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A kinetic theory of classical simple liquids*†

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A dynamical equation for simple classical liquids is presented which is obtained by a systematic approximation for the memory function of the conventional, equilibrium-averaged, phase-space correlation function. This "kinetic" equation is non-Markovian and spatially nonlocal. It agrees with the known limiting behavior at high and low frequencies ω and wave vectors $\vec{k}$ even for dense liquids. For intermediate k and ω, our equation represents an explicit interpolation model from which virtually all measurable dynamical properties of the simple one-component fluid can be obtained. This equation can be solved analytically. As an example, the dynamical structure factor $S_{nn}(k,\omega)$ for liquid argon near its triple point was calculated. Our results are in excellent agreement with both coherent-neutron-scattering experiments (for $k = 1$–4 Å^{-1}) and computer-dynamics results (for $k < 1$ Å^{-1}). We want to emphasize that no adjustable parameters are introduced. We believe that this is the first kinetic theory which gives satisfactory results for $S_{nn}(k,\omega)$ for the full range k,ω for which data are available.

I. INTRODUCTION

The foremost goal of any microscopic theory of dynamical processes in simple fluids is to calculate the fluctuations of the particle density, summarized in the wave-vector- ($\vec{k}$) and frequency-(ω) dependent structure factor $S_{nn}(k,\omega)$. This quantity is important because almost all conventional probes excite density fluctuations. Thus, for example, $S_{nn}(k,\omega)$ for small k and ω can be measured by light scattering, while for larger values of k and ω it can be obtained by coherent neutron scattering, or derived from computer-dynamics "experiments." Because most quantities of interest are proportional to the number of particles that contribute to them, a calculation of $S_{nn}(k,\omega)$, for any system, is of fundamental importance. In this paper, we report on such a calculation for a dense classical liquid, namely, liquid argon near its triple point.

The theoretical analysis of $S_{nn}(k,\omega)$ naturally separates into three regions: When k and ω are so small that $kl \ll 1$ and $\omega\tau \ll 1$, where l is a mean free path and τ a collision time, $S_{nn}(k,\omega)$ is easily obtained from linearized hydrodynamics.[1] For very large frequencies, $\omega\tau \gg 1$, $S_{nn}(k,\omega)$ describes the instantaneous response of the liquid,[2] and can be calculated from the static average structure of the liquid, which is accurately known. Our calculation here concerns the difficult intermediate region which in gases could be described by Boltzmann's equation.[3,4] In liquid argon, the region in question comprises wavelengths between, say, 0.1 and 10 Å and frequencies between 10^{11} and 10^{13} sec^{-1}. For this region, there is no good microscopic theory. Yet, the wave vectors and frequencies probed in neutron scattering and obtained from computer dynamics fall into this region.

The primary quantity which the present theory is aimed to calculate is the equilibrium-averaged one-particle phase-space correlation function[5,6] ($\mathrm{Im}\, z > 0$)

$$S(\vec{k}z;\vec{\xi}\vec{\xi}\,') = i\int_0^\infty d(t-t') \times \int d(\vec{r}-\vec{r}\,')e^{iz(t-t')-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}[\ ],$$

$$[\ ] = (mv_0)^6\langle[f(\vec{r}\vec{p}t) - \langle f(\vec{r}\vec{p}t)\rangle_{\mathrm{eq}}] \times [f(\vec{r}\,'\vec{p}\,'t') - \langle f(\vec{r}\,'\vec{p}\,'t')\rangle_{\mathrm{eq}}]\rangle_{\mathrm{eq}}, \quad (1.1)$$

where the one-particle density is given by

$$f(\vec{r}\vec{p}t) = \sum_\alpha \delta(\vec{r}-\vec{r}^{\,\alpha}(t))\delta(\vec{p}-\vec{p}^{\,\alpha}(t)). \quad (1.2)$$

$\vec{r}^{\,\alpha}(t)$ and $\vec{p}^{\,\alpha}(t)$ are the position and momentum of the αth particle at time t, and dimensionless momentum variables are defined by

$$\vec{\xi} = \vec{p}/mv_0, \quad v_0^2 = (m\beta)^{-1}, \quad (1.3)$$

where m is the mass of the particle, and $\beta^{-1} = k_B T$. The system which we investigate is specified by the Hamiltonian

$$H = \sum_\alpha \frac{p^{\alpha 2}}{2m} + \tfrac{1}{2}\sum_{\alpha\neq\beta} \mathcal{V}(|\vec{r}^{\,\alpha} - \vec{r}^{\,\beta}|), \quad (1.4)$$

where $\mathcal{V}(r)$ is the pair potential.

$S(\vec{k}z;\vec{\xi}\vec{\xi}\,')$ summarizes a host of measurable correlation functions. The dynamical liquid structure factor is extracted from it as

$$S_{nn}(k,\omega) = 2\,\mathrm{Im}\int d\vec{\xi}\int d\vec{\xi}\,' S(\vec{k}z;\vec{\xi}\vec{\xi}\,')|_{z=\omega+i0}, \quad (1.5)$$

and other quantities of interest are similarly obtained.

More in particular, our theory is based on an explicit approximation for the memory function associated with $S(\vec{k}z;\vec{\xi}\vec{\xi}')$, namely, the matrix $\Sigma(\vec{k}z)$, which is defined to fulfill the "kinetic" equation[7]

$$(z-v_0\vec{k}\cdot\vec{\xi})S(\vec{k}z;\vec{\xi}\vec{\xi}')-\Sigma(\vec{k}z;\vec{\xi}\vec{\bar{\xi}})S(\vec{k}z;\vec{\bar{\xi}}\vec{\xi}')=-S^0(\vec{k};\vec{\xi}\vec{\xi}'),\quad(1.6)$$

where S^0 is known in terms of the static pair-correlation function. In this equation, and throughout this paper, an integration $\int d^3\bar{\xi}$ over the barred variable is understood.

Many authors have discussed Eq. (1.6), or equivalent representations. Mazenko,[8] and Boley and Desai[9] have shown that for low particle density (1.6) is the linearized Boltzmann equation as one would expect, and they have considered corrections to this equation. Forster and Martin[6] have calculated $\Sigma(\vec{k}z)$ for a system of weakly interacting particles. A formal microscopic representation for $\Sigma(\vec{k}z)$ has been given by Akcasu and Duderstadt.[5] More recently, Mazenko[10] has discussed the self-consistent structure of $\Sigma(\vec{k}z)$. His techniques elucidate the processes which enter $\Sigma(\vec{k}z)$ although they have not, as yet, led to practical approximations applicable to dense liquids.

The approximation made in this paper is based on a suggestion made recently by Forster[7] (F): While little can be rigorously said about the functional dependence of $\Sigma(\vec{k}z)$ in the intermediate region of wave vector and frequency, we have certain knowledge about its asymptotic behavior for large z, where sum rules are available, and in the hydrodynamic region. Properties of $\Sigma(\vec{k}z)$, pertaining to either region, have been collected in F. In a gas, these two regions are separated by a wide gap in k and ω, and the asymptotic properties are not overly helpful. In liquid argon, however, hydrodynamics is a good theory even down to wavelengths as short as about 10 times the first-neighbor distance. The suggestion is therefore to construct an interpolation model for $\Sigma(\vec{k}z;\vec{\xi}\vec{\xi}')$ which is in accord with the known asymptotic properties. Since simple liquids display far less dynamical structure than do, for example and obviously, crystalline solids, the hope seems justified that quantities like $S_{nn}(k,\omega)$ are not overly sensitive to many details of such a model. Our results seem to bear out this expectation.

The explicit expression for $\Sigma(\vec{k}z)$ which we have analyzed is of the following form: It is generally true that $\Sigma(\vec{k}z)$ separates into two pieces,

$$\Sigma(\vec{k}z;\vec{\xi}\vec{\xi}')=\Sigma^{(s)}(\vec{k};\vec{\xi})+\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}'),\qquad(1.7)$$

where the first part summarizes the short-time response which is driven by an effective mean field, and is given by

$$\Sigma^{(s)}(\vec{k};\vec{\xi})=-nc(k)v_0(\vec{k}\cdot\vec{\xi})\phi(\xi),\qquad(1.8)$$

where $c(k)$ is the direct correlation function, n is the particle density, and

$$\phi(\xi)=(2\pi)^{-3/2}e^{-\xi^2/2}.\qquad(1.9)$$

$\Sigma^{(s)}$ determines[7] the initial value S^0, which appears in Eq. (1.6), to be of the form

$$(1/n)S^0(\vec{k};\vec{\xi}\vec{\xi}')=\phi(\xi)\delta(\vec{\xi}-\vec{\xi}')+\phi(\xi)nh(k)\phi(\xi'),\qquad(1.10)$$

where

$$h(k)=c(k)[1-nc(k)]^{-1}\qquad(1.11)$$

is the Fourier transform of $h(r)=g(r)-1$, and $g(r)$ is the pair-correlation function. It is the collision term $\Sigma^{(c)}$ which we have approximated, by an expression of the structure $(\vec{\partial}\equiv\partial/\partial\vec{\xi})$

$$\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')\phi(\xi')=A^{(0)}(\vec{\partial}\cdot\vec{\partial}')\phi(\xi)\delta(\vec{\xi}-\vec{\xi}')+\{A_{ij}^{(1)}\xi_i\xi_j'+A_{ijkl}^{(2)}(\xi_i\xi_j-\delta_{ij})(\xi_k'\xi_l'-\delta_{kl})$$
$$+A_{ij}^{(3)}[(\vec{k}\cdot\vec{\xi})(\xi_i'\xi_j'-\delta_{ij})+(\vec{\xi}\leftrightarrow\vec{\xi}')]\}\phi(\xi)\phi(\xi').\qquad(1.12)$$

This expression is here meant only to elucidate the momentum dependence of our approximate collision kernel. The first term in (1.12) describes the forward scattering of individual particles. This term is familiar from the theory of Brownian motion[11] and the Fokker-Planck equation.[12,13] The other terms in (1.12) are backflow terms which are required by momentum and energy conservation. Because the eigenfunctions of the Fokker-Planck term are known (namely, the Hermite polynomial tensors, the first few of which occur also in the backflow terms), Eq. (1.12) allows an explicit analytic solution of the integral equation (1.6). Obviously, this is a highly welcome feature of this theory since it enables us to scrutinize the impact which various approximation steps might have on the final results.

We do not want to give the impression that the approximation (1.12) is simply an *ad hoc* ansatz. Rather, we have derived it from the microscopic theory in a systematic fashion. Therefore, the coefficients $A^{(\nu)}(\vec{k},z)$ in (1.12) are all explicit functions of $\vec{k}$ and z which can be calculated from the static structure of the liquid. We will explain the ideas on which the derivation is based in Sec. II, delegating much of the necessary but not very informative algebraic detail to Appendix A. In Sec. III, we will exhibit the approximate $\Sigma^{(c)}$ in a form which makes the coefficients $A^{(\nu)}(\vec{k},z)$ explicit, and we will explain the microscopic parameters which enter this theory. In Sec. IV, we will show that $\Sigma^{(c)}$ satisfies all the asymptotic properties of the kinetic memory function which have been discussed in F.

The solution of our kinetic equation (1.6) is given in Sec. V, with some detail deferred to Appendix B. In Sec. VI we will discuss numerical results for liquid argon which we have obtained, and compare these with experimental data. A summary and discussion concludes the paper.

II. DERIVATION OF THE APPROXIMATE MEMORY KERNEL

The separation (1.7) of the memory function $\Sigma(\vec{k}z)$ is one that is natural if one considers very high frequencies z or, equivalently, the short-time response. Namely, the mean-field term $\Sigma^{(s)}(\vec{k})$ is the limit of $\Sigma(\vec{k}z)$ as $z\to\infty$. Since the collision kernel $\Sigma^{(c)}(\vec{k}z)$, therefore, vanishes in this limit,[14] an expansion in powers of $1/z$ will result in high-frequency sum rules of which the first,

$$\Sigma_\infty^{(c)}(\vec{k};\vec{\xi}\vec{\xi}')=\lim_{z\to\infty} z\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}'), \tag{2.1}$$

has been given by several authors.[6,7,15,16] $\Sigma_\infty^{(c)}(\vec{k})$, which is also given in Eq. (3.1a) below, is of a very simple structure, and can be explicitly computed from the pair-correlation function and the pair potential.

It is therefore suggestive to approximate $\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')$ by

$$\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')=\Sigma_\infty^{(c)}(\vec{k};\vec{\xi}\vec{\xi}')f(k,z), \tag{2.2}$$

where the numerical function $f(k,z)$ must equal $1/z$ at large z. Such an approximation is guaranteed to give valid results at high frequencies, and if one uses

$$f(k,z)=1/[z+i\tau^{-1}(k)], \tag{2.3}$$

one has an explicit and soluble theory which lumps many unresolved microscopic processes into one k-dependent relaxation time $\tau(k)$. Sum-rule-inspired approximations of this sort have become a standard tool in the analysis of time correlation functions.[17,18] In the present context, Eq. (2.2) has been considered by Lebowitz, Percus, and Sykes,[16] and applied to argon by Duderstadt and Akcasu.[15] The numerical results are quite good for large k and ω but fail when k becomes smaller than about 1 Å^{-1}.

The reason is obvious. Equation (2.2) is in accord with the requirements of mass and momentum conservation but it does not conserve energy. As a consequence it will not, for small k and ω, give the correct hydrodynamic behavior. Since, as k decreases, the dynamics is strongly channeled into the hydrodynamic modes, Eq. (2.2) fails in this region. It is safe to predict that for liquid rubidium, which Copley and Rowe[19] and Rahman[20] have recently investigated experimentally, Eq. (2.2) would do even worse.

A side remark may be helpful. Effectively, Eqs. (2.2) and (2.3) lump into one relaxation time all of those processes which are not explicitly carried by the one-particle property $f(\vec{r}\vec{p}t)$. This is likely to be successful if all of these processes do in fact decay on a similar microscopic time scale. If they do not, it will fail. An example of a much simpler sort concerns the one-particle velocity autocorrelation function in a liquid, $\langle v(t)v(0)\rangle$. The approximation, which for this function corresponds to Eqs. (2.2) and (2.3), would predict simple exponential decay. In fact, in all except hard-sphere liquids, $\langle v(t)v(0)\rangle$ has a damped oscillatory behavior.[17] The reason is that hydrodynamic backflow, imposed by momentum conservation in this case, fluctuates on a much slower time scale than do almost all other microscopic processes.

If the side remark has been helpful, the remedy is obvious. Since, at least for small k, there is a slow mode (which becomes heat conduction as $k\to 0$) required by energy conservation, this mode has to be separately accounted for. There are several ways of doing that. The simplest by far appears to be to expand our set of explicitly considered dynamical variables by one, namely, the total energy density

$$\epsilon(\vec{r}t)=\int d\vec{p}\,\frac{p^2}{2m}f(\vec{r}\vec{p}t) + \tfrac{1}{2}\sum_{\alpha\neq\beta}\upsilon(|\vec{r}^{\,\alpha}-\vec{r}^{\,\beta}|)\delta(\vec{r}-\vec{r}^{\,\alpha}), \tag{2.4}$$

whose potential part is important in a liquid, but is not a moment of the one-particle density $f(\vec{r}\vec{p}t)$.

Instead of the "$\infty\times\infty$" matrix $S(\vec{k}z;\vec{\xi}\vec{\xi}')$ (with matrix indices $\vec{\xi}$ and $\vec{\xi}'$), we thus consider the "$(\infty+1)\times(\infty+1)$" matrix

$$\begin{pmatrix} G_{ff}(\vec{k}z;\vec{\xi}\vec{\xi}') & G_{f\epsilon}(\vec{k}z;\vec{\xi}) \\ G_{\epsilon f}(\vec{k}z;\vec{\xi}') & G_{\epsilon\epsilon}(\vec{k}z) \end{pmatrix} \equiv G_{\mu\nu}(\vec{k}z) \tag{2.5}$$

of correlation functions of the dynamical variables

$$\{A_\mu(\vec{r},t)\}\equiv\{f(\vec{r}\vec{\xi}t),\epsilon(\vec{r},t)\}. \tag{2.6}$$

μ serves as a counting index, comprising the matrix indices $\vec{\xi}$ and ϵ. The correlation functions are defined as in (1.1), by

$$G_{\mu\nu}(\vec{k}z) = i\int_0^\infty dt\, e^{izt} G_{\mu\nu}(\vec{k},t), \tag{2.7a}$$

$$G_{\mu\nu}(\vec{k},t) = \int d(\vec{r}-\vec{r}')e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')} \times \langle \delta A_\mu(\vec{r},t)\delta A_\nu(\vec{r}',0)\rangle_{\text{eq}}, \tag{2.7b}$$

where

$$\delta A_\mu(\vec{r},t) = A_\mu(\vec{r},t) - \langle A_\mu(\vec{r},t)\rangle \ .$$

While for the one-particle correlation function $S \equiv G_{ff}$ energy conservation is not easily expressed, it is a simple matter for the matrix $G_{\mu\nu}$ since it essentially reduces to the equations

$$\partial_t G_{\epsilon f}(\vec{k}t;\vec{\xi}') = 0, \quad \partial_t G_{\epsilon\epsilon}(\vec{k},t) = 0 \quad \text{as } k \to 0, \tag{2.8}$$

which standard approximations will not violate.

A memory-function representation for $G_{\mu\nu}(\vec{k}z)$, formally similar to Eq. (1.6), is

$$[z\delta_{\mu\lambda} - \hat{\Omega}_{\mu\lambda}(\vec{k}) - \hat{\Sigma}_{\mu\lambda}(\vec{k}z)]\, G_{\lambda\nu}(\vec{k}z) = -G^0_{\mu\nu}(\vec{k}), \tag{2.9}$$

where the caret is used to differentiate the "matrix" memory function $\hat{\Sigma}$ and frequency term $\hat{\Omega}$ from the corresponding quantities in Eq. (1.6). Note that $\hat{\Sigma}_{ff}$ is not equal to Σ or to $\Sigma^{(c)}$. $G^0_{\mu\nu}$ is the matrix of equal-time correlation functions,

$$G^0_{\mu\nu}(\vec{k}) = G_{\mu\nu}(\vec{k}; t=0), \tag{2.10}$$

and $\hat{\Omega}_{\mu\nu}$ is obtained as

$$\hat{\Omega}_{\mu\nu}(\vec{k}) = i\mathring{G}_{\mu\lambda}(\vec{k}; t=0)G^{0\,-1}_{\lambda\nu}(\vec{k}). \tag{2.11}$$

Both matrices can be obtained explicitly as to their $\vec{\xi}$ dependence, and they involve a few $\vec{k}$-dependent equilibrium correlation functions; see Appendix A.

$\hat{\Sigma}_{\mu\nu}(\vec{k}z)$ vanishes as $z \to \infty$. Asymptotically, it is given by the sum rule

$$\hat{\Sigma}_{\mu\nu}(\vec{k}z) = (1/z)\,\hat{\Sigma}^\infty_{\mu\nu}(\vec{k}) + O(1/z^2), \tag{2.12}$$

$$\hat{\Sigma}^\infty_{\mu\nu}(\vec{k}) = -[\ddot{G}(\vec{k}; t=0)G^{0\,-1}(\vec{k}) + \hat{\Omega}^2(\vec{k})]_{\mu\nu}, \tag{2.13}$$

which can be calculated explicitly as to its $\vec{\xi}$ dependence, and in terms of static correlation functions as to its numerical value. If we now approximate $\hat{\Sigma}_{\mu\nu}(\vec{k}z)$ by

$$\hat{\Sigma}_{\mu\nu}(\vec{k}z) = \hat{\Sigma}^\infty_{\mu\nu}(\vec{k})\sigma(k,z), \tag{2.14}$$

we have in Eqs. (2.9)–(2.14) an explicit approximation which can be solved, in principle and in practice, for $G_{ff}(\vec{k}z;\vec{\xi}\vec{\xi}') = S(\vec{k}z;\vec{\xi}\vec{\xi}')$. This is the approximation on which this paper is based. For the relaxation function $\sigma(k,z)$ we have used a simple exponential-decay model,

$$\sigma(k,z) = 1/[z + i\tau^{-1}(k)] \quad (\operatorname{Im} z > 0), \tag{2.15}$$

so that the sum rule (2.12) is fulfilled. We will describe below how the relaxation time $\tau(k)$ is determined.

As described here, our approximation appears as a straightforward generalization of the Duderstadt-Akcasu ansatz (2.2). However, because we have included the energy fluctuations explicitly, the major shortcomings of that ansatz are remedied. The penalty we pay is that our approximation involves additional coefficients. Again, we will show below how these are determined.

Since kinetic theory has been previously discussed within the context of the Eq. (1.6), it is convenient to cast Eq. (2.9) in the standard form (1.6) once an approximation for $\hat{\Sigma}$ is found. This procedure will allow us to draw on previous work.[7] Given $\hat{\Sigma}_{\mu\nu}$, it is a trivial if laborious matter to extract the corresponding $\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')$ from Eq. (2.9), so long as $G^0_{\mu\nu}$ is sufficiently simple that its matrix inverse can be obtained. This is the case. Delegating the awful details to the Appendix A, the approximate kernel $\Sigma^{(c)}$ which emerges is given in Sec. III.

III. THE EXPLICIT FORM OF $\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')$

The considerations described in Sec. II result in the following approximation for the kinetic memory function:

$$\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}') = \sigma(k,z)\Sigma^{(c)}_\infty(\vec{k};\vec{\xi}\vec{\xi}') + \Sigma^{(c)}_\epsilon(\vec{k}z;\vec{\xi}\vec{\xi}'), \tag{3.1}$$

where the first term is the one utilized by Duderstadt and Akcasu,[15] namely,

$$\begin{aligned}\Sigma^{(c)}_\infty(\vec{k};\vec{\xi}\vec{\xi}')\phi(\xi') = {}& -\tfrac{1}{3}\nu^2_{ii}(0)\vec{\partial}\cdot(\vec{\partial}+\vec{\xi})\phi(\xi)\delta(\vec{\xi}-\vec{\xi}') \\ & - [\nu^2_{ij}(\vec{k}) - mv_0^2 k_i k_j c(k)] \\ & \times \xi_i\xi_j'\phi(\xi)\phi(\xi'),\end{aligned} \tag{3.1a}$$

with coefficients which are explained below. The second term in (3.1) accounts for the influence of energy-density fluctuations, and can be written in the form

$$\begin{aligned}\Sigma^{(c)}_\epsilon(\vec{k}z;\vec{\xi}\vec{\xi}')\phi(\xi') &= (\beta/n)[\tilde{\chi}^2_{T\epsilon}(k)/\tilde{\chi}_{\epsilon\epsilon}(k)] \\ &\quad \times[-\sigma(k,z)v_0^2(\vec{k}\cdot\vec{\xi})(\vec{k}\cdot\vec{\xi}') \\ &\quad + \hat{\sigma}(k,z)\hat{g}(\vec{k}z;\vec{\xi})\hat{g}(\vec{k}z;\vec{\xi}')]\phi(\xi)\phi(\xi'),\end{aligned} \tag{3.1b}$$

where we have used the abbreviation

$$\hat{g}(\vec{k}z;\vec{\xi}) = v_0(\vec{k}\cdot\vec{\xi}) - \tfrac{1}{2}\sigma(k,z)[\beta\tilde{\chi}_{T\epsilon}(k)/n]^{-1} \times\hat{\nu}_{ij}(\vec{k})(\xi_i\xi_j - \delta_{ij}). \tag{3.1c}$$

The relaxation function $\sigma(k,z)$ which we have used is given by (2.15). It determines the function

$\hat{\sigma}(k,z)$ as

$$\hat{\sigma}(k,z)=[z-\omega_\epsilon^2(k)\sigma(k,z)]^{-1}. \tag{3.2}$$

Equation (3.1) is obviously of the form heralded in Eq. (1.12). We will now explain the various k-dependent coefficients.

A. Susceptibilities

For any two densities $A(\vec{r}), B(\vec{r})$, the susceptibility $\chi_{AB}(\vec{k})$ is defined by[21]

$$\chi_{AB}(\vec{k})=\beta\int d(\vec{r}-\vec{r}\,')e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \times[\langle A(\vec{r})B(\vec{r}\,')\rangle-\langle A(\vec{r})\rangle\langle B(\vec{r}\,')\rangle]. \tag{3.3}$$

Then Eq. (3.1) involves the k-dependent combinations

$$\tilde{\chi}_{\epsilon\epsilon}\equiv\chi_{\epsilon\epsilon}-\chi_{\epsilon n}\chi_{nn}^{-1}\chi_{n\epsilon}-\tfrac{3}{2}nk_BT, \tag{3.4}$$

$$\tilde{\chi}_{\tau\epsilon}\equiv\chi_{\tau\epsilon}-\chi_{\tau n}\chi_{nn}^{-1}\chi_{n\epsilon}-nk_BT, \tag{3.5}$$

which can be understood as the (many-particle-) correlated contributions to the respective susceptibilities. The density-density susceptibility is of course related to the static structure factor $S_{nn}(k)$ or to the direct correlation function $c(k)$ by

$$\beta^{-1}\chi_{nn}(k)=nS_{nn}(k)=n[1-nc(k)]^{-1}. \tag{3.6}$$

$\tau(r)$ is the longitudinal stress density,

$$\chi_{\tau A}(k)\equiv(k_ik_j/k^2)\chi_{\tau_{ij}A}(\vec{k}). \tag{3.7}$$

χ_{nn}, $\chi_{\tau n}$, and $\chi_{\tau\epsilon}$ can be calculated from the pair-correlation function $g(r)$. In fact,

$$\chi_{\tau n}(k)=n, \tag{3.8}$$

which is simply the longitudinal f-sum rule, while

$$\chi_{\tau\epsilon}(k)=\tfrac{5}{2}nk_BT+\tfrac{1}{2}n^2\int d\vec{r}\,g(r)\left(1-\frac{\sin(\vec{k}\circ\vec{r})}{k^2}(\vec{k}\cdot\nabla)\right) \times\mathcal{V}(r), \tag{3.9}$$

so that, as $k\to0$,

$$\lim_{k\to0}\chi_{\tau\epsilon}(k)=\epsilon^0+p, \tag{3.10}$$

which expresses Galilei invariance. ϵ^0 and p are the equilibrium energy density and pressure.

$\chi_{\epsilon\epsilon}(k)$ involves the static triple and quadruple correlation functions, and since these are not available, it will have to be approximated. Note, however, that

$$\lim_{k\to0}\tilde{\chi}_{\epsilon\epsilon}(k)=nT(mc_V-\tfrac{3}{2}k_B) \tag{3.11}$$

and also that

$$\lim_{k\to0}\tilde{\chi}_{\tau\epsilon}(k)=T\left[\left(\frac{dp}{dT}\right)_n-nk_B\right]. \tag{3.12}$$

B. Sum rules

Three more quantities are involved in Eq. (3.1) which originate in high-frequency sum rules. These are given by

$$\nu_{ij}^2(\vec{k})=(n/m)\int d\vec{r}\,g(r)\cos(\vec{k}\cdot\vec{r})\nabla_i\nabla_j\mathcal{V}(r), \tag{3.13}$$

$$k^2\alpha(k)=(n/k_BT)\int d\vec{r}\,g(r)\sin(\vec{k}\circ\vec{r})(\vec{k}\cdot\vec{\nabla})\mathcal{V}(r), \tag{3.14}$$

$$\gamma_\epsilon(k)=[nv_0^2k^2(k_BT)^2]^{-1} \times\int d\vec{r}\cos(\vec{k}\cdot\vec{r})\langle\dot{\epsilon}(\vec{r})\dot{\epsilon}(0)\rangle -(nk_BT)^{-2}\chi_{\tau\epsilon}^2(k)-\tfrac{5}{2}. \tag{3.15}$$

The last two terms in (3.15) eliminate those contributions to the energy-current correlation function which could be obtained from $g(r)$. An explicit expression for $\gamma_\epsilon(k)$ can be obtained which involves the static triple-correlation function $g_3(\vec{r},\vec{r}\,')$. We have decided not to utilize the sparse information on g_3 which one has, but instead to approximate $\gamma_\epsilon(k)$ in a different manner, described below. The sum rules occur in Eqs. (3.1c) and (3.2) in the combinations

$$\hat{\nu}_{ij}^2(\vec{k})\equiv\nu_{ij}^2(\vec{k})+\nu_{ij}^2(0)-v_0^2k_ik_j\alpha(k), \tag{3.16}$$

$$\omega_\epsilon^2(k)\equiv[n/\beta\tilde{\chi}_{\epsilon\epsilon}(k)]\,[\nu_{ii}^2(k)-v_0^2k^2\alpha(k)+v_0^2k^2\gamma_\epsilon(k)]. \tag{3.17}$$

This completes our exposition of the approximate kinetic memory function. Except for the quantities $\chi_{\epsilon\epsilon}(k)$, $\chi_{n\epsilon}(k)$, $\gamma_\epsilon(k)$, and of course $\tau(k)$ all coefficients are known in terms of the pair-correlation function $g(r)$ and pair potential $\mathcal{V}(r)$. At $k=0$, $\chi_{\epsilon\epsilon}$ and $\chi_{n\epsilon}$ can be obtained from the thermodynamics, via Eqs. (3.11) and (3.12), while γ_ϵ and τ can be related to the heat conductivity and the viscosity; see Eqs. (4.7) and (4.8) below. For their k dependence, we will suggest approximations in Sec. VI.

IV. PROPERTIES OF $\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}\,')$

In F, a number of general properties of $\Sigma^{(c)}(\vec{k}z)$ have been collected, statements which can be proved microscopically and rigorously. We will now show that the approximation (3.1) satisfies these properties, and that it is therefore guaranteed to give an asymptotically correct description of the dynamics.

A. General properties

It is apparent that our $\Sigma^{(c)}(\vec{k}z;\, \overrightarrow{\xi\xi}')$ has all the symmetries which follow from the invariance of a liquid under translations, rotations, parity, and time reversal. These also include detailed balance. Of course, the relaxation ansatz (2.15) for $\sigma(k,z)$ builds in irreversibility. To maintain time-reversal invariance we would define $-\sigma(k,-z) = \sigma(k,z)$. From the construction of our approximation in Sec. II, it is also clear that the stability requirement that $-\mathrm{Im}\Sigma^{(c)}(\vec{k}z)$ be a positive matrix for $\mathrm{Im} z > 0$ is satisfied, so long as $\tau(k) > 0$ and the coefficients of Eq. (3.1) have their usual thermodynamic positivity properties. Finally, the first high-frequency sum rule, namely Eq. (2.1) above, is of course satisfied.

Note, however, that the next sum rule on $\Sigma^{(c)}$, namely Eq. (F2.10), cannot be fulfilled by our approximation. Indeed, because of the relaxation ansatz (2.15) for $\sigma(\vec{k},z)$, the integral $\int d\omega\, \omega\, \mathrm{Im}\Sigma^{(c)}(\vec{k},\omega)$ diverges. It would be desirable in one sense to modify $\Sigma^{(c)}$ so that this sum rule is finite as well since it would open the way for the utilization of additional microscopic information. While it is not difficult to find such a modification we have decided not to pursue this goal in this work. Namely, from the structure of the second sum rule (F2.10) it is apparent that a theory which incorporates it will not likely be analytically soluble. We enjoy this feature of Eq. (3.1) but point out that in the computer age its value has limits.

B. Conservation laws

From the construction of our approximation as described in Sec. II, it is apparent that it must satisfy the conservation laws. Indeed, the local and Markovian collision operator

$$K(\vec{\xi},\vec{\xi}') = \lim_{z\to i0}\lim_{k\to 0} i\Sigma^{(c)}(\vec{k}z;\, \overrightarrow{\xi\xi}') \tag{4.1}$$

has the simple and interesting form

$$K(\vec{\xi},\vec{\xi}')\phi(\xi) = -\nu^2\tau\{\vec{\partial}\cdot(\vec{\partial}+\vec{\xi})\phi(\xi)\delta(\vec{\xi}-\vec{\xi}') + \phi(\xi)[\vec{\xi}\circ\vec{\xi}' + \tfrac{1}{3}(\xi^2-3)(\xi'^2-3)]\phi(\xi')\}, \tag{4.2}$$

where

$$\nu^2 = (n/3m)\int d\vec{r}\, g(r)\nabla^2 v(r) \tag{4.3}$$

is the square of the Kirkwood[22] friction constant, and $\tau \equiv \tau(k=0)$. Equation (4.2) is the Fokker-Planck collision operator studied by Yip and Ranganathan,[12] who obtained it by linearizing a conserving, stochastic collision model, and applied it to fluctuations in gases. The present microscopic derivation of Eq. (4.2) is new. It is interesting to note that our derivation makes no reference to low density. However, only in a gas would it be a good approximation to replace $i\Sigma^{(c)}(\vec{k}z;\, \overrightarrow{\xi\xi}')$ by its local and Markovian limit $K(\vec{\xi},\vec{\xi}')$.

Even in a liquid, however, the equations

$$\int d\vec{\xi}\,\{1,\vec{\xi},\xi^2\}K(\vec{\xi},\vec{\xi}') = 0, \tag{4.4}$$

which are satisfied by the kernel (4.2), do in fact express conservation of mass, momentum, and energy as has been pointed out in F. Apart from the five vanishing eigenvalues which correspond to the conservation laws, the eigenvalues of $K[\nu^2\tau]^{-1}$ are all positive integers. This means, of course, that our approximate $\Sigma^{(c)}(\vec{k}z)$ is not blessed with, or plagued by, the long time tails which have made headlines recently.[23] We also note that for finite k and ω the damping operator $-\mathrm{Im}\Sigma^{(c)}(\vec{k}\omega;\, \overrightarrow{\xi\xi}')$ has only one eigenfunction with eigenvalue zero, namely, $\psi(\xi)=1$. As $k\to 0$, three more "invariant" eigenfunctions appear, namely, ξ_i, $i=1$, 2, and 3. Only as $\omega\to 0$ does the eigenvalue corresponding to ξ^2 go to zero, too.

C. Local equilibrium

An occasional reader might want to know the form of the potential stress tensor T_{ij}, energy E, and energy current J_i^ϵ functions which have been introduced in (F2.14). They emerge from the present approximation in the transparent form

$$T_{ij}(\xi) = \delta_{ij}\,\beta n^{-1}\tilde{\chi}_{T\epsilon}(0)(\xi^2-3)/3, \tag{4.5a}$$

$$E(\xi) = \beta n^{-1}\tilde{\chi}_{\epsilon\epsilon}(0)(\xi^2-3)/3, \tag{4.5b}$$

$$J_i^\epsilon(\vec{\xi}) = \beta n^{-1}\tilde{\chi}_{T\epsilon}(0)\xi_i\,. \tag{4.5c}$$

Because of the thermodynamic relations (3.11) and (3.12), the requirements (F2.20) and (F2.21) are thus fulfilled, namely,

$$\frac{1}{v_0 k}\langle \xi_3|\Sigma^{(c)}(\vec{k}z)|\,\xi^2/2\rangle|_{k\to 0,z\to i0} = \frac{1}{nk_B}\left(\frac{dp}{dT}\right)_n - 1, \tag{4.6a}$$

$$-\frac{1}{z}\langle \xi^2/2|\Sigma^{(c)}(\vec{k}z)|\,\xi^2/2\rangle|_{k\to 0,z\to i0} = \frac{mc_V}{k_B} - \frac{3}{2}\ , \tag{4.6b}$$

where the scalar-product notation is as defined in F or by Eq. (5.1) below. These are the properties which have been shown in F, and also by Mazenko,[23] to be necessary and sufficient (with the usual analyticity caveat) if the dynamical operator $\Sigma^{(c)}(\vec{k}z)$ is to establish local equilibrium properly. Hence, our approximation (3.1) is guaranteed to yield the correct hydrodynamic mode intensities, the Laplacean expression for the speed of sound, and indeed all the properties discussed by Kadanoff and Martin[1] on the basis of the Navier-Stokes equations.

D. Transport coefficients

In F, general expressions for the shear and bulk viscosities η and ζ and for the heat conductivity κ have been obtained, namely, Eqs. (F3.16), (F3.20), and (F3.21). The approximate $\Sigma^{(c)}$ is so simple that these formulas can be explicitly evaluated. The method applied in F gives each transport coefficient as the sum of two contributions which one might call "kinetic" (primed) and "correlational" (double-primed). The results are

$$\eta'/mn = \tfrac{1}{2}v_0^2[\nu^2\tau]^{-1}, \tag{4.7a}$$

$$\begin{aligned}\eta''/mn &= \tau[\nu^2 - \nu_{11}^2(k)]\,k^{-2}|_{k\to 0}\\ &= 2\tau[c_{t\infty}^2(0) - v_0^2],\end{aligned} \tag{4.7b}$$

$$\kappa'/nk_B = \tfrac{5}{6}[\nu^2\tau]^{-1}, \tag{4.8a}$$

$$\kappa''/nk_B = \tau v_0^2\gamma_\epsilon(0). \tag{4.8b}$$

Here ν is the Kirkwood friction constant (4.3), $\tau \equiv \tau(0)$ is the collision time, and $mnc_{t\infty}^2(0)$ is the high-frequency shear modulus which has been studied by Zwanzig and Mountain,[24] and used in viscosity calculations by Forster *et al.*[25] The collisional bulk viscosity ζ' vanishes; the correlational part ζ'' can be easily written down but is not needed here.

Equations (4.7) and (4.8) involve the two parameters $\tau = \tau(k=0)$ and $\gamma_\epsilon(0)$ for which we have not given explicit expressions above. If one is willing to utilize those sum rules which involve the triple-correlation function $g_3(\vec{r}, \vec{r}')$, both parameters can be microscopically calculated. The present theory would then also constitute an approximate calculation of transport coefficients. However, since similar calculations have in fact been done,[25] and since our main interest here centers on the spectrum of fluctuations outside the transport regime, we have decided instead to utilize experimental values for η and κ in order to determine the parameters τ and $\gamma_\epsilon(0)$ via Eqs. (4.7) and (4.8).

V. SOLUTION OF THE KINETIC EQUATION

Since our approximate kinetic theory, codified in Eqs. (1.6)–(1.8) and (3.1), has all these good properties, we can now proceed with confidence to solve the integral equation in momentum space. $\Sigma^{(c)}(\vec{\xi}, \vec{\xi}')$ is essentially a Fokker-Planck kernel which allows an analytic solution. It is again convenient to utilize the scalar-product notation for matrix elements in $\vec{\xi}$ space, namely,

$$\langle\varphi|M|\psi\rangle \equiv \int d\vec{\xi}\int d\vec{\xi}'\,\varphi(\vec{\xi})M(\vec{\xi}, \vec{\xi}')\phi(\xi')\psi(\vec{\xi}'), \tag{5.1}$$

which has already been introduced in F. For purely technical reasons which will be explained in Appendix B, no complex conjugation for the function $\varphi(\vec{\xi})$ appears in (5.1). In fact, (5.1) is used for real functions φ and ψ here.

Equation (1.6) then leads one to consider the matrix

$$S_{\mu\nu}(\vec{k}z) = \langle\varphi_\mu|[z - \omega^0(\vec{k}) - \Sigma(\vec{k}z)]^{-1}|\varphi_\nu\rangle, \tag{5.2}$$

with

$$\omega^0(\vec{k}; \vec{\xi}\vec{\xi}') \equiv v_0(\vec{k}\cdot\vec{\xi})\delta(\vec{\xi} - \vec{\xi}'), \tag{5.3}$$

for the following four Hermite polynomials ($\mu = 0$ to 3)

$$\{\varphi_\mu(\xi)\} = \{1;\ \xi_3;\ (\xi_3^2 - 1)/\sqrt{2}\ ;\ (\xi_1^2 + \xi_2^2 - 2)/2\}, \tag{5.4}$$

which are invariant under rotations about the 3-axis which is chosen to be the direction of $\vec{k}$. There is, therefore, no matrix element of S which would connect any of the functions (5.4) to the transverse momentum density ξ_1, say. Equation (5.2) is, of course, the formal solution of the kinetic equation (1.6) from which we obtain, in particular, the dynamical liquid structure factor in the form

$$S_{nn}(k, \omega) = [-2k_BT\chi_{nn}(k)]\,\mathrm{Im}S_{00}(k, \omega + i0). \tag{5.5}$$

Equation (1.6) with (3.1) is soluble because we known the eigenfunctions of the Fokker-Planck operator $\vec{\partial}\cdot(\vec{\partial} + \vec{\xi})$, and the remaining, polynomial, terms in (3.1) are separable. Solutions to essentially similar equations have appeared in the literature.[11,13,16] We can therefore be brief, giving only an outline of the method of solution.

The essential part of the integral operator in (5.2) is the Fokker-Planck matrix

$$A(\vec{k}z; \vec{\xi}\vec{\xi}') = [v_0(\vec{k}\cdot\vec{\xi}) - \nu^2\sigma(k, z)\vec{\partial}\cdot(\vec{\partial} + \vec{\xi})]\,\delta(\vec{\xi} - \vec{\xi}'). \tag{5.6}$$

The remainder

$$R(\vec{k}z; \vec{\xi}\vec{\xi}') \equiv [\omega^0(\vec{k}) + \Sigma(\vec{k}z) - A(\vec{k}z)](\vec{\xi}, \vec{\xi}') \tag{5.7}$$

contains all the polynomial contributions to $\Sigma^{(s)}$ and to $\Sigma^{(c)}$; see Eqs. (1.8) and (3.1). If we therefore define

$$S_{\mu\nu}^0(\vec{k}z) = \langle\varphi_\mu|[z - A(\vec{k}z)]^{-1}|\varphi_\nu\rangle, \tag{5.8}$$

we obtain for $S_{\mu\nu}(\vec{k}z)$ the following 4×4 matrix equation:

$$S_{\mu\nu} = S_{\mu\nu}^0 + S_{\mu\lambda}^0 R_{\lambda\kappa} S_{\kappa\nu}, \tag{5.9}$$

where

$$R_{\mu\nu}(\vec{k}z) \equiv \langle \varphi_\mu | R(\vec{k}z) | \varphi_\nu \rangle \tag{5.10}$$

and where the implied index sums in (5.9) only extend over $\mu = 0$ to 3 as defined in (5.4). The R matrix is easily read off from Eqs. (1.8) and (3.1). For example, $R_{00} = 0$, and

$$R_{22}(kz) = \tfrac{1}{2}[n/\beta\tilde{\chi}_{\epsilon\epsilon}(k)]\,\hat{\sigma}(k,z)[\sigma(k,z)\hat{\nu}_{33}(k)]^2. \tag{5.11}$$

Thus it remains to calculate the Fokker-Planck functions $S^0_{\mu\nu}(\vec{k}z)$. For the inversion of the operator A of (5.6), everybody seems to have his own favorite method. Chandrasekhar[11] and Gross,[13] in whose treatment σ is a negative-imaginary constant, solved the associated equation in real time. Lebowitz *et al.*[16] inverted $[z - A]$ by Fourier transforming in the $\vec{\xi}$ variable. We prefer an operator technique which is briefly explained in the Appendix B. Suffice it here to say that all functions $S^0_{\mu\nu}(\vec{k}z)$ can be simply expressed in terms of the incomplete γ function, defined by[26]

$$\gamma(\alpha, x) = \int_0^x d\tau\, e^{-\tau}\tau^{\alpha-1} \quad (\mathrm{Re}\,\alpha > 0), \tag{5.12}$$

which is tabulated.

With this, the 4×4 matrix equation (5.9) can be easily solved, and the dynamical liquid structure factor (or other functions of interest) calculated.

Transverse fluctuations. The transverse momentum-density correlation function $S_t(kz)$ is defined by

$$S_t(kz) = i\int_0^\infty dt \int d(\vec{r} - \vec{r}\,')e^{izt - i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \times \langle g_x(\vec{r}t) g_x(\vec{r}\,'0)\rangle. \tag{5.13}$$

It is even simpler to calculate. Taking $\varphi_4(\xi) \equiv \xi_1$, it is given by

$$S_t(kz) = -n(mv_0)^2 S_{44}(kz). \tag{5.14}$$

Since ξ_1 does not couple to any of the other Hermite polynomials contained in R, one obtains

$$S_{44}(kz) = \frac{S^0_{44}(kz)}{1 + \nu^2_{11}(k)\sigma(k,z)S^0_{44}(kz)}\,. \tag{5.15}$$

This is identical to the result obtained and discussed by Duderstadt and Akcasu[15] who used the approximation codified here as Eq. (2.2). Indeed, since our improvement over that approximation concerns the impact of energy-density fluctuations, it should not affect the purely transverse modes.

VI. DYNAMICAL STRUCTURE FACTOR (COMPARISON WITH EXPERIMENTS)

From the present theory, we have calculated the dynamical liquid structure factor $S_{nn}(k,\omega)$ for liquid argon at 85.2 K and a mass density of $mn = 1.416$ g cm^{-3}. This is the temperature and density for which Sköld *et al.*[27] have reported an absolute neutron scattering measurement of $S_{nn}(k,\omega)$, taken on a coherent sample. It is also essentially the state for which Levesque *et al.*[28] have performed molecular-dynamics experiments. The triple point of argon is at $T = 83.78$ K. We have chosen the customary Lennard-Jones potential

$$\mathcal{V}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \tag{6.1}$$

with the parameters $\epsilon/k_B = 119.8$ K and $\sigma = 3.405$ Å which have been used in the computer experiments by Levesque *et al.*[28] For the pair-correlation function $g(r)$, we have used the experimental data obtained by Yarnell *et al.*[29] by neutron scattering from liquid argon.[30] From these data, we computed[31] $\chi_{nn}(k)$, $\chi_{Tn}(k)$, and $\chi_{T\epsilon}(k)$ as well as the coefficients $\nu^2_{ij}(\vec{k})$ and $\alpha(k)$ defined in Eqs. (3.13) and (3.14).

To obtain $\chi_{\epsilon\epsilon}(0)$ and $\chi_{n\epsilon}(0)$, we have used the thermodynamic statements (3.11) and (3.12). We inserted the experimental specific heats[32] $mc_V/k_B = 2.32$ and $mc_p/k_B = 5.06$, which determine $(dp/dT)_n$ since

$$mn(c_p - c_V)\chi^{-1}_{nn}(0) = T(dp/dT)^2_n. \tag{6.2}$$

$(n\beta)^{-1}\chi_{nn}(0) = S(k=0) = 0.0522$ is the extrapolated experimental value from Yarnell *et al.* The k dependence of $\chi_{\epsilon\epsilon}(k)$ and $\chi_{n\epsilon}(k)$ cannot be determined from available data. Arguing that fluctuations of the energy and the particle densities should be locally proportional to each other, we have used the approximations

$$\chi_{\epsilon\epsilon}(k) \approx [\chi_{\epsilon\epsilon}(0)/\chi_{nn}(0)]\,\chi_{nn}(k), \tag{6.3a}$$

$$\chi_{n\epsilon}(k) \approx [\chi_{n\epsilon}(0)/\chi_{nn}(0)]\,\chi_{nn}(k). \tag{6.3b}$$

There remain the two dissipative coefficients $\tau^{-1}(k)$ and $\gamma_\epsilon(k)$. Following Duderstadt and Akcasu,[33] we argue that for large k, $\tau(k)$ and $\gamma^{-1}_\epsilon(k)$ should vanish. We have used the simplest possible interpolation, namely,

$$\tau^{-1}(k) = \tau^{-1}(0)[1 + (k/k_0)^2], \tag{6.4a}$$

$$\gamma_\epsilon(k) = \gamma_\epsilon(0)[1 + (k/k_0)^2]. \tag{6.4b}$$

For k_0, we used the reasonable value 1.5 Å^{-1} used also by Ref. 33. We did not vary k_0 to obtain a best fit. As indicated in Sec. IV D, we found $\tau^{-1}(0)$ and $\gamma_\epsilon(0)$ from experimental values of the shear viscosity η and the heat conductivity κ. The values used are[32] $\eta = 0.28$ cP and $\kappa = 2.9\times10^{-4}$ cal/K sec cm.

Our results are given in Figs. 1–4, covering a range in wave vector from 0.183 to 4 Å^{-1}. Frequencies are given in units of τ_0^{-1}, where $\tau_0 = (m\sigma/48\epsilon)^{1/2} = 3.112\times10^{-13}$ sec serves as a natural reference time for argon. In Fig. 1, we have com-

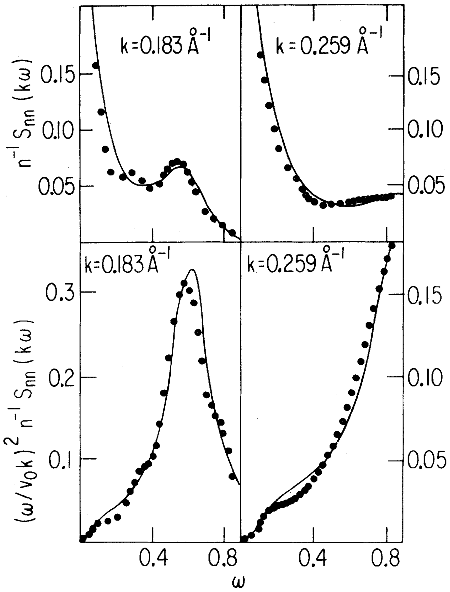

FIG. 1. $n^{-1}S_{nn}(k,\omega)$ (in units of $\tau_0=3.112\times10^{-13}$ sec) as a function of ω, given in units of τ_0^{-1}. These units are also used in all later figures. The lower graphs give the longitudinal momentum-density correlation function. The solid line gives our theoretical results for liquid argon. The dots are data from the computer experiments of Ref. 28.

pared our results with the molecular-dynamics data of Levesque *et al.*,[28] for very small wave vectors. It is seen that we obtain good agreement in the over-all shape of the spectrum. The most prominent feature at small k is the incipient Brillouin sidepeak which has not been obtained before from a kinetic theory. While the experimental Brillouin peak levels off at about $k\simeq0.26$ Å^{-1}, it is slightly more persistent in our theory, where it disappears at $k\simeq0.3$ Å^{-1}. Only at $\omega\approx0$ is the fit to experiment poor; our theory gives a value for $S_{nn}(k,0)$ which is 1.5 times larger than the experimental one. However, computer-dynamics results for very small ω are unreliable since they involve times longer than those that can be reached by computer dynamics. Also drawn in Fig. 1 is the longitudinal momentum-density correlation function

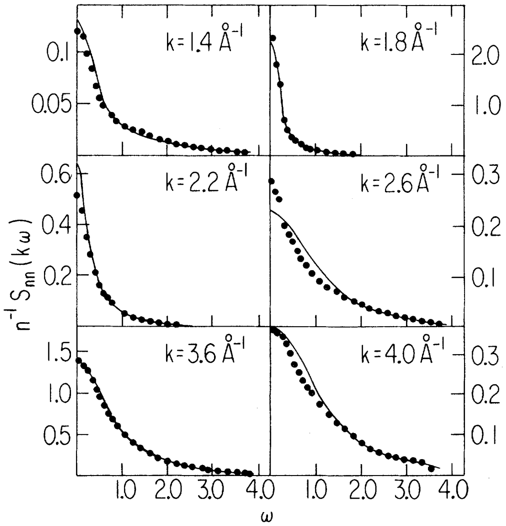

FIG. 2. Dynamical liquid structure factor for liquid argon as a function of frequency, for six values of k as given. The dots are data from coherent neutron scattering, Ref. 27.

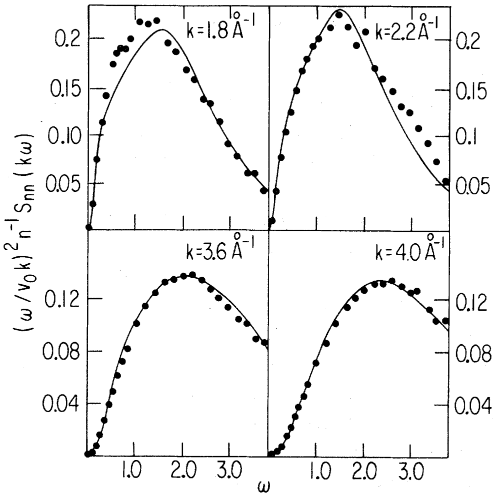

FIG. 3. Longitudinal momentum-density correlation function for liquid argon, for selected values of k. The dots are the neutron scattering results of Ref. 27.

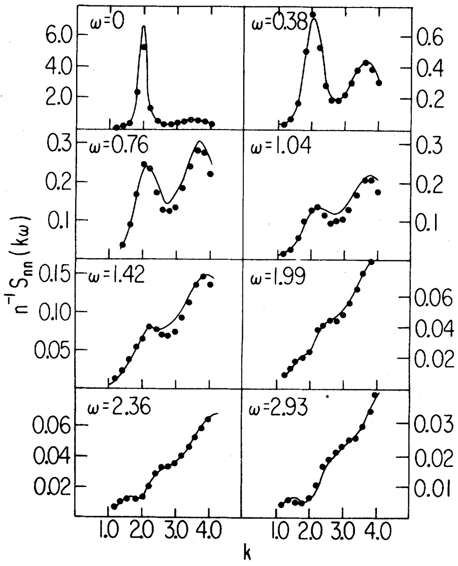

FIG. 4. Dynamical liquid structure factor $S_{nn}(k,\omega)$ as a function of wave number k, for eight values of ω in units of τ_0^{-1} as given. The dots are neutron scattering results taken from Ref. 27.

$$S_l(k,\omega)=(m^2\omega^2/k^2)S_{nn}(k,\omega). \qquad (6.5)$$

For larger values of k, a comparison can be made with the neutron scattering data of Sköld *et al.*[27] In Fig. 2, we show our results for k ranging from 1.4 to 4.0 Å^{-1}. Figure 3 gives the corresponding results for the longitudinal momentum-density correlation function. Again, there is excellent over-all agreement. The small discrepancy in the region from $k\approx 2$ Å^{-1} to $k\approx 3$ Å^{-1} could be due to several factors. It appears most probable that the simple interpolation (6.4) for the relaxation times is the reason. We have not attempted, however, to adjust the value of k_0 to aim for a better fit, or to complicate the dependence of $\tau^{-1}(k)$ and $\gamma_\epsilon(k)$ on k.

In Fig. 4, we have plotted the dynamical structure factor $S_{nn}(k,\omega)$ as a function of k, for a range of frequencies. The agreement with neutron scattering experiments is impressive.

VII. SUMMARY AND DISCUSSION

We have presented a kinetic theory of dynamical fluctuations in simple fluids which has several appealing features. From a pragmatic point of view, it is satisfying that the theory gives very good agreement with experimental data over the full range of wave vector and frequency where those are available. It is also very appealing that the theory is not only very simple mathematically, but that it can be derived microscopically. We note that the derivation which we have presented in Sec. II does not impose an explicit restriction to the very high density for which we have tested our approximation. Indeed, not only does our theory properly reduce to hydrodynamics for small k and ω, and agree with the rigorous sum rules for large ω, but it also reduces, in the low-density-gas regime, to the local and Markovian Fokker-Planck equation,[12] which gives a satisfactory description of gas kinetics. No previous theory has been able to describe, in a unified fashion, such a wide range. This is not to say that quantitative agreement with experiment can be expected to be as good in a gas as it is at liquid density. In a gas, the region in k and ω over which we interpolate is much larger than it is in a liquid. Nevertheless, the Fokker-Planck model does describe this region satisfactorily if not fully quantitatively.[34]

It is interesting to notice that in our application to a liquid we find that the transport coefficients are largely correlational. Our fit to Eqs. (4.7) and (4.8) gives $\eta''\gg\eta'$ and $\kappa''\gg\kappa'$. In a gas, the opposite would be true. This is an indication of the fact that, although the approximation (3.1) is reminiscent of models used in gas kinetics,[12,34] the role which the various terms in $\Sigma^{(c)}(\vec{k}z)$ play is very different at liquid density.

We would like to point out that our use of experimental values for κ and η is sensible for the present purpose, but that it is not necessary as a matter of principle. Explicit calculations[25] have demonstrated that transport coefficients can be microscopically obtained from sum rules of higher order. If we were willing to use the triple-correlation function, or a superposition approximation for it, it would be a simple matter to calculate the k-dependent relaxation frequencies $\tau^{-1}(k)$ and $\gamma_\epsilon(k)$ as well. Indeed, there is hope that such a procedure might improve the results in the region of $k\approx 2$ Å^{-1} to $k\approx 3$ Å^{-1}. A similar comment applies to the static susceptibilities. In this sense, our theory is free of adjustable parameters.

We have not, in our figures, included the results obtained on the basis of previous theories, mainly because these have been tested for argon at different temperature and density. Earlier theories have been compared in the paper by Rowe and Sköld.[35] These authors have also recomputed some results for the temperature and density considered here. The best of these theories appears to be that of Pathak and Singwi,[36] at least for sufficiently large values of k. Even in this region, our theory compares very favorably with that of Pathak and Singwi.

Most of the earlier theories are quite different from ours in purpose and approach. They represent $S_{nn}(k,\omega)$ in terms of a collective memory function[18] or a similar object,[36] use an *ad hoc* ansatz for the latter, and determine its parameters from microscopic sum rules. Even when this approach is successful, it yields little microscopic understanding of the dynamics.[37] By contrast, the kinetic-theory approach is on a level much closer to the microscopic dynamics, a level which is intermediate between that of generalized hydrodynamics where the microstructure is ignored, and a full-scale attack on the N-body problem. Although we have not done so, it would be interesting to investigate how sensitive quantities like $S_{nn}(k,\omega)$ are to changes in the structure of the collision kernel $\Sigma^{(c)}(\vec{k}z)$. This could provide some additional justification for the ansatz procedure of generalized hydrodynamics. Although we have at present only calculated $S_{nn}(k,\omega)$, it is worth pointing out that many additional and interesting correlation functions could be easily obtained from our kinetic theory.

We want to point out, finally, that our approximation is restricted to simple classical fluids, but not to the special case of Lennard-Jones fluids. An interesting case for future investigation is liquid rubidium. For this system, both neutron scattering data[19] and a computer simulation[20] have been reported recently. The prominent feature of these experiments is a Brillouin sidepeak which persists to wave numbers k as large as 1 Å^{-1}, corresponding to a wavelength of the order of the first-neighbor distance. It seems likely that the relatively much softer core of the rubidium potential is responsible for this persistent oscillatory mode. We will report on an application of our theory to this system in the near future.

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APPENDIX A: DERIVATION OF $\Sigma^{(c)}(\vec{k}z;\vec{\xi}\vec{\xi}')$

In this appendix, we furnish some of the calculational details which enter the derivation of the approximate memory kernel $\Sigma^{(c)}$ which we have described in Sec. II. The calculation is tedious if straightforward, and the lengthy formulas which are written down here are given in the hope that they might be useful for other purposes as well. It is apparent from Eqs. (2.9) through (2.13) that we have to compute the matrices $G_{\mu\nu}$, $\dot{G}_{\mu\nu}$, and $\ddot{G}_{\mu\nu}$ each at $t=0$.

1. Static correlation functions

The matrix $G^0_{\mu\nu}(\vec{k})$ is easily obtained. Its elements are given by

$$G^0_{ff}(\vec{k};\vec{\xi}\vec{\xi}')=n\phi(\xi)\delta(\vec{\xi}-\vec{\xi}') +[\beta^{-1}\chi_{nn}(k)-n]\,\phi(\xi)\phi(\xi'), \tag{A1a}$$

$$G^0_{f\epsilon}(k;\,\xi)=G^0_{\epsilon f}(k;\,\xi) =[n\epsilon_0(\xi)+\beta^{-1}\chi_{n\epsilon}(k)]\,\phi(\xi), \tag{A1b}$$

$$G^0_{\epsilon\epsilon}(k)\equiv\beta^{-1}\chi_{\epsilon\epsilon}(k). \tag{A1c}$$

Equation (A1a) is identical to (1.10) above, of course, the susceptibilities $\chi_{AB}(k)$ are as defined in (3.3), and

$$\epsilon_0(\xi)\equiv\tfrac{1}{2}mv_0^2(\xi^2-3). \tag{A2}$$

Equations (A1) can be written down because classically canonical averages over momenta and over positions factorize, and the potential-energy density does not depend on the particle momenta. The matrix inverse $G^{0\,-1}_{\mu\nu}(\vec{k})$, defined in the obvious sense, can then be found. It has the elements

$$(G^0)^{-1}_{ff}(\vec{k};\vec{\xi}\vec{\xi}')=[n\phi(\xi)]^{-1}\delta(\vec{\xi}-\vec{\xi}')+\Delta^{-1}(k) \times\{\chi_{nn}(k)\epsilon_0(\xi)\epsilon_0(\xi') +\chi_{n\epsilon}(k)[\epsilon_0(\xi)+\epsilon_0(\xi')] +[\chi_{\epsilon\epsilon}(k)-\tfrac{3}{2}n\beta^{-1}-(\beta/n)\Delta(k)]\}, \tag{A3a}$$

$$(G^0)^{-1}_{f\epsilon}(k;\,\xi)=(G^0)^{-1}_{\epsilon f}(k;\,\xi) =-\Delta^{-1}(k)[\chi_{nn}(k)\epsilon_0(\xi)+\chi_{n\epsilon}(k)], \tag{A3b}$$

$$(G^0)^{-1}_{\epsilon\epsilon}(k)=\Delta^{-1}(k)\chi_{nn}(k), \tag{A3c}$$

where

$$\beta\Delta(k)=\chi_{nn}(k)[\chi_{\epsilon\epsilon}(k)-\tfrac{3}{2}(n/\beta)]-\chi^2_{n\epsilon}(k). \tag{A3d}$$

2. First time derivatives

The matrix $\dot{G}_{\mu\nu}(\vec{k};t=0)$ is also easy to calculate. Most conveniently, one uses the classical fluctuation-dissipation theorem

$$\langle\dot{A}B\rangle=\beta^{-1}\langle[A,B]\rangle, \tag{A4}$$

where here [,] are the Poisson brackets, to derive the following expressions:

$$i\dot{G}_{ff}(\vec{k};\vec{\xi}\vec{\xi}')=nv_0(\vec{k}\cdot\vec{\xi})\phi(\xi)\delta(\vec{\xi}-\vec{\xi}'), \tag{A5a}$$

$$i\dot{G}_{f\epsilon}(\vec{k};\vec{\xi})=i\dot{G}_{\epsilon f}(\vec{k};\vec{\xi}) =v_0(\vec{k}\cdot\vec{\xi})\phi(\xi)[\chi_{\tau\epsilon}(k)-(n/\beta)+n\epsilon_0(\xi)], \tag{A5b}$$

$$i\dot{G}_{\epsilon\epsilon}(k)=0. \tag{A5c}$$

The last equation is a consequence of time-reversal invariance. Equation (A5b) is in accord with momentum conservation. Given Eqs. (A5) and (A3), the elements of the matrix $\hat{\Omega}_{\mu\nu}(\vec{k})$ of Eq. (2.11) are found by straightforward if laborious matrix multiplication. They will not be written down here.

3. Second time derivatives

Similarly, the second time derivatives $\ddot{G}_{\mu\nu}(\vec{k};t=0)$ can be calculated which are needed to find $\hat{\Sigma}^{\infty}_{\mu\nu}(\vec{k})$. They are given by

$$\ddot{G}_{ff}(\vec{k};\vec{\xi}\vec{\xi}')=-nv_0^2(\vec{k}\cdot\vec{\xi})\phi(\xi)\delta(\vec{\xi}-\vec{\xi}') +n\nu^2_{ij}(0)\partial_i(\partial_j+\xi_j)\phi(\xi)\delta(\vec{\xi}-\vec{\xi}') +n\nu^2_{ij}(\vec{k})\partial_i\partial'_j\phi(\xi)\phi(\xi'), \tag{A6a}$$

$$\ddot{G}_{f\epsilon}(\vec{k};\vec{\xi})=\ddot{G}_{\epsilon f}(\vec{k};\vec{\xi}) =-n\left[\tfrac{1}{2}mv_0^2\xi^2+\tfrac{1}{2}n\int d\vec{r}\,g(r)\mathcal{V}(r)\right]v_0^2(\vec{k}\cdot\vec{\xi})^2\phi(\xi) +\tfrac{1}{2}n\beta^{-1}v_0^2k^2\alpha(k)\phi(\xi)+\tfrac{1}{2}n\beta^{-1} \times[\nu^2_{ij}(\vec{k})-\nu^2_{ij}(0)](\xi_i\xi_j-\delta_{ij})\phi(\xi), \tag{A6b}$$

$$\ddot{G}_{\epsilon\epsilon}(k) = -\int d\vec{r}\cos(\vec{k}\cdot\vec{r})\langle\dot{\epsilon}(r)\dot{\epsilon}(0)\rangle. \tag{A6c}$$

The coefficients in these formulas are those defined in Sec. III B. Matrix multiplication, as indicated in Eq. (2.13), gives the elements of the matrix $\hat{\Sigma}^{\infty}_{\mu\nu}(\vec{k})$ which shall not be reproduced here.

Given $\hat{\Omega}$, $\hat{\Sigma}$, and G^0 as they enter Eq. (2.9), it is then a simple matter to rewrite this equation in the form (1.6) for $G_{ff} \equiv S$, and thus to extract the kinetic memory function $\Sigma(\vec{k}z)$ which is given in Eqs. (1.7), (1.8), and (3.1).

APPENDIX B: FOKKER-PLANCK FUNCTIONS

Because $\partial_1(\partial_1+\xi_1)\phi(\xi)=0$, the calculation of $S^0_{00}(kz)$, as well as the other matrix elements defined in (5.8), is essentially a one-dimensional problem, involving only the 3-coordinate if $\xi_3 = (\vec{k}\cdot\vec{\xi})/k$. It is convenient to define the operators

$$a = (\partial_3+\xi_3) \text{ and } a^\dagger = -\partial_3, \tag{B1}$$

which are indeed adjoined within a "scalar-product" definition as in (5.1), in the sense that $\langle\varphi|a|\psi\rangle = \langle\psi|a^\dagger|\varphi\rangle$, and for which

$$[a, a^\dagger] = 1. \tag{B2}$$

Moreover, the "vacuum," defined by

$$a|0\rangle = 0 \text{ and } \langle 0|a^\dagger = 0, \tag{B3}$$

corresponds to the function $\varphi_0(\xi)=1$ of (5.4). Therefore

$$S^0_{00}(kz) = [\nu^2\sigma(k,z)]^{-1}E(\zeta,\lambda), \tag{B4}$$

where

$$\begin{aligned}\lambda &= v_0 k/\nu^2\sigma(k,z),\\ \zeta &= [z/\nu^2\sigma(k,z)]+\lambda^2,\end{aligned} \tag{B5}$$

and

$$E(\zeta,\lambda) = \langle 0|[\zeta-\lambda(a^\dagger+a)-a^\dagger a-\lambda^2]^{-1}|0\rangle. \tag{B6}$$

E can thus be calculated with the algebraic methods used when one discusses harmonic oscillators. The transformation

$$\tilde{a} = a+\lambda \text{ and } \tilde{a}^\dagger = a^\dagger+\lambda, \tag{B7}$$

which is generated by

$$U = e^{\lambda(a^\dagger - a)} = e^{\lambda(\tilde{a}^\dagger - \tilde{a})}, \tag{B8}$$

produces a new vacuum,

$$\tilde{a}|\tilde{0}\rangle = 0 \text{ and } \langle\tilde{0}|\tilde{a}^\dagger = 0, \tag{B9}$$

which is given by

$$|0\rangle = U|\tilde{0}\rangle. \tag{B10}$$

With the excited states given by

$$|\tilde{n}\rangle = (n!)^{-1/2}(\tilde{a}^\dagger)^n|\tilde{0}\rangle, \tag{B11}$$

one obtains

$$\begin{aligned}E(\zeta,\lambda) &= \langle 0|[\zeta-\tilde{a}^\dagger\tilde{a}]^{-1}|0\rangle\\ &= \sum_{n=0}^{\infty}\frac{\langle 0|\tilde{n}\rangle\langle\tilde{n}|0\rangle}{\zeta-n}.\end{aligned} \tag{B12}$$

One easily finds that

$$\langle 0|\tilde{n}\rangle = \langle\tilde{n}|0\rangle = e^{-\lambda^2/2}\lambda^n(n!)^{-1/2}, \tag{B13}$$

so that

$$E(\zeta,\lambda) = e^{-\lambda^2}\sum_{n=0}^{\infty}\frac{\lambda^{2n}}{n!(\zeta-n)}. \tag{B14}$$

It is related to the incomplete γ function quoted in Eq. (5.12) by

$$E(\zeta,\lambda) = -e^{-\lambda^2}(i\lambda)^{2\zeta}\gamma(-\zeta,-\lambda^2). \tag{B15}$$

This determines $S^0_{00}(kz)$. The other functions $S^0_{\mu\nu}(\vec{k}z)$ of (5.8) are most easily obtained by using relations such as

$$v_0 k S^0_{10}(kz) = z S^0_{00}(kz) - 1, \tag{B16}$$

etc., which follow directly from (5.6). Note that

$$S^0_{33}(kz) = [\nu^2\sigma(k,z)]^{-1}E(\zeta-2,\lambda), \tag{B17}$$

which can be further reduced since

$$\zeta E(\zeta,\lambda) = 1+\lambda^2 E(\zeta-1,\lambda), \tag{B18}$$

and also that $S^0_{3\mu}(kz)=0$ for $\mu=0$, 1, and 2. Finally, the function which occurs in the formula (5.15) for the transverse fluctuations is

$$S^0_{44}(kz) = [\nu^2\sigma(k,z)]^{-1}E(\zeta-1,\lambda). \tag{B19}$$

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