for some values of $k\sigma$ corresponding to peaks and valleys of $S(\vec{k})$. This figure evidently suggests that the normalized intermediate scattering function contains a damped oscillatory function, the oscillations arising from the collective peak in $S(\vec{k}, \omega)$, for the smaller values of k and, of course, the ideal-gas Gaussian shape for large k .

The Gaussian ansatz $G_{\vec{k}}^o(t)/G_{\vec{k}}^o(0)$ used in this calculation is shown for comparison in Fig. 7 for the value $k\sigma = 7.13$, where the correction $\Delta(k)$ is near

FIG. 7. Time decay of the computed intermediate scattering function $nG_{\vec{k}}(t)$, normalized to unity at $t=0$, for liquid argon at several values of $k\sigma$; broken line is the corresponding Gaussian "ansatz" for $k\sigma = 7.13$.

FIG. 8. Computed van Hove correlation function $G(\vec{r}, t)$, normalized to zero at large r , for liquid argon at several values of the time in 10^{-12} sec; function at $t=0$ includes a δ function at the origin.

its maximum. The change produced by Eq. (23) is seen to be considerable, except for times less than about 2.5×10^{-13} sec, where the corrected and uncorrected curves merge. As expected, the difference between $G_k^0(t)$ and the final $G_k(t)$ is less significant for larger values of k , where $\Delta(k)$ is much smaller.

A final Fourier sine transform over k yields the van Hove function $G(\vec{r}, t)$ shown in Fig. 8 as a function of r for succeeding values of the time. Note that these curves contain both the "self" and "distinct" parts of $G(\vec{r}, t)$. The peculiar behavior of the computed $G(\vec{r}, t)$ for short times in the vicinity

FIG. 9. Comparison of computed $G(\vec{r}, t)$ with Rahman's molecular dynamics results for the "distinct" part of $G(\vec{r}, t)$ at $t = 10^{-12}$ sec.

of the hard core region is obvious. Here the function takes on some values below -1 , which is clearly an error. This anomalous behavior is apparently not a result of the approximation in Eq. (7), in that similar behavior is evidenced by the numerical inversion of just the Gaussian G_k^0 and is also apparently not a numerical difficulty in calculating the "distinct" part of $G(\vec{r}, t)$ in the hard core region, in that the numerical inversion of G_k alone yields a well behaved result. It appears thus to be a numerical difficulty in accounting for the behavior of the "self" part of $G(\vec{r}, t)$, which is evolving from a Dirac δ function at the origin at $t=0$. In any case, the anomaly disappears for longer times.

Quantitative agreement with Rahman's "distinct" part $G_d(\vec{r}, t)$ is poor. This comparison is illustrated in Fig. 9 for $t = 10^{-12}$ sec, where it is seen that the extrema of $|G(\vec{r}, t)|$ computed here are too large. [We are assuming in this comparison that the "self" term of $G(\vec{r}, t)$ does not contribute significantly for $r/\sigma > 1$.] That is, $G(\vec{r}, t)$ is decaying too slowly compared to the molecular dynamics results. Part of the divergence in Fig. 9 is due directly to the approximate Percus-Yevick results used here for the initial form of $G(\vec{r}, 0)$. This is evident from Fig. 10, where in particular we find that the main peak exceeds the peak obtained in the numerical experiments. Since $G(\vec{r}, t)$ is directly proportional to $G(\vec{r}, 0)$, this would result in consistently too large values of this peak at all times, in the best of cases. In addition, however, this initial error enters into the time development of $G(\vec{r}, t)$ in a more complex fashion through the computed frequencies $\omega_0(k)$ and $\omega_1(k)$. The latter quantity is particularly sensitive to the first peak of $G(\vec{r}, 0)$. This feature makes it evidently quite difficult to

FIG. 10. Comparison of the initial form of $G(\vec{r}, 0)$ obtained from the Percus-Yevick equation with Rahman's molecular dynamics results.

specify the principal source of the error in the final results. Nevertheless, on the basis of a comparison with other numerical calculations⁷ also using the Percus-Yevick approximation and Eq. (7) but with a different form of the modeled func-

tion $G^\circ(\vec{r}, t)$, it is believed that the principal error stems from the Gaussian form [Eq. (15)] used here rather than the imperfections in $G(\vec{r}, 0)$ or the limitations of the general approximation [Eq. (7)].

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Coherent-State Representation of Elementary Excitations in Liquid ⁴He at Low Temperatures*

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The coherent states of two-dimensional harmonic oscillators are introduced to describe the elementary excitations of liquid helium. It allows a simple derivation of the liquid-⁴He density matrix at low temperatures, first obtained by Penrose.

I. INTRODUCTION

Feenberg¹ has recently given an evaluation of the density matrix of liquid ⁴He at low temperatures using a set of orthonormal basis functions obtained from the paired-phonon analysis.² His result is in agreement with the earlier result of Penrose,³ who interprets the long-wavelength excitations as small density fluctuations. (In Penrose's calculation the generalized Hermite polynomials were used as orthonormal basis functions.) These two treatments, though distinct, are essentially equivalent.¹ In particular, both sets of orthonormal basis functions are solutions of the Schrödinger equation for a two-dimensional isotropic harmonic oscillator. The purpose of the present note is mainly pedagogical. We show that the helium density matrix at low temperatures has a diagonal representation in terms of the coherent states⁴ for two-dimensional oscillators. Such a representation frequently occurs in the quantum mechanical description of op-

tical fields,⁵ and we shall make extensive use of these quantum optical results. The coordinate space form of the density matrix can be easily evaluated in the coherent-state formalism and in fact gives a much simpler derivation of the Penrose result. In Sec. II we briefly summarize some pertinent properties of the coherent states for two-dimensional oscillators, and in Sec. III we give the coherent-state representation and rederive the Penrose result. We believe that the new coherent-state representation [Eq. (18) below] will be useful in elucidating many properties of elementary excitations in liquid helium.

II. COHERENT STATES OF HARMONIC OSCILLATOR IN TWO DIMENSIONS

The Hamiltonian of a two-dimensional harmonic oscillator is given by

$$H = \frac{1}{2}(p_1^2 + \omega^2 q_1^2) + \frac{1}{2}(p_2^2 + \omega^2 q_2^2) = \hbar\omega(a_1^\dagger a_1 + a_2^\dagger a_2 + 1),$$