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Time-dependent self-correlations in fluids at intermediate wave numbers

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A new type of infinite-order perturbation treatment of the incoherent intermediate scattering function $F_s(\vec{k},t)$ yields analytic expressions for the spectrum $S_s(\vec{k},\omega)$ and the Van Hove self-correlation function $G_s(\vec{r},t)$ valid at intermediate to very large values of the wave number k. Predictions of this "intermediate-k" theory agree quantitatively with the results of computer simulations of fluid argon for k as small as 6.75 Å^{-1} at the triple point and 2 or 3 Å^{-1} away from the triple point. The present theory is qualitatively and quantitatively superior to competing large-k theories and predicts a scaling of dynamical variables associated with $S_s(\vec{k},\omega)$ that differs from that predicted by generalized Boltzmann-Enskog theory. The deviation of the Boltzmann-Enskog "scaling law" from experiment is fully accounted for in the present theory, with its new "scaling law." Relations between the "intermediate-k" model and previous models in various limits are discussed.

I. INTRODUCTION

Neutron scattering has become a standard technique for investigating the structure and dynamics of condensed phases.[1] The *incoherent* contribution to the cross section for thermal inelastic neutron scattering is proportional to the (incoherent) spectral function $S_s(\vec{k},\omega)$, where $\hbar\vec{k}$ and $\hbar\omega$ are, respectively, the momentum and energy *transferred* from the scattered neutron.[1,2] In turn, the spectral function is expressed as

$$S_s(\vec{k},\omega)=(2\pi)^{-1}\int_{-\infty}^{\infty} dt\exp(-i\omega t)F_s(\vec{k},t), \tag{1a}$$

$$F_s(\vec{k},t)=\int d^3r\exp(i\vec{k}\cdot\vec{r})G_s(\vec{r},t), \tag{1b}$$

in terms of $F_s(\vec{k},t)$, the (incoherent) intermediate scattering function and $G_s(\vec{r},t)$, the Van Hove[3] self-correlation function,

$$G_s(\vec{r},t)=N^{-1}\left\langle\sum_{i=1}^{N}\delta(\vec{r}+\vec{r}_i(0)-\vec{r}_i(t))\right\rangle. \tag{2}$$

In (2) $\vec{r}_i$ is the position of the ith particle, there being a total of N particles in the system. For a pure homogeneous fluid, each particle is equivalent, and so the scattering function (1b) assumes the form

$$F_s(\vec{k},t)=\langle\exp[i\vec{k}\cdot\vec{r}_1(0)]\exp[-i\vec{k}\cdot\vec{r}_1(t)]\rangle, \tag{3}$$

where $\vec{r}_1$ is the position of a typical, or "test", particle.

From (1)–(3) it is clear that the scattering cross section [proportional to $S_s(\vec{k},\omega)$] is intimately connected with the test-particle density fluctuations and hence that neutron scattering is potentially quite useful in the experimental study of single-particle molecular motions in fluids.[4]

From a theoretical viewpoint the problem of obtaining $S_s(\vec{k},\omega)$ can be reduced to that of determining the intermediate scattering function $F_s(\vec{k},t)$, i.e., the time-autocorrelation function (TACF) of the dynamical quantity

$$A\equiv\exp[i\vec{k}\cdot\vec{r}_1(t)].$$

Now, assuming that the system obeys the classical laws of motion, we can rewrite the scattering function as

$$F_s(\vec{k},t)=\langle A(0)A^*(t)\rangle$$
$$=\langle A(0)\exp(\hat{\mathcal{L}}t)A^*(0)\rangle,$$

where Liouville's operator is given by

$$\hat{\mathcal{L}}\equiv\sum_{i=1}^{N}\left[\left(\frac{\partial H}{\partial\vec{p}_i}\right)\cdot\frac{\partial}{\partial\vec{r}_i}-\left(\frac{\partial H}{\partial\vec{r}_i}\right)\cdot\frac{\partial}{\partial\vec{p}_i}\right],$$

with $\vec{p}_i$ denoting the (conjugate) momentum of the ith particle and H the total Hamiltonian. We shall further assume H to be infinitely differentiable with respect to $\vec{r}_i$ and $\vec{p}_i$, so as to exclude from consideration impulsive interactions. Then, $F_s(\vec{k},t)$ may be *formally* expanded in a Maclaurin series:

$$F_s(\vec{k},t)=\sum_{n=0}^{\infty}(-1)^n a_n(\vec{k})\frac{t^{2n}}{(2n)!}. \tag{4}$$

Note that odd powers of t are absent in (4) on account of the anti-Hermiticity of $\hat{\mathcal{L}}$:

$$\langle X(\hat{\mathcal{L}}Y)^*\rangle=-\langle(\hat{\mathcal{L}}X)Y^*\rangle.$$

The coefficient $a_n(\vec{k})$, defined by

$$a_n(\vec{k})\equiv\langle(\hat{\mathcal{L}}^nA)(\hat{\mathcal{L}}^nA^*)\rangle, \tag{5}$$

is the $2n$th moment of the spectrum, i.e.,

$$a_n(\vec{k})=\int_{-\infty}^{\infty}d\omega\,\omega^{2n}S_s(\vec{k},\omega).$$

Let us momentarily entertain a discursion on TACF's of a more general nature. Let A represent the (arbitrary) dynamical quantity of princi-

pal interest, i.e., the one whose TACF $C_A(t) = \langle AA^*(t)\rangle$ we set out to find, and define the set of dynamical functions

$$B_n(t) = \hat{\mathfrak{L}}^n A(t), \quad n = 0, 1, 2, \ldots .$$

Next, transform the set $\{B_n\}_{n=0}^{\infty}$ into the Schmidt-orthogonalized set[5-9] $\{Z_n\}_{n=0}^{\infty}$, where

$$Z_0 = B_0 = A ,$$
$$Z_n = B_n - \sum_{k=0}^{n-1} \langle B_n Z_k^*\rangle \langle Z_k Z_k^*\rangle^{-1} Z_k .$$

Now, under the restriction of infinite differentiability introduced above, it can be shown[6-9] that

$$\hat{\mathfrak{L}} Z_n = Z_{n+1} - \lambda_n Z_{n-1} ,$$

where the *lowering coefficient* λ_n is given by

$$\lambda_n \equiv \langle Z_n Z_n^*\rangle \langle Z_{n-1} Z_{n-1}^*\rangle^{-1}, \quad n \geq 1 . \tag{6}$$

We have recently pointed out[10] that the moments [of the Fourier transform of $\langle AA^*(t)\rangle$] are related to the lowering coefficients as follows:

$$a_n = \langle Z_0 Z_0^*\rangle \sum_{k_1=1}^{1} \lambda_{k_1} \sum_{k_2=1}^{k_1+1} \lambda_{k_2} \cdots \sum_{k_n=1}^{k_{n-1}+1} \lambda_{k_n} . \tag{7}$$

Using (7), we find the first four moments [corresponding to the normalized TACF $\bar{C}_A(t) = C_A(t)\langle AA^*\rangle^{-1}$] to be

$$\bar{a}_1 = \lambda_1 ,$$
$$\bar{a}_2 = \lambda_1(\lambda_1 + \lambda_2) ,$$
$$\bar{a}_3 = \lambda_1(\lambda_1 + \lambda_2)^2 + \lambda_1\lambda_2\lambda_3 ,$$
$$\bar{a}_4 = \lambda_1(\lambda_1 + \lambda_2)^3 + 2\lambda_1^2\lambda_2\lambda_3 + \lambda_1\lambda_2\lambda_3^2 + 2\lambda_1\lambda_2^2\lambda_3 + \lambda_1^2\lambda_2\lambda_3\lambda_4 . \tag{8}$$

Finally, we note that the Laplace transform of the TACF can be conveniently represented[11] as an infinite continued fraction:

$$\int_0^{\infty} dt \exp(-st)\bar{C}_A(t) = \frac{1}{s} + \frac{\lambda_1}{s} + \frac{\lambda_2}{s} + \cdots . \tag{9}$$

Returning now to our central problem, namely, the determination of $F_s(\vec{k}, t)$, we observe that a variety of approximate approaches have been taken by previous workers. These include methods based on Brownian-motion concepts,[4] the generalized Boltzmann equation,[12] the generalized Langevin equation,[13] generalized hydrodynamics,[4,13] and the cumulant expansion.[14] In addition, several molecular dynamics studies[15,16] have been carried out.

The purpose of this article is to present a new approach to the calculation of $F_s(\vec{k}, t)$, which is based on a type of "perturbation" correction to the limit of $F_s(\vec{k}, t)$ at very large wave numbers $k = |\vec{k}|$ in which the λ's, introduced in (6), play a central role. The procedure, to be presented fully in Sec. III, is outlined as follows. We note first that the $2n$th moment $a_n(\vec{k})$ of $S_s(\vec{k}, \omega)$ can be expressed as an even polynomial in k of degree $2n$. Neglecting contributions to $a_n(\vec{k})$ of order k^{2n-4} and less, we then obtain a closed expression for $a_n(\vec{k})$. Next, we effectively solve the nonlinear equations (7) for the lowering coefficients, obtaining $\lambda_n(\vec{k})$ explicitly to $O(k^{-2})$. By stopping at this order in k we can guarantee the required positivity of the λ's for all values of k, an important feature that is lost at higher orders in k. It is this fact that sets the present calculation apart from all other large-k theories. The form of the lowering coefficients permits us to obtain an analytic expression for $F_s(\vec{k}, t)$. Finally, we compute $S_s(\vec{k}, \omega)$ and $G_s(\vec{r}, t)$ using relations (1).

The treatment just outlined is rigorous only at very large, yet still finite, wave numbers. In practice, it appears to give good results even at intermediate values of k. It seems helpful to view the approach as defining an "intermediate-k" (or IK) model that becomes rigorously valid only at very large (but finite) k.

In the next section we shall briefly derive an algorithm by which (7) can be solved recursively. We shall next employ this algorithm to obtain an explicit expression for the lowering coefficients associated with the IK model.

In Secs. IV and V analytic results of the IK model will be established and compared with those of other models, such as free particle, hydrodynamic, Enskog,[2] and cumulant, in various limits.

In Sec. VI we shall compare the results of the IK model with computer-simulation data[15,16] on fluid argon.

II. DYNAMICAL EMBEDDING[17]

A convenient method of solving (7) for the lowering coefficients in terms of the moments can be derived from the observation that all of the information required to compute the TACF of $B_n = \hat{\mathfrak{L}}^n A$, i.e., $C_{B_n}(t)$, is already contained in the TACF of A itself. This is easily seen by examining the sequence

$$C_{B_1} = C_{\dot{A}} = \sum_{n=0}^{\infty} (-1)^n a_n^{(1)} \frac{t^{2n}}{(2n)!}$$
$$= \sum_{n=0}^{\infty} (-1)^n a_{n+1} \frac{t^{2n}}{(2n)!}$$
$$= \frac{-d^2 C_A}{dt^2} .$$

We say that $C_{\dot{A}}$ is "dynamically embedded" in C_A, inasmuch as the moments of $C_{\dot{A}}$, $\{a_n^{(1)}\}_{n=0}^{\infty} = \{a_n\}_{n=1}^{\infty}$ form a subset of those of $C_A(\{a_n\}_{n=0}^{\infty})$. It can be shown[17] that the lowering coefficients associated with $C_{\dot{A}}$ and C_A are connected by the relations

$$\lambda_{2n-1}^{(1)}\lambda_{2n}^{(1)} = \lambda_{2n}^{(0)}\lambda_{2n+1}^{(0)}, \quad n \geq 1 \tag{10a}$$

$$\lambda_{2n}^{(1)} + \lambda_{2n+1}^{(1)} = \lambda_{2n+1}^{(0)} + \lambda_{2n+2}^{(0)}, \quad n \geq 0 \tag{10b}$$

where the superscripts 0 and 1, respectively, refer to C_A and $C_{\dot{A}}$. Note that $\lambda_0^{(k)} = 0$, for all k.

The embedding procedure can be immediately generalized. Consider the TACF of $\hat{\mathfrak{L}}^k A$:

$$C_{\hat{\mathfrak{L}}^k A}(t) = \sum_{n=0}^{\infty} (-1)^n a_n^{(k)} \frac{t^{2n}}{(2n)!}$$

$$= \sum_{n=0}^{\infty} (-1)^n a_{n+k} \frac{t^{2n}}{(2n)!}$$

$$= (-1)^k \frac{d^{2k} C_A}{dt^{2k}} .$$

The generalization of (10) is then

$$\lambda_{2n-1}^{(k)}\lambda_{2n}^{(k)} = \lambda_{2n}^{(k-1)}\lambda_{2n+1}^{(k-1)}, \quad n \geq 1 \tag{11a}$$

$$\lambda_{2n}^{(k)} + \lambda_{2n+1}^{(k)} = \lambda_{2n+1}^{(k-1)} + \lambda_{2n+2}^{(k-1)}, \quad n \geq 0 . \tag{11b}$$

The moments of the kth embedded (normalized) TACF are given by

$$\bar{a}_{n+1}^{(k)} \prod_{l=k}^{n+k} \lambda_1^{(l)} = \frac{a_{n+1}^{(k)}}{C_{\hat{\mathfrak{L}}^k A}(0)} . \tag{12}$$

Equations (11) and (12) constitute a convenient algorithm for generating the lowering coefficients of a given TACF from its moments and *vice versa*. The procedure is nicely illustrated with the Gaussian $C_G(t) = \exp(-t^2/2)$ as a model TACF. From the Maclaurin expansion the moments of C_G are easily found to be $\bar{a}_n^{(0)} = a_n = (2n-1)!!$. Then from (12) the $\lambda_1^{(l)}$ are calculated (up to $l=5$) and entered into Table I as the first column. Clearly, $\lambda_1^{(l)}$ is the first moment of the lth embedded TACF derived from C_G. Now from (11b) we have

$$\lambda_2^{(l-1)} = \lambda_1^{(l)} - \lambda_1^{(l-1)}, \quad l = 1, 2, \ldots, 5$$

which generates the second column of Table I. Next, we rearrange (11a) to obtain

$$\lambda_3^{(l-1)} = \lambda_2^{(l)}\lambda_1^{(l)}/\lambda_2^{(l-1)}, \quad l = 1, 2, 3, 4$$

which gives us the third column. Then we return to (11b) to compute

$$\lambda_4^{(l-1)} = \lambda_3^{(l)} + \lambda_2^{(l)} - \lambda_3^{(l-1)}, \quad l = 1, 2, 3 . \tag{13}$$

Equation (13) yields the fourth column. Continuing in this fashion alternately using (11a) and (11b), we eventually fill in the entire embedding table. Then the lowering coefficient $\lambda_j^{(0)}$ of C_G is simply the jth entry of the first ($l=0$) row.

Of course, the above procedure can be "reversed" to calculate the first column of the table, and from (12) the moments, if we are given the first row, i.e., the lowering coefficients. We shall employ dynamical embedding to calculate the lowering coefficients of the IK model in the next section.

TABLE I. Embedding table for the Gaussian $C_G(t) = \exp(-t^2/2)$.

l \ n	1	2	3	4	5	6
0	1	2	3	4	5	6
1	3	2	5	4	7	
2	5	2	7	4		
3	7	2	9			
4	9	2				
5	11					

III. DERIVATION OF THE INTERMEDIATE-k MODEL

We first derive an approximate expression for the $2n$th moment of $S_s(\vec{k}, \omega)$, namely, $a_n(\vec{k})$ [see (5)]. Operating upon $A(0) = \exp(i\vec{k}\cdot\vec{r}_1)$, with $\mathfrak{L}^n$ and retaining only terms of order k^{n-2} or greater, we find

$$B_n \equiv \hat{\mathfrak{L}}^n A \simeq A\left[\left(\frac{i\vec{k}\cdot\vec{p}_1}{m}\right)^n + n(n-1)\left(\frac{i\vec{k}\cdot\vec{p}_1}{m}\right)^{n-2}\left(\frac{i\vec{k}\cdot\vec{F}_1}{m}\right)\Big/2 + n(n-1)(n-2)\left(\frac{i\vec{k}\cdot\vec{p}_1}{m}\right)^{n-3}\left(i\vec{k}\cdot\frac{d\vec{F}_1}{dt}/m\right)\Big/3!\right.$$

$$\left. + 3n(n-1)(n-2)(n-3)\left(\frac{i\vec{k}\cdot\vec{p}_1}{m}\right)^{n-4}\left(\frac{i\vec{k}\cdot\vec{F}_1}{m}\right)^2\Big/4!\right], \tag{14}$$

where

$$\frac{\vec{p}_1}{m} = \hat{\mathfrak{L}}\vec{r}_1 = \frac{d\vec{r}_1}{dt} ,$$

$$\vec{F}_1 = \hat{\mathfrak{L}}\vec{p}_1 = \frac{d\vec{p}_1}{dt} ,$$

$$\frac{d\vec{F}_1}{dt} = \hat{\mathcal{L}}\,\vec{F}_1 ,$$

and m is the mass of the test particle. Mathematical induction provides a straightforward proof of (14). Next, from (14) we compute the approximate (i.e., intermediate-k) expression

$$\begin{aligned} a_n(\vec{k}) = \langle B_n B_n^* \rangle = &\left\langle \left(\frac{\vec{k}\cdot\vec{p}_1}{m} \right)^{2n} \right\rangle + n^2(n-1)^2 \left\langle \left(\frac{\vec{k}\cdot\vec{p}_1}{m} \right)^{2n-4} \left(\frac{\vec{k}\cdot\vec{F}_1}{m} \right)^2 \right\rangle \Big/ 4 \\ &- n(n-1)(n-2) \left\langle \left(\frac{\vec{k}\cdot\vec{p}_1}{m} \right)^{2n-3} \left(\vec{k}\cdot\frac{d\vec{F}_1}{dt}/m \right) \right\rangle \Big/ 3 \\ &- n(n-1)(n-2)(n-3) \left\langle \left(\frac{\vec{k}\cdot\vec{p}_1}{m} \right)^{2n-4} \left(\frac{\vec{k}\cdot\vec{F}_1}{m} \right)^2 \right\rangle \Big/ 4 + O(k^{2n-4}), \end{aligned} \tag{15}$$

wherein terms of order k^{2n-4} and less have been neglected. Using the relations

$$\left\langle \left(\frac{\vec{k}\cdot\vec{p}_1}{m} \right)^{2n-3} \left(\vec{k}\cdot\frac{d\vec{F}_1}{dt}/m \right) \right\rangle = -(2n-3) \left\langle \left(\frac{\vec{k}\cdot\vec{p}_1}{m} \right)^{2n-4} \left(\frac{\vec{k}\cdot\vec{F}_1}{m} \right)^2 \right\rangle ,$$

$$\langle (\vec{k}\cdot\vec{p}_1/m)^{2n-4} (\vec{k}\cdot\vec{F}_1/m)^2 \rangle = \langle (\vec{k}\cdot\vec{p}_1/m)^{2n-4} \rangle \langle (\vec{k}\cdot\vec{F}_1/m)^2 \rangle ,$$

$$\langle (\vec{k}\cdot\vec{p}_1/m)^{2n} \rangle = (2n-1)!!\,\lambda_1^n ,$$

$$\langle (\vec{k}\cdot\vec{F}_1/m)^2 \rangle = k^2 \langle \vec{F}_1\cdot\vec{F}_1 \rangle / (3m^2) = \lambda_1\mu_1 ,$$

where

$$\begin{aligned} &\mu_1 = \langle \vec{F}_1\cdot\vec{F}_1 \rangle \langle \vec{p}_1\cdot\vec{p}_1 \rangle^{-1} , \\ &\lambda_1 \equiv k^2/m\beta = a_1(\vec{k}) , \\ &\beta \equiv (k_B T)^{-1} , \end{aligned} \tag{16}$$

k_B is Boltzmann's constant, and T is the absolute temperature, we can simplify (15) to

$$a_n(k) = (2n-1)!!\,[\lambda_1 + n(n-1)\mu_1/6]\,\lambda_1^{n-1} + O(k^{2n-4}) . \tag{17}$$

Note that λ_1 and μ_1 are, respectively, the second moments associated with $F_s(\vec{k}, t)$ and the test-particle velocity TACF.

We next utilize the embedding relations (11) to derive an explicit formula for the lowering coefficients. The procedure is precisely analogous to the one followed in Sec. II to generate Table I. After one computes the first several columns of the embedding table, it becomes apparent that, in general,

$$\lambda_{2j}^{(n)}(k) = \{2j + [4jn + j(2j-1)\mu_1/\lambda_1]\}\,\lambda_1 + O(k^{-2}) , \tag{18a}$$

$$\lambda_{2j+1}^{(n)}(k) = [2j+1+2n+(n+3j)(2n+2j+1)\mu_1/(3\lambda_1)]\,\lambda_1 + O(k^{-2}) . \tag{18b}$$

In the derivation of (18) all terms are retained exactly to order k^0 at each stage of computation, terms of $O(k^{-2})$ being discarded. The rationale for this procedure is that the inclusion of higher orders leads to negative values for some of the lowering coefficients at some values of $\vec{k}$. But the lowering coefficients are strictly positive [see (6)]. Thus, the embedding procedure provides a means for disposing of dynamically inconsistent information in a set of approximately derived moments.

As in the case of expression (14) for $a_n(\vec{k})$, it is convenient to use mathematical induction (on j) to prove (18). Finally, setting $n=0$ in (18), we have

$$\lambda_j(k) = \lambda_j^{(0)} = \lambda_1(k)j + \mu_1 j(j-1)/2 + O(k^{-2}) , \quad \text{all } j . \tag{19}$$

Now, *by definition*, we shall take the intermediate-k (IK) model to be characterized by a scattering function having lowering coefficients

$$\lambda_j(k) = \lambda_1(k)j + \mu_1 j(j-1)/2 , \quad j \geq 1 . \tag{20}$$

Employing an identity[18] from the analytic theory of continued fractions, we can invert the Laplace transform (9), with λ's given explicitly by (20), to obtain

$$F_s^{(\mathrm{IK})}(\vec{k}, t) = \{\mathrm{sech}\,[(\mu_1/2)^{1/2}t]\}^{2\lambda_1/\mu_1} , \tag{21}$$

where of course the superscript (IK) denotes the intermediate-k model. Then inverting (1b), we find

$$\begin{aligned} G_s^{(\mathrm{IK})}(\vec{r}, t) &= (2\pi)^{-3} \int d\vec{k}\, \exp(i\vec{k}\cdot\vec{r}) F_s^{(\mathrm{IK})}(\vec{k}, t) \\ &= [4\pi\rho(t)]^{-3/2} \exp[-r^2/4\rho(t)] , \end{aligned} \tag{22}$$

where

$$\rho(t) \equiv [2/(m\beta\mu_1)] \ln\{\cosh[(\mu_1/2)^{1/2}t]\}.$$

Since $F_s(\vec{k}, t)$ is even in t, expression (1a) can be rewritten as

$$S_s(\vec{k}, \omega) = \pi^{-1} \int_0^\infty dt \cos(\omega t) F_s(\vec{k}, t). \tag{23}$$

Substituting (21) into (23) brings $S_s^{(IK)}(\vec{k}, \omega)$ into a more or less standard form, which can be evaluated[19] as

$$S_s^{(IK)}(\vec{k}, \omega) = (2\mu\pi)^{-1/2} [\Gamma(\lambda_1/\mu_1)/\Gamma(\lambda_1/\mu_1 + \tfrac{1}{2})] \times \prod_{n=0}^{\infty} \left[1 + \left(\frac{\omega^2}{2\mu_1}\right) \Big/ \left(n + \frac{\lambda_1}{\mu_1}\right)^2\right]^{-1}, \tag{24}$$

where $\Gamma(x)$ is the gamma function.

Observe that in (19) the omitted terms vanish as $k \to \infty$. This suggests that the intermediate-k model can be viewed as a sort of perturbation expansion in which the order parameter is k. In the usual theory, the order parameter λ vanishes for the unperturbed system and corrections account for additional interactions that are "turned on" as λ increases from zero to unity. In the present treatment, the zeroth order is characterized by $k = \infty$. The corrections, the "first order" of which is the term $\mu_1 j(j-1)/2$ [see (19)], account essentially for the fact that k may be finite.

We note that for finite k, $\lambda_j \sim O(j^2)$ in the limit of large j. It can be shown[20] that in this case the corresponding TACF, namely, $F_s^{(IK)}(\vec{k}, t)$, though regular at the origin, is not analytic everywhere in the complex-t plane. On the other hand, the form of $F_s(\vec{k}, t)$ obtained using (4) with $a_n(k)$ truncated at order k^{2n-4} [Eq. (17)] is an entire function. Hence, there appears to be a "price," i.e., loss of analyticity, for whatever advantages may come with the IK model.

IV. RELATION OF INTERMEDIATE-k MODEL TO PREVIOUS MODELS

If one retains only the term of order k^{2n}, the intermediate-k expression (17) for the $2n$th moment simplifies to

$$a_n(\vec{k}) \simeq (2n-1)!! \lambda_1^n, \tag{25}$$

which, upon insertion into (4), yields the well-known[4] free-particle model scattering function

$$F_s^{(G)}(\vec{k}, t) = \exp(-\lambda_1 t^2/2), \tag{26}$$

the superscript G denoting "Gaussian." The corresponding self-correlation and spectral functions are given, respectively, by

$$G_s^{(G)}(\vec{r}, t) = (2\pi v_0^2 t^2)^{-3/2} \exp[-(r/v_0 t)^2/2], \tag{27}$$

$$S_s^{(G)}(\vec{k}, \omega) = \exp[-(\omega/kv_0)^2/2]/(\sqrt{2\pi} k v_0), \tag{28}$$

where

$$v_0^2 = 1/\beta m. \tag{29}$$

Now from the second term [of $O(k^{2n-2})$] in (17), we deduce, via (4), the first-order cumulant correction[4,14] to $F_s^G(\vec{k}, t)$, namely,

$$F_s^{(1)}(\vec{k}, t) = (\mu_1 \lambda_1 / 4!) t^4 \exp(-\lambda_1 t^2/2). \tag{30}$$

Thus, we have

$$F_s^{(C)}(\vec{k}, t) = F_s^{(G)}(\vec{k}, t) + F_s^{(1)}(\vec{k}, t), \tag{31}$$

where the superscript C refers to "cumulant."

Expression (31) agrees with the exact Maclaurin expansion through $O(t^4)$, i.e., gives the second moment of $S_s(\vec{k}, \omega)$ exactly. An alternate approximation

$$F_s^{(Z)}(\vec{k}, t) = \{1 + (\mu_1 \lambda_1 / 4!)[4 \exp(-\mu_1 t^2/2) - 3] t^4\} \times \exp(-\lambda_1 t^2/2), \tag{32}$$

which is based on the Zassenhaus formula[9] for the "propagator" $\exp(\hat{\mathfrak{L}} t)$, also coincides with the exact Maclaurin series through $O(t^4)$. However, although $F_s^{(C)}$ and $F_s^{(Z)}$ agree at short times, they exhibit very different long-time behavior. Indeed,

$$\lim_{t \to \infty} F_s^{(Z)}(\vec{k}, t)/F_s^{(C)}(\vec{k}, t) = -3.$$

The point is simply that alternate expansions of the TACF, which are equally rigorous, may yield quite disparate approximations when truncated so as to give the same subset of moments exactly.

One may be concerned that $F_s^{(C)}$ does not agree with $F_s^{(IK)}$ given by (21), since both functions are derived from (15). The crucial difference, however, is that $F_s^{(C)}$ is based on the moment expression (17), whereas $F_s^{(IK)}$ derives from the expression (20) for the lowering coefficients. This distinction may be appreciated more fully as follows. Recall that the IK model is defined by (20). The corresponding moments may be calculated by substituting λ_j's given by (20) into (7). It is clear that the $2n$th moment computed in this way is an even polynomial in k encompassing all powers of k from 0 to $2n$. These *exact* IK model moments cannot, therefore, agree with those given by (17). However, in the limit $k \to \infty$, $\lambda_n \to \lambda_1 n$ [see (19)]. Since these limiting lowering coefficients correspond exactly to the limiting moments given by (25), it follows that

$$\lim_{k \to \infty} F^{(IK)}(\vec{k}, t) = F_s^{(G)}(\vec{k}, t).$$

Thus, in view of the intermediate-k model as a first-order perturbation treatment presented in

Sec. III, we can regard $F_s^{(G)}$ as the "zero-order" scattering function.

In closing this section, we summarize, for future reference, the hydrodynamic model[4] (i.e., $k \to 0$ limit):

$$\begin{aligned} F_s^{(H)}(\vec{k}, t) &= \exp(-D_s k^2 t), \\ G_s^{(H)}(\vec{k}, t) &= (4\pi D_s t)^{-3/2} \exp(-r^2/4D_s t), \\ S_s^{(H)}(\vec{k}, \omega) &= \pi^{-1} D_s k^2/[\omega^2 + (D_s k^2)^2], \end{aligned} \tag{33}$$

where D_s is the self-diffusion coefficient.

V. ADDITIONAL ANALYTIC RESULTS FOR THE INTERMEDIATE-k MODEL

We begin with the (normalized) longitudinal self-current TACF, defined by

$$\begin{aligned} C_s(\vec{k}, t) &\equiv \langle [\vec{k}\cdot\vec{p}_1(t)/m] \exp[i\vec{k}\cdot\vec{r}_1(t)] [\vec{k}\cdot\vec{p}_1(0)/m] \exp[-i\vec{k}\cdot\vec{r}_1(0)] \rangle \langle [\vec{k}\cdot\vec{p}_1(0)/m]^2 \rangle^{-1} \\ &= \left(\frac{\partial^2 F_s(\vec{k}, t)}{\partial t^2}\right)\left[\left(\frac{\partial^2 F_s(\vec{k}, t)}{\partial t^2}\right)_{t=0}\right]^{-1}. \end{aligned} \tag{34}$$

From (34) and (21) we compute

$$\begin{aligned} C_s^{(IK)}(\vec{k}, t) = &\{\operatorname{sech}[(\mu_1/2)^{1/2} t]\}^{2\lambda_1/\mu_1} \\ &\times \{(1 + 2\lambda_1/\mu_1) \operatorname{sech}^2[(\mu_1/2)^{1/2} t] - 2\lambda_1/\mu_1\}. \end{aligned}$$

Employing the relation

$$\phi(t) = \lim_{k\to 0} C_s(\vec{k}, t), \tag{35}$$

where ϕ is the test-particle velocity TACF, we obtain

$$\phi^{(IK)}(t) = \operatorname{sech}^2[(\mu_1/2)^{1/2} t]. \tag{36}$$

The implied self-diffusion coefficient is given by

$$D_s^{(IK)} = v_0^2 \int_0^\infty \phi^{(IK)}(t)\, dt = v_0^2 (2/\mu_1)^{1/2}. \tag{37}$$

In terms of (37), we can rewrite (36) as

$$\phi^{(IK)}(t) = \operatorname{sech}^2(v_0^2 t/D_s^{(IK)}), \tag{38}$$

from which we deduce the following limits:

$$\phi^{(IK)}(t) \sim \begin{cases} 1 - \mu_1 t^2/2 + O(t^4), & \text{small } t \\ \exp(-2v_0^2 t/D_s^{(IK)}), & \text{large } t. \end{cases} \tag{39}$$

Thus, the velocity TACF implied by the IK model exhibits free-particle–like behavior at small times and Enskog-like[21] behavior at large times. Note that the small-time expansion is exact through order t^2.

It should be emphasized that $D_s^{(IK)}$ cannot be identified with the macroscopic diffusion coefficient D_s given by

$$D_s = v_0^2 \int_0^\infty \phi(t). \tag{40}$$

It has been shown[22] that D_s can be cast as

$$D_s = v_0^2 \lim_{l\to\infty} \mu_2\mu_4\mu_6 \cdots \mu_{2l} f_l / \mu_1\mu_3\mu_5 \cdots \mu_{2l-1}(\mu_{2l+1})^{1/2}, \tag{41}$$

where f_l is a known functional of $\{\mu_j\}_{j=1}^{2l+1}$ and μ_j is the jth lowering coefficient associated with $\phi(t)$. Then from (37) and (41) we compute the ratio

$$D_s^{(IK)}/D_s = \lim_{l\to\infty} (2\mu_1)^{1/2} \mu_3\mu_5 \cdots \mu_{2l-1}(\mu_{2l+1})^{1/2} / \mu_2\mu_4\mu_6 \cdots \mu_{2l} f_l,$$

which is clearly not equal to one, except possibly for some special thermodynamic states.[23]

Using (29) and (37), we can rewrite the Van Hove self-correlation function (22) for the IK model as

$$G_s^{(IK)}(\vec{r}, t) = [4\pi (D_s^{(IK)})^2/v_0^2]^{-3/2} \{\ln[\cosh(v_0^2 t/D_s^{(IK)})]\}^{-3/2} \exp(-v_0^2 r^2/\{4(D_s^{(IK)})^2 \ln[\cosh(v_0^2 t/D_s^{(IK)})]\}). \tag{42}$$

Again calculating the limit of $G_s^{(IK)}(\vec{r}, t)$ at small and large times, we find

$$G_s^{(IK)}(\vec{r}, t) \sim \begin{cases} (2\pi v_0^2 t^2)^{-3/2} \exp(-r^2/2v_0^2 t^2), & \text{small } t \\ (4\pi D_s^{(IK)} t)^{-3/2} \exp(-r^2/4D_s^{(IK)} t), & \text{large } t. \end{cases} \tag{43}$$

Thus, again in the small-time limit, the intermediate-k model displays free-particle behavior; at large times it mimics the hydrodynamic model [see (33)], except that the macroscopic diffusion coefficient is replaced by $D_s^{(IK)}$.

The mean-square displacement in the IK model is given by

$$\langle r^2(t)\rangle_{(\mathrm{IK})} = \int d^3r\, r^2 G_s^{(\mathrm{IK})}(\vec{r}, t)$$

$$= 6(D_s^{(\mathrm{IK})})^2 \ln[\cosh(v_0^2 t/D_s^{(\mathrm{IK})})]/v_0^2, \quad (44)$$

where the second line of (44) follows from the first by inserting expression (42). Then, as expected on the basis (43), we find

$$\langle r^2(t)\rangle_{(\mathrm{IK})} \sim \begin{cases} 3v_0^2 t^2, & \text{small } t \\ 6D_s^{(\mathrm{IK})} t, & \text{large } t \end{cases}$$

which are, respectively, the free-particle and hydrodynamic limits.

To make additional connections with previous models, it is helpful to introduce the quantity

$$y^{-1} \equiv \sqrt{2}\, k D_s^{(\mathrm{IK})}/v_0, \quad (45)$$

which takes on the significance of the collision parameter appearing in the linearized Boltzmann treatment of single-particle motions in the hard-sphere fluid,[12] provided that we interpret the quantity $v_0^2/D_s^{(\mathrm{IK})} = (\mu_1/2)^{1/2}$ as a "collision frequency." Such an interpretation can be made plausible by the following argument. Note first that

$$\tau = \left(\frac{2}{\mu_1}\right)^{1/2} = \int_0^\infty dt\, \phi^{(\mathrm{IK})}(t) \quad (46)$$

can be taken as a characteristic time for single-particle momentum relaxation. Were $\phi^{(\mathrm{IK})}(t)$ a decaying exponential, for example, then the integral (46) would be the decay constant. Since the momentum of a particle generally relaxes after a few collisions, it is reasonable to take $\tau^{-1} = (\mu_1/2)^{1/2}$ as a rough measure of the frequency of collisions. The collision parameter also appears in the Enskog kinetic equation for hard spheres,[12,16] except that $D_s^{(\mathrm{IK})}$ is replaced by D_E.

Now in terms of the collision parameter y^{-1} we can recast the IK model scattering function as

$$F_s^{(\mathrm{IK})}(\vec{k}, t) = [\mathrm{sech}(v_0^2 t/D_s^{(\mathrm{IK})})]^{1/2y^2},$$

which possesses the temporal limits

$$F_s^{(\mathrm{IK})}(\vec{k}, t) \sim \begin{cases} 1 - \lambda_1 t^2/2 + \lambda_1(\mu_1 + 3\lambda_1) t^4/4! + O(t^6), & \text{small } t \\ \exp(-k^2 D_s^{(\mathrm{IK})} t), & \text{large } t. \end{cases} \quad (47)$$

Thus, at small times the IK model scattering function agrees with the exact one through fourth order in t. Again, the hydrodynamic limit [see (33)] obtains at large t, but with $D_s^{(\mathrm{IK})}$ replacing the macroscopic diffusion coefficient.

In (47) the large-time limit holds, regardless of the value of k. As a consequence, one would expect a plot of $\ln F_s(\vec{k}, t)$ against t to be linear at large times over those ranges of k for which the IK model is valid. Computer-simulation data[16] representative of liquid argon in the thermodynamic state $\rho^* = 0.3$, $T^* = 2.16$ display such behavior for values of k up to 1.55 Å^{-1}, the largest value of k considered. It appears that, at least for some thermodynamic states, the large-time limit given in (47) may be qualitatively correct for all k. These results suggest the existence of a function $D_s(k)$ with the following properties:

$$F_s(\vec{k}, t) \sim \exp[-k^2 D_s(k) t], \quad \text{large } t$$

where

$$D_s(k) \sim \begin{cases} D_s, & k \to 0 \\ D_s^{(\mathrm{IK})}, & k \to \infty. \end{cases}$$

Indeed, Zwanzig[24] has demonstrated the existence of such a function, generalized to include frequency dependence in order to treat $S_s(\vec{k}, \omega)$. The intermediate-k model naturally gives rise to this generalized diffusion coefficient, which in the limits of large wave number and small frequency is $D_s^{(\mathrm{IK})}$.

In connection with the Enskog kinetic theory[12,16] one introduces a reduced frequency $x \equiv \omega/\sqrt{2}\, k v_0$, which, along with the collision parameter $y_E \equiv v_0/\sqrt{2}\, k D_E$ [see (45)], allows the spectral function to be written as $S_s^{(E)}(\vec{k}, \omega) \propto S_s^{(E)}(x, y_E)$, i.e., as a function only of the reduced variables. Thus, in the Enskog theory the scattering function obeys an "(x, y_E) scaling law." This law does not apply to the intermediate-k model. Rather,

$$(2\mu_1)^{1/2} S_s^{(\mathrm{IK})}(\vec{k}, \omega) \equiv \mathcal{S}_s(y, u)$$

$$= \pi^{-1/2}[\Gamma(1/4y^2)/\Gamma(1/4y^2 + \tfrac{1}{2})] \times \prod_{n=0}^{\infty} \left(1 + \frac{16y^4u^2}{(4ny^2+1)^2}\right)^{-1}, \quad (48)$$

where the reduced frequency is now given by

$$u \equiv \omega/(2\mu_1)^{1/2},$$

and the collision parameter y is defined by (45). Thus, the IK model conforms to a (u, y) scaling law. Chen and Rahman[16] have shown that Enskog (x, y_E) scaling breaks down at high densities and low temperatures for large k. Results presented in the next section show that (u, y) scaling cor-

rectly describes this thermodynamic regime and is essentially indistinguishable from the Enskog result at lower densities and higher temperatures, *within the range of wave numbers where the* IK *model applies.*

The IK model is capable of yielding spectral functions $S_s^{(IK)}(\vec{k}, \omega)$ that display a wide variety of functional dependences. For example, if $1/2y^2 = n$, where n is integer, then (48) simplifies[19] to

$$s_s^{(IK)}(1/2m^{1/2}, u) = \{4^m u/[2(2m-1)!\sinh(\pi u)]\} \times \prod_{l=1}^{m-1}(u^2+l^2), \quad n=2m$$

$$s_s^{(IK)}(1/2(m+1/2)^{1/2}, u) = \{4^m/[(2m)!\cosh(\pi u)]\} \times \prod_{l=1}^{m}[u^2+(l-1/2)^2], \quad n=2m+1.$$

From these expressions it is evident that $s_s^{(IK)}$ exhibits rather strong variations in its ω dependence as k varies. This contrasts sharply with the cumulant and Zassenhaus results, neither of which conform to (u, y) scaling. From (26) and (30)–(32) we compute[4,19]

$$S_s^{(C)}(\vec{k}, \omega) = (1/2\pi\lambda_1)^{1/2}\{1 + [\mu_1/4!(4\lambda_1)]\, H_4(\omega/(2\lambda_1)^{1/2})\}\exp(-\omega^2/2\lambda_1)$$

and

$$S_s^{(Z)}(\vec{k}, \omega) = (1/2\pi\lambda_1)^{1/2}\{1 - [3\mu_1/(4!4\lambda_1)]\, H_4(\omega/(2\lambda_1)^{1/2})\}\exp(-\omega^2/2\lambda_1) + [1/2\pi(\mu_1+\lambda_1)]^{1/2}\{\mu_1\lambda_1/[4!(\mu_1+\lambda_1)^2]\}\, H_4(\omega/[2(\mu_1+\lambda_1)]^{1/2})\exp[-\omega^2/2(\mu_1+\lambda_1)],$$

where H_4 is the Hermite polynomial of the fourth degree.

To gain some insight into the origins of the wide variations in ω dependence of $S_s(\vec{k}, \omega)$ permitted by the IK model, face-to-face with the cumulant and Zassenhaus models, consider the velocity TACF's implied by the various models. That which corresponds to the IK model is given by (38). Then from (34), (35), (39), and (40) we compute

$$\varphi^{(C)}(t) = 1 - \mu_1 t^2/2 \tag{49}$$

and

$$\phi^{(Z)}(t) = 1 + [3\mu_1 - 4\mu_1\exp(-\mu_1 t^2/2)]t^2/2 + (3\mu_1^2 t^4/2 - \mu_1^3 t^6/6)\exp(-\mu_1 t^2/2). \tag{50}$$

Clearly, since both $\phi^{(C)}$ and $\phi^{(Z)}$ diverge quadratically at large t, the implied diffusion coefficients, given by (37), do not exist. It seems reasonable to attribute the differences in the ω dependence of S_s to these disparate temporal dependences of the velocity TACF [see (49) and (50)].

It is possible to employ the Zassenhaus formula in connection with the generalized Langevin equation (GLE) to obtain yet another model for which the implied diffusion coefficient does exist. The single-variable GLE for $F_s(\vec{k}, t)$ is[5,13]

$$\dot{F}_s(\vec{k}, t) = -\lambda_1\int_0^t dt' K_s(\vec{k}, t')F_s(\vec{k}, t-t'), \tag{51}$$

where the *normalized* memory function K_s satisfies the relation[4,15]

$$\lim_{k\to 0} K_s(\vec{k}, t) = \phi(t). \tag{52}$$

Now, $K_s(\vec{k}, t)$ itself is a TACF of the so-called "random force" with associated lowering coefficients given by[20]

$$\nu_i = \lambda_{i+1}.$$

The leading term of the Zassenhaus expansion of K_s is then

$$K_s^{(Z)}(\vec{k}, t) = \exp(-\nu_1 t^2/2) = \exp[-(\mu_1+2\lambda_1)t^2/2], \tag{53}$$

and from (52) we compute

$$\phi^{(ZM)}(t) = \exp(-\mu_1 t^2/2),$$

where the superscript ZM denotes the Zassenhaus formula applied to the memory function K_s. The diffusion coefficient implied by this model is computed [by means of (37)] to be

$$D_s^{(ZM)} = v_0^2(\pi/2\mu_1)^{1/2}. \tag{54}$$

Now using the Zassenhaus memory function (53) in (51), we can solve for $F_s^{(ZM)}$ in the large- and small-k limits. The method is detailed in the Appendix. We obtain

$$F_s^{(ZM)}(\vec{k}, t) \sim \begin{cases} \exp(-k^2 D_s^{(ZM)} t) & \text{large } t, \text{ small } k \quad (55a) \\ \exp[-k(\pi/4m\beta)^{1/2}t] & \text{large } t, \text{ large } k. \quad (55b) \end{cases}$$

It is interesting that although the ZM model yields a hydrodynamic (i.e., small k) limit, with $D_s^{(ZM)}$ replacing D_s, it fails to give the correct free-particle limit (see Appendix). This example illustrates that not every model for which the

implied diffusion coefficient exists leads to the broad range of qualitative agreement found for the IK model.

We close this section with a brief consideration of the limiting properties of $S_s^{(IK)}(\vec{k}, \omega)$. Recalling from the definition (45) of the collision parameter that the limit $k \to 0$ corresponds to $y \to \infty$, we have[19]

$$\Gamma(1/4y^2) \sim 4y^2,$$

$$\pi^{1/2}/\Gamma(1/2 + 1/4y^2) \sim 1,$$

$$16y^4u^2/(4ny^2+1)^2 \sim u^2/n^2, \quad n \neq 0, \quad k \sim 0.$$

Thus,

$$s_s^{(IK)}(y,u) \sim \pi^{-1}\left(\frac{4y^2}{1+16y^4u^2}\right)\prod_{n=1}^{\infty}\left(1+\frac{u^2}{n^2}\right)^{-1}$$

$$= \left(\frac{4y^2}{1+16y^4u^2}\right)\frac{u}{\sinh \pi u},$$

which becomes Lorentzian for sufficiently small u, i.e., for u such that

$$\omega \ll (2\mu_1)^{1/2}/\pi.$$

VI. COMPARISON OF INTERMEDIATE-k MODEL WITH COMPUTER EXPERIMENTS

We shall base our comparisons largely on the shape of the spectral function $S_s(\vec{k}, \omega)$, two measures of which have become essentially standard. One measure is the half-width at half-height W normalized to the hydrodynamic limit

$$\Delta(k) \equiv W(k)/k^2 D_s;$$

the other is the peak height at zero frequency normalized to that of the hydrodynamic limit

$$\Sigma(k) = \pi k^2 D_s S_s(\vec{k}, 0).$$

If the implied diffusion coefficient is D_I, then

$$\lim_{k\to 0} \Delta(k) = D_I/D_s,$$

$$\lim_{k\to \infty} \Sigma(k) = D_s/D_I.$$

Thus, a model for which $D_I = D_s$ yields the correct hydrodynamic limit. Although the small-k limit is of little relevance to our comparisons with experimental data, we note, for sake of completeness, that D_I is finite and positive for the IK model, $+\infty$ for the free-particle limit [since $\phi^{(G)}(t) = 1$], and for the Zassenhaus expansion, but $-\infty$ for the cumulant expansion.

Two sets of "data" on $S_s(\vec{k}, \omega)$ for computer "argon" are available.[15,16] The thermodynamic states and corresponding values of μ_1 and D_s are listed in Table II. Note that Chen and Rahman[16] place the critical point of computer argon at $\rho_c^* = 0.36$, $T_c^* = 1.36$, and the triple point at $\rho_t^* = 0.8422$, $T_t^* = 0.722$, although others[25] estimate that $T_t^* \approx 0.68$. Thus, states labeled I and III correspond to the triple point, II corresponds to a dense gas, and IV corresponds to a liquid of intermediate density.

TABLE II. Thermodynamic states of "computer" argon and corresponding normalized mean-square accelerations μ_1 and the self-diffusion constants. Units are those of Ref. 15.

State	ρ^*	T^*	μ_1	D_s
I[a]	0.8442	0.679	5.5[c]	0.0045
II[a]	0.2976	2.15	1.84[c]	0.1197
III[b]	0.8442	0.722	5.68	0.0048
IV[b]	0.65	1.827	5.15	0.031

[a] Data from Ref. 16.
[b] Data from Ref. 15.
[c] These values of μ_1 are extrapolated from data of Ref. 15.

Figures 1–3 display plots of $\Delta(k)$ vs k for these four thermodynamic states. The values of the $\Delta(k)$ for the IK model were calculated to a precision of about one percent by generating $S_s^{(IK)}(\vec{k}, \omega)$ from expression (24). Without exception, we find quantitative agreement between IK-model and computer results long before the free-particle limit is attained.

Of course, we expect the IK model to be valid only for sufficiently large values of k, or more

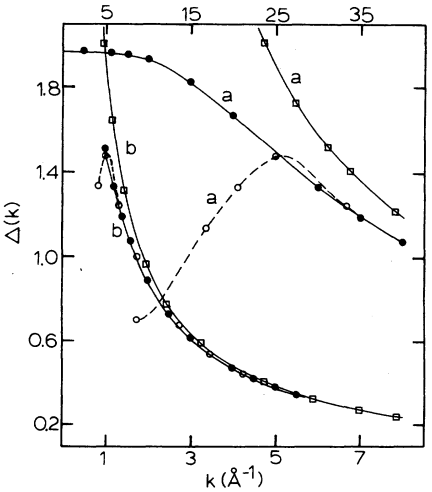

FIG. 1. $\Delta(k)$ vs k for the thermodynamic state I (see Table II). Curves labeled with a correspond to the abscissa at the bottom of the graph; those labeled with b correspond to the abscissa at the top of the graph. ○, simulated data; □, free-particle limit; ●, the intermediate-k model.

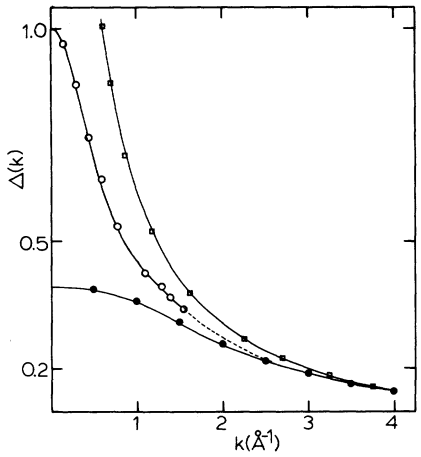

FIG. 2. $\Delta(k)$ vs k for thermodynamic state II. Curves labeled as in Fig. 1.

precisely, only for values of k so large that

$$\eta \equiv 2\lambda_1/\mu_1 = 2k^2/m\beta\mu_1 \gg 1 . \quad (56)$$

We now define k_{min} as the smallest value of k for which $\Delta^{(IK)}(k)$ agrees *quantitatively* with the simulated $\Delta(k)$, by which we mean here that the plots of Figs. 1–3 have merged. In Table III we list k_{min}, and the corresponding η_{min} calculated from (56) for the various thermodynamic states considered. One sees that η_{min} varies only slightly, from about 3 to 4. The corresponding range of the collision parameter y [see (45)] is from 0.34 to 0.43. Thus, in summary, the IK model yields a $\Delta(k)$ in essentially *quantitative* agreement with the simulated spectra for the collision parameter in the range $0 \leq y \leq 0.4$.

Similarly good agreement is observed for the cumulant expansion, although the Zassenhaus formula gives quite poor agreement. In fact, reasonable coincidence between the Zassenhaus and simulated results does not obtain until well after the free-particle limit is reached. Over the range of k values for which the intermediate-k and cumulant treatments are valid, both yield a $\Delta(k)$ in better agreement with the simulated $\Delta(k)$ at the triple point than does the linearized Enskog-Boltzmann approximation.[16] Away from the triple point all three approximations are in agreement with the simulation, over the appropriate range of k.

TABLE III. k_{min}, η_{min}, and y_{max} for which the "intermediate-k" model yields quantitative agreement with computer experiment. Thermodynamic states are given in Table I.

State	k_{min}(Å^{-1})	η_{min}	y_{max}
I	6.75	2.71	0.43
II	2.5	3.52	0.38
III	8.0	3.92	0.36
IV	5.0	4.28	0.34

Considering now $\Sigma(k)$, we find the intermediate-k results to be superior to those of the cumulant expansion in several respects. In Figs. 4 and 5 are plots of $\Sigma(k)$ vs k in various approximations for thermodynamic states III and IV. One sees that the IK model $\Sigma^{(IK)}$ converges to the simulated Σ well before the cumulant $\Sigma^{(C)}$. Indeed, it appears that $\Sigma^{(C)}$ converges to the free-particle $\Sigma^{(G)}$ before $\Sigma^{(G)}$ merges with Σ, whereas $\Sigma^{(IK)}$ seems to converge to Σ well ahead of $\Sigma^{(G)}$. Finally, we note that $\Sigma^{(IK)}$ converges to Σ at about the same value of k as $\Delta^{(IK)}$ merges with Δ.

In closing we compare the mean-square displacement predicted by the IK model [see (44)] with the simulated result. Figure 6 shows plots

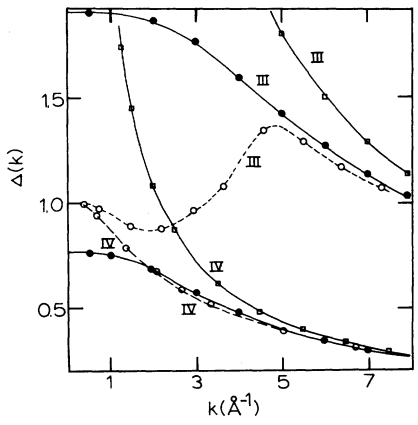

FIG. 3. $\Delta(k)$ vs k for thermodynamic states III and IV. ○, simulated data; □, free-particle limit; ●, the intermediate-k model.

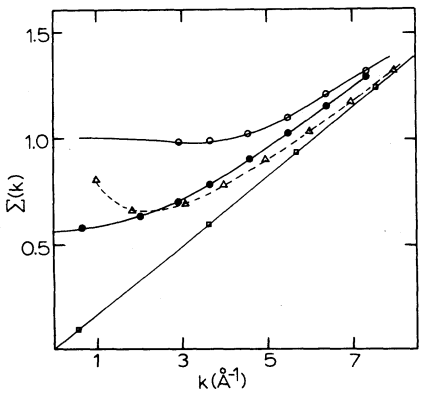

FIG. 4. $\Sigma(k)$ vs k for thermodynamic state III. ○, simulated data; □, free-particle limit; ●, intermediate-k model; △, cumulant expansion.

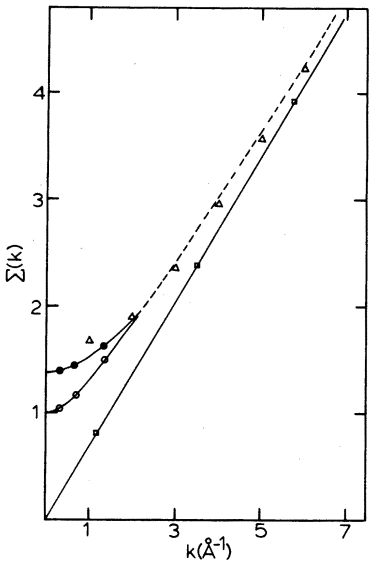

FIG. 5. $\Sigma(k)$ vs k for thermodynamic state IV. Curves are labeled as in Fig. 4. Dashed line corresponds to both open and filled circles in range when the intermediate-k and simulated curves coincide.

of $\langle r^2(t)\rangle/6Dt$ for the thermodynamic state II. Note that $D = D_s^*$ for the simulated result and $D = D_s^{(IK)*}$ for the IK model. (The star denotes the use of reduced units.) The disparity in slopes at small t stems from the difference in magnitude between D_s^* and $D_s^{(IK)*}$, whereas at larger t differences in the shapes of $\phi^{(IK)}(t)$ and the simulated ϕ also come into play. Larger qualitative differences in the two plots are expected near the triple point since $\phi^{(IK)}$ fails to mimic the negative minimum observed in the simulated ϕ at higher densities.

VII. SUMMARY AND CONCLUSIONS

In Sec. II we presented a general approach to the calculation of time-autocorrelation functions

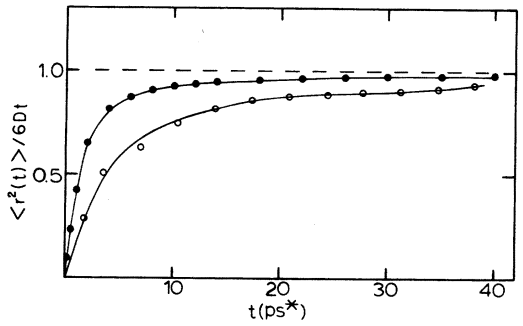

FIG. 6. $\langle r^2(t)\rangle/6Dt$ vs t (in units of Ref. 15) for thermodynamic state II. ○, computer simulation result ($D = D_s^* = 0.1197$); ●, intermediate-k model ($D = D_s^{(IK)*} = 0.03$).

(TACF's) based upon the concept of dynamical embedding (itself a specialization of the quotient-difference algorithm[17]). The significance of (11) lies in the fact that it provides an algorithm to construct, from appropriate knowledge of moments, the infinite continued-fraction representation of the Laplace transform of the TACF to which the moments correspond. Such a procedure lends itself to series summation, particularly when the series has a finite radius of convergence. In the latter case, the continued fraction represents the analytic continuation of the series into the region (of t) where the series fail to converge.[6]

In Sec. III we applied dynamical embedding to develop a model for the incoherent thermal inelastic neutron scattering function $F_s(\vec{k}, t)$ [and corresponding spectrum $S_s(\vec{k}, \omega)$] valid for large, finite wave numbers k. The analysis began with a calculation of the moments of $S_s(\vec{k}, \omega)$ to order k^{2n-2}. We then "cycled" the moments through the embedding relations, keeping terms through order k^0 at each stage. It should be noted that this procedure loses information contained in the original moments since terms of order k^{-2}, k^{-4}, etc., are neglected on each "cycle." We arrived finally at the lowering coefficients (20) which define the intermediate-k model. Since the form of these lowering coefficients coincides with an identity from the analytic theory of continued fractions, we were able to obtain an analytic expression (24) for $F_s(\vec{k}, t)$; i.e., we were able to invert the Laplace transform analytically.

In Secs. V and VI we found that the intermediate-k model gives broader and better agreement with certain previous theoretical models and with simulated data than does either the cumulant or the Zassenhaus expansion. We argue that this agreement is not fortuitous, as one might suspect, since less information appears to be used in the IK model than is contained in the cumulant expansion. From the definition (6), it is clear that the lowering coefficients are all strictly positive. Inasmuch as this positivity follows solely from the fact that the system obeys the classical equations of motion, we may regard it as a law of motion in the same sense as the conservation of total energy, or of total momentum, is a law of motion. To illustrate the deficiencies of the cumulant expansion, we consider a thermodynamic state (near $\rho^* = 0.85$, $T^* = 0.76$) for which $\mu_1 = 6$ and a value of $k \simeq 1.65$ Å^{-1}. Then $\lambda_1 = \frac{1}{2}$ and from (17) we have the moments of the cumulant expansion

$$a_n(\vec{k}) = (2n-1)!!\,[1/2 + n(n-1)]\,2^{1-n}.$$

Using the embedding relations (11) and retaining *all* terms, we find the corresponding lowering

coefficients: $\lambda_1 = \frac{1}{2}$, $\lambda_2 = 7$, and $\lambda_3 = -\frac{15}{14}$. We conclude therefore that the cumulant expansion somehow uses information about the moments in a manner that is not dynamically consistent, since it yields negative lowering coefficients, thereby disobeying the "semi-invariants" of motion $\lambda_j > 0$. The merit of the intermediate-k model is that its lowering coefficients are manifestly strictly positive [see (20)]. It would appear that whatever extra information is born by the approximate moments (17), and subsequently lost in the transition to lowering coefficients (20), is irrelevant, and indeed deleterious, to the dynamical description of self-correlations at large wave numbers.

Perhaps even more important than the good agreement between the IK-model and simulated results is the qualitatively correct description of test-particle dynamics even at small k. For example, the implied single-particle velocity TACF is given by

$$\phi^{(\mathrm{IK})}(t) = \mathrm{sech}^2(v_0^2 t / D_s^{(\mathrm{IK})}) .$$

Thus, one finds an Enskog-like[21] behavior at large t reconciled with evenness in t *via* the hyperbolic secant. Such forms have been previously suggested[9] for similar purposes, but the intermediate-k model provides a more or less rigorous basis for this form, at least in the present context. The hyperbolic secant has also been suggested[26-27] as an interpolative *ansatz* for Raman line shapes. Equally interesting is that the IK model obeys a different kind of scaling law for $S_s(\vec{k}, \omega)$ than that predicted by Boltzmann-Enskog kinetic theory. Away from the triple point both theories give the same results at large k and both are in good agreement with computer experiment. At liquid densities, and particularly near the triple point, Boltzmann-Enskog scaling is known to break down, most notably at large k. The intermediate-k scaling, on the other hand, is in quantitative accord with simulated data in this regime. Further, neither the cumulant nor the Zassenhaus models give the proper scaling law.

As noted in Sec. IV, the intermediate k, in contrast to other models, predicts wide variations in the functional dependence of $S_s(\vec{k}, \omega)$ upon ω. Unfortunately, no data over the appropriate range of wave numbers are available to permit an unambiguous test of the competing theories. Given the broad range of both qualitative and quantitative agreement of IK-model predictions with previous results, we believe this feature [i.e., wide variations in functional form of $S_s^{(\mathrm{IK})}(\vec{k}, \omega)$] merits serious consideration as a discriminant among the various theoretical models considered. For this reason, in addition to those delineated by Chen and Rahman,[16] we believe it is desirable to have neutron-scattering data for argon at its triple point at wave numbers in the range 8 to 15 Å^{-1}.

APPENDIX: DERIVATION OF RELATIONS (55)

Substituting (53) into (51) and replacing λ_1 by $k^2/m\beta$ [see (16)], we obtain

$$\dot{F}_s(\vec{k}, t) = -\frac{k^2}{m\beta}\int_0^t du\, F_s(\vec{k}, t-u) \exp\left[-\left(\mu_1 + \frac{2k^2}{m\beta}\right)\frac{u^2}{2}\right] . \tag{A1}$$

It is easily seen from (15) that the Maclaurin expansion coefficients of $F_s(\vec{k}, t)$ after the first are factored by k^2. It follows from (A1) that in the limit of small k, $F_s(\vec{k}, t)$ is slowly varying for $t \ll (m\beta/k^2)^{1/2}$. Observe that t can be made as large as one wishes simply by choosing k sufficiently small. Let us now expand $F_s(\vec{k}, t-u)$ in a Taylor series about t:

$$F_s(\vec{k}, t-u) = F_s(\vec{k}, t) - u\dot{F}_s(\vec{k}, t) + O(u^2) . \tag{A2}$$

The leading term of the Maclaurin expansion of $\dot{F}_s(\vec{k}, t)$ is $-k^2 t/m\beta$. Since $0 \leq u \leq t$, the second term of (A2) is negligible for sufficiently small k. Then (A1) becomes

$$\dot{F}_s(\vec{k}, t) = -\frac{k^2}{m\beta} F_s(\vec{k}, t)\int_0^t du \exp\left[-\left(\mu_1 + \frac{2k^2}{m\beta}\right)\frac{u^2}{2}\right] . \tag{A3}$$

Equation (55a) immediately follows since in the limit of small k the integral factor in (A3) is proportional to $D_s^{(\mathrm{ZM})}$ [see (54)] for t large enough. Note that this argument does not depend on the form of $K_s(\vec{k}, u)$. Thus the same argument can be employed rigorously to derive, from the generalized Langevin equation, the small-k solution in the form

$$F_s(\vec{k}, t) = \exp\left(-\frac{k^2}{m\beta}\int_0^t dv \int_0^v dw\, K_s(\vec{k}, w)\right),$$

from which the hydrodynamic limit (large t) is easily obtained.

To derive the large-k limiting form (55b), we employ the following representation of the Dirac delta function[28]:

$$\delta(u) = \lim_{\sigma\to\infty} (2\sigma/\pi)^{1/2} \exp(-\sigma u^2/2) \quad 0 \leq u \leq \infty .$$

Taking $\sigma = (\mu_1 + 2k^2/m\beta)$, we obtain from (A1)

$$\begin{aligned}\dot{F}_s(\vec{k}, t) &= -\left(\frac{k^2}{m\beta}\right)\left[\pi \Big/ \left(2\mu_1 + \frac{4k^2}{m\beta}\right)\right]^{1/2} \\ &\quad \times \int_0^t du\, F_s(\vec{k}, t-u)\delta(u) \\ &\approx -k(\pi/4m\beta)^{1/2} F_s(\vec{k}, t) ,\end{aligned} \tag{A4}$$

the last line following in the limit of large k and large t. Equation (55b) follows immediately upon integrating (A4).

Fourier transformation of (55b) suggests that the line shape function in the limit of large k takes the form

$$S_s^{(ZM)}(\vec{k},\omega)=\pi^{-1}k(\pi/4m\beta)^{1/2}/[\omega^2+(\pi k^2/4m\beta)],$$

and the associated (reduced) width and height are, respectively,

$$\Sigma^{(ZM)}(k)\approx(4m\beta/\pi)^{1/2}D_s k, \quad \text{large } k$$
$$\Delta^{(ZM)}(k)\approx(\pi/4m\beta)^{1/2}/D_s k, \quad \text{large } k. \tag{A5}$$

These results may be compared with the correct limits [see (28)]

$$\Sigma(k)\approx(\pi m\beta/2)^{1/2}D_s k, \quad \text{large } k$$
$$\Delta(k)\approx[2\ln(2)/m\beta]^{1/2}/D_s k, \quad \text{large } k.$$

Thus, although the proper limiting k dependence is displayed by the ZM model, the numerical prefactors in $\Sigma^{(ZM)}$ and $\Delta^{(ZM)}$ are too small by factors of 0.90 and 0.75, respectively. This failure of the Gaussian kernel in connection with the GLE has been noted in a slightly different context,[15] but still within the generalized Langevin equation formalism.

These derivations contain an element of irony. The delta-function kernel is usually invoked for the small-k limit[4] on the basis of a time-scale argument. We find this unnecessary. Instead, we exploit the fact that the moments vary as polynomials in k^2, which allows a rigorous small-time expansion in the small-k limit. An important result is the reconciliation of evenness in time with exponential decay asymptotically.

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