Journal of Statistical Physics, Vol. 21, No. 1, 1979

"Thought-Experiments" by Molecular Dynamics

G. Ciccotti,[1] G. Jacucci,[2] and I. R. McDonald[3]

Received November 2, 1978

A method for studying the dynamical properties of liquids by molecular dynamics simulation is described. Its basis is the measurement of the response to a weak applied field of appropriate character. The explicit form of the mechanical perturbation is worked out in several cases, and details are given of the numerical techniques used in implementing the method.

KEY WORDS: Molecular dynamics; transport properties; linear response theory.

1. INTRODUCTION

The purpose of this paper is to present in general form a nonequilibrium method for studying the dynamical properties of liquids in the context of molecular dynamics calculations. The conventional approach is to compute the time correlation functions that describe the decay of spontaneous fluctuations in the variables of interest. The correlation functions in question are properties of the system in equilibrium, but from linear response theory we know that they can also be related to the response of the system to a weak external field of appropriate character. Our approach is more direct, since we choose to measure the response itself; to that extent our work may be regarded as a realization of the "thought-experiments" of Kubo and Luttinger.(1–4) A number of results obtained in this way have already been reported,(5–7) but until now we have progressed in a largely intuitive fashion. The more formal development given here is intended to give a firm theoretical basis to the method. Given this starting point, it should be easy to generalize the approach to cover a much wider range of phenomena than those we discuss explicitly. At the same time we take the opportunity of describing in

---

[1] Istituto di Fisica "G. Marconi," Università di Roma, Rome, Italy.
[2] Dipartimento di Matematica e Fisica, Libera Università di Trento, Povo, Trento, Italy.
[3] Department of Chemistry, Royal Holloway College, Egham, Surrey, England.

greater detail than hitherto the numerical techniques used in implementing the method.

In attempting to characterize the dynamical behavior of a system in terms of the response to a weak applied field we encounter at once two major problems. The first is the old question of how to represent in mechanical terms the generalized forces required to excite the responses that are of interest, including in particular the representation of the gradients necessary to induce a current of momentum or of energy. This has as a corollary the question of how to incorporate such forces into the molecular dynamics algorithm. The second difficulty concerns the measurement of the response, since in the linear regime this will be, at best, comparable in magnitude with the thermal fluctuations in the system. If these two problems can be overcome, we shall have at our disposal a method for probing systematically the dynamics of systems of interacting particles, including a variety of small cross effects which are impractical to study by the usual equilibrium techniques.

Let us first formulate the problem in very general terms. If $\langle\dot{\alpha}_\mu(\mathbf{r})\rangle_t$ is the flux induced in a microscopic variable $\alpha_\mu(\mathbf{r})$, then in a linear approximation we can write

$$\langle\dot{\alpha}_\mu(\mathbf{r})\rangle_t = \sum_\nu \int_{-\infty}^{t} dt' \int dr\, L_{\mu\nu}(\mathbf{r} - \mathbf{r}', t - t')F_\nu(\mathbf{r}', t') \tag{1.1}$$

where $\langle\cdots\rangle_t$ denotes an average on a nonequilibrium ensemble and F_ν is an external field conjugate to the variable α_ν, i.e., we assume that the interaction with the system is described by the Hamiltonian

$$\mathscr{H}_I(t) = -\sum_\nu \int dr\, \alpha_\nu(\mathbf{r})F_\nu(\mathbf{r}, t) \tag{1.2}$$

Given the correct choice of α_i, the system of equations (1.1) reduces to the phenomenological laws of irreversible thermodynamics in the limit when the applied fields vary slowly in space and time. This means that with any *thermodynamic* force appearing in the phenomenological laws we may associate a *mechanical* force, which is the gist of the indirect Kubo method.(4) In the more general case ($k, \omega > 0$) we may rewrite Eq. (1.1) in the form

$$\langle\dot{\alpha}_\mu(\mathbf{k})\rangle_\omega = \sum_\nu L_{\mu\nu}(\mathbf{k}, \omega)\hat{F}_\nu(\mathbf{k}, \omega) \tag{1.3}$$

If we choose the set of variables $\alpha_\mu(\mathbf{r})$ to be the microscopic conserved variables associated with the independent fluxes appearing in the expression for entropy production, the quantities $L_{\mu\nu}(\mathbf{k}, \omega)$ form the tensor of kinetic coefficients which in the limit $k, \omega \to 0$ (taken in the right order) yields the transport coefficients of hydrodynamics.

Given the correspondence between thermodynamic and mechanical forces, it is clear that once we have identified the explicit form of the mechanical forces the method of molecular dynamics can be used to study irreversible processes in a direct way by exploitation of Eq. (1.1). By computing the fluxes induced by weak external fields of appropriate character we could, in particular, evaluate the various elements in the matrix of kinetic coefficients. Before this program can be carried through successfully, a solution must be found to the second problem mentioned above. The device we use is a "subtraction" technique, the justification for which is the fact that a nonequilibrium average obtained by applying a perturbation to the system can be transformed into an average over an equilibrium ensemble by the operation

$$\langle A\rangle_t \equiv (A, \rho(t)) = (A, \exp(i\mathscr{L}t)\, \rho_0) = (\exp(-i\mathscr{L}t)\, A, \rho_0)$$
$$\equiv \langle \exp(-i\mathscr{L}t)\, A\rangle_0 \qquad (1.4)$$

where $\mathscr{L}$ is the Liouville operator of the perturbed system, ρ_0 is the equilibrium probability distribution, and $\rho(t)$ is the perturbed probability distribution, with $\rho(t = 0) = \rho_0$; the symbol $(\cdots, \cdots)$ is used to denote an integral over phase space and $\langle\cdots\rangle_0$ denotes an equilibrium average. Thus, in order to improve the signal-to-noise ratio in the calculation of $\langle A\rangle_t$, we subtract from $\exp(-i\mathscr{L}t)\, A$ the quantity $\exp(-i\mathscr{L}_0 t)\, A$, where $\mathscr{L}_0$ is the unperturbed Liouville operator, and compute the difference

$$\Delta A(t) = \exp(i\mathscr{L}t)\, A - \exp(-i\mathscr{L}_0 t)\, A \qquad (1.5)$$

the equilibrium average of which is

$$\langle \Delta A(t)\rangle_0 = \langle A\rangle_t - \langle A\rangle_0 \qquad (1.6)$$

This procedure yields the dynamical response we wish to measure with an accuracy which is high if t is not too large. The reason for this is simply the fact that *random* fluctuations in the two terms in Eq. (1.5) are highly correlated and therefore largely cancel, leaving only the systematic part, i.e., the response to the perturbation.

At this point it might be helpful to describe briefly what we do in practice. We carry out a molecular dynamics run in the normal way, but in addition, at regular intervals in time, we apply a small perturbation to the system, which in the general case involves adjusting the coordinates and momenta of all particles in a prescribed way. Thereafter the paths of the particles in perturbed and unperturbed trajectories are followed simultaneously and the time variation of the response is calculated as the difference in the relevant dynamical variable. This yields the *mechanical* response defined by Eq. (1.5), and the *statistical* response represented by Eq. (1.6) is obtained via the ergodic theorem by averaging the mechanical response over a number (typically 50–100) of such pairs of trajectories. In each case the maximum useful information is obtained if the perturbed trajectory is followed for a time which is somewhat larger than the longest relaxation time characterizing the dynamical process under investigation.

The outline of the remainder of the paper is as follows. In Section 2 we give a general account of the method in the framework of linear response theory; in Section 3 we discuss the choice of mechanical perturbation and the character of the different responses; in Section 4 we give some details concerning the numerical solution of the equations of motion; and in Section 5 we summarize the advantages and limitations of method and consider some possible generalizations. For simplicity we restrict the detailed discussion to the case of monatomic systems.

2. GENERAL DEVELOPMENT

Let $\alpha(\mathbf{r})$ be a dynamical variable of the form

$$\alpha(\mathbf{r}) = \sum_{i=1}^{N} \alpha_i \, \delta(\mathbf{r} - \mathbf{r}_i) \tag{2.1}$$

with

$$\alpha(\mathbf{r}, t) = \exp(-i\mathscr{L}_0 t)\, \alpha(\mathbf{r}) \tag{2.2}$$

where α_i is a property of particle i, and may, however, be a function of the phase space coordinates $\mathbf{r}_j$, $\mathbf{p}_j$ of *all* particles j ($j = 1$ to N). Now suppose that the system is subjected to a weak external field $\phi(\mathbf{r}, t)$ which couples to the variable α. The total Hamiltonian in the presence of the perturbation is

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_I(t) \tag{2.3}$$

where $\mathscr{H}_0$ is the equilibrium Hamiltonian and $\mathscr{H}_I(t)$ represents the interaction between the system and the field

$$\mathscr{H}_I(t) = -\int d\mathbf{r}\, \alpha(\mathbf{r})\phi(\mathbf{r}, t) = -\sum_{i=1}^{N} \alpha_i \phi(\mathbf{r}_i, t) \tag{2.4}$$

If the perturbation is applied at $t = 0$, then for any observable property of the system, O say, the mean change $\langle O(\mathbf{r})\rangle_t$ induced by the perturbation after a time t is given by$^{(1,8)}$

$$\langle O(\mathbf{r})\rangle_t = \beta \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, \langle O(\mathbf{r}, t)\dot{\alpha}(\mathbf{r}', t')\rangle_0 \phi(\mathbf{r}', t') \tag{2.5}$$

where $\beta = 1/k_B T$ and, for simplicity, we have assumed that $\langle O(\mathbf{r})\rangle_0 = 0$; clearly Eq. (2.5) corresponds to the statistical response of Eq. (1.6). In writing

Eqs. (2.4) and (2.5) we have omitted the appropriate contraction of vectorial indices which must appear if α is not a scalar.

We now consider the special case when α is a conserved quantity, obeying a conservation law of the general form

$$\dot{\alpha}(\mathbf{r}, t) + \nabla \cdot \mathcal{J}^{\alpha}(\mathbf{r}, t) = 0 \tag{2.6}$$

where $\mathcal{J}^{\alpha}$ is the corresponding current; $\mathcal{J}^{\alpha}$ may be either a vector (if α is a scalar) or a second-rank tensor (if α is a vector). Equation (2.5) can then be rewritten as

$$\langle O(\mathbf{r})\rangle_t = \beta \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, \langle O(\mathbf{r}, t)\mathcal{J}^{\alpha}(\mathbf{r}', t')\rangle_0 \, \nabla\phi(\mathbf{r}', t') \tag{2.7}$$

or, since the time correlation function appearing in Eq. (2.7) is a function only of the differences $\mathbf{r} - \mathbf{r}'$ and $t - t'$, as

$$\langle O(\mathbf{r})\rangle_t = \beta \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, \langle O(\mathbf{r} - \mathbf{r}', t - t')\mathcal{J}^{\alpha}(0, 0)\rangle_0 \, \nabla\phi(\mathbf{r}', t') \tag{2.8}$$

Taking the Fourier transform in space, we obtain

$$\langle \hat{O}(\mathbf{k})\rangle_t = \beta V \int_{-\infty}^{t} dt' \, \langle \hat{O}(\mathbf{k}, t)\hat{\mathcal{J}}^{\alpha}(-\mathbf{k}, t')\rangle_0 i\mathbf{k}\hat{\phi}(\mathbf{k}, t') \tag{2.9}$$

where for the transform of a function $f(\mathbf{r})$ we use the definition

$$\hat{f}(\mathbf{k}) = (1/V) \int d\mathbf{r} \, f(\mathbf{r}) \exp(-i\mathbf{k}\cdot\mathbf{r}) \tag{2.10}$$

In interpreting Eq. (2.8) or Eq. (2.9) it is again necessary to incorporate the appropriate contraction between $\mathcal{J}^{\alpha}$ and $\nabla\phi$ or between $\hat{\mathcal{J}}^{\alpha}$ and $\mathbf{k}\hat{\phi}$.

Given an interaction of the type displayed in Eq. (2.4), the equations of motion in Hamiltonian form are

$$\dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m} - \phi(\mathbf{r}_i, t)\frac{\partial \alpha_i}{\partial \mathbf{p}_i} \tag{2.11}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -\frac{\partial \mathcal{H}_0}{\partial \mathbf{r}_i} + \sum_{j=1}^{N} \phi(\mathbf{r}_j, t)\frac{\partial \alpha_j}{\partial \mathbf{r}_i} + \alpha_i \frac{\partial \phi(\mathbf{r}_i, t)}{\partial \mathbf{r}_i} \tag{2.12}$$

and in Newtonian form are

$$m\ddot{\mathbf{r}}_i = -\frac{\partial \mathcal{H}_0}{\partial \mathbf{r}_i} + \sum_{j=1}^{N} \phi(\mathbf{r}_j, t)\frac{\partial \alpha_j}{\partial \mathbf{r}_i} + \alpha_i \frac{\partial \phi(\mathbf{r}_i, t)}{\partial \mathbf{r}_i} - m\frac{d}{dt}\left(\phi(\mathbf{r}_i, t)\frac{\partial \alpha_i}{\partial \mathbf{p}_i}\right) \tag{2.13}$$

The final term on the right-hand side of (2.13) appears only when the perturbation is dependent on velocity, as is true in the cases discussed in Sections 3.4 and 3.5. If the perturbation is an impulsive force, care is needed in taking the derivative with respect to time; note that d/dt denotes a total derivative.

In writing Eq. (2.4) we have assumed that the nature of the applied field is such that the interaction with the system can be represented by an additional term in the Hamiltonian. However, we may also wish to study induced transverse currents (of number, mass, charge, etc.). In such cases the perturbation is a transverse field and cannot be described in this simple way. Nonetheless, if the applied field is a function only of coordinates, an equation similar to Eq. (2.5) can still be derived, the quantity $\dot{\alpha}$ taking the form

$$\dot{\alpha}(\mathbf{r}) = \sum_{i=1}^{N} \gamma_i \dot{\mathbf{r}}_i \, \delta(\mathbf{r} - \mathbf{r}_i) \tag{2.14}$$

where γ_i is the particle property which couples to the external field. Thus Jackson and Mazur(3) have shown that if the system is subjected at time $t = 0$ to a weak vectorial field $\boldsymbol{\xi}(\mathbf{r}, t)$ such that

$$\nabla \times \boldsymbol{\xi} \neq 0, \qquad \nabla \cdot \boldsymbol{\xi} = 0 \tag{2.15}$$

and the force acting on particle i is given by

$$\mathbf{F}(\mathbf{r}_i, t) = \gamma_i \boldsymbol{\xi}(\mathbf{r}_i, t) \tag{2.16}$$

then the mean change in a variable O is

$$\begin{aligned} \langle O(\mathbf{r}) \rangle_t = \beta \int d\mathbf{r}' \int_{-\infty}^{t} dt' \, \langle O(\mathbf{r}, t) \sum_{i=1}^{N} \gamma_i \dot{\mathbf{r}}_i(t') \\ \times \, \delta\{\mathbf{r}' - \mathbf{r}_i(t')\} \rangle_0 \cdot \boldsymbol{\xi}(\mathbf{r}', t') \end{aligned} \tag{2.17}$$

or

$$\begin{aligned} \langle \hat{O}(\mathbf{k}) \rangle_t = \beta V \int_{-\infty}^{t} dt' \, \langle \hat{O}(\mathbf{k}, t) \sum_{i=1}^{N} \gamma_i \dot{\mathbf{r}}_i(t') \\ \times \, \exp\{i\mathbf{k} \cdot \mathbf{r}_i(t')\} \rangle_0 \cdot \hat{\boldsymbol{\xi}}(\mathbf{k}, t') \end{aligned} \tag{2.18}$$

The total Hamiltonian of the system is now unchanged by the applied field, which appears instead as an additional term in the equations of motion. The latter now take the simpler form given by

$$\dot{\mathbf{r}}_i = \partial \mathscr{H}_0 / \partial \mathbf{p}_i = \mathbf{p}_i / m \tag{2.19}$$

$$\dot{\mathbf{p}}_i = -\partial \mathscr{H}_0 / \partial \mathbf{r}_i + \gamma_i \boldsymbol{\xi}(\mathbf{r}_i, t) \tag{2.20}$$

We have so far said nothing about the explicit time dependence of the applied field. This can be separated from the spatial dependence of the perturbation by writing

$$\phi(\mathbf{r}, t) = \phi(\mathbf{r}) f(t) \tag{2.21}$$

or, in the case of a transverse field,

$$\boldsymbol{\xi}(\mathbf{r}, t) = \boldsymbol{\xi}(\mathbf{r})f(t) \tag{2.22}$$

which in either event represents a spatial field modulated by a scalar function $f(t)$. The form of $f(t)$ is arbitrary, but the choice of greatest practical interest is

$$f(t) = \delta(t - t_0) \tag{2.23}$$

where $\delta(t)$ is the Dirac delta function. This represents an impulsive force applied at $t = t_0$; to simplify the formulas we shall always assume that $t_0 = 0$. From Eqs. (2.9) and (2.17) it is easy to see that the response to a delta-function perturbation is the time correlation function itself. In some earlier calculations we used a step-function perturbation of the form

$$\begin{aligned} f(t) &= 0 \qquad \text{if} \quad t < t_0 \\ &= 1 \qquad \text{if} \quad t > t_0 \end{aligned} \tag{2.24}$$

representing a steady field switched on at $t = t_0$. In this case the response is the time integral of the correlation function. It follows that with a proper choice of the variables α and O the limiting drift current, namely

$$\lim_{t \to \infty} \langle \hat{O}(\mathbf{k}) \rangle_t$$

is closely related to a certain transport coefficient. In most circumstances, however, the structure of the correlation function is also of interest and for that reason alone use of a delta-function perturbation has generally more to recommend it. In addition, when the applied field is velocity dependent, integration of the equations of motion is more cumbersome when a step function is used. The subsequent discussion is therefore limited to the case of delta-function perturbations.

3. FORM OF THE MECHANICAL PERTURBATION

We want now to show how the general formalism of Section 2 can be adapted to specific cases. To avoid widening the discussion too far, we shall focus most of our attention on the important case of dynamical variables satisfying a conservation law. It is clear on general grounds that the most straightforward way of exciting a current $\mathscr{J}^\alpha$, say, is by applying a field which couples directly to the corresponding conserved variable α. This allows a study of the autocorrelation function of the quantity $\hat{\mathscr{J}}^\alpha(\mathbf{k}, t)$ from which, in the limit $k, \omega \to 0$, a transport coefficient can be extracted. It is equally clear, however, that any such perturbation will simultaneously give rise to the full set of cross effects described by the matrix of kinetic coefficients. In multicomponent systems the number of cross effects is much larger than in pure fluids; this makes it natural to attempt the measurement of cross transport coefficients such as thermal diffusivity, quantities which are extremely difficult to determine by the standard molecular dynamics method.

The detailed way in which the mechanical equations of motion are modified by the perturbation depends on the character of the variable α. Thus the mechanical perturbation has a different form according to whether α_i is (i) independent of the phase space variables (as when $\mathscr{J}^\alpha$ is the longitudinal particle current); (ii) a function of the momentum $\mathbf{p}_i$ (as when $\mathscr{J}^\alpha$ is a component of the stress tensor); or (iii) a function of $\mathbf{p}_i$ and of all coordinates $\mathbf{r}_j$, $j = 1$ to N (as when $\mathscr{J}^\alpha$ is the energy current). We shall consider each of these in turn, together with the extension of (i) to the case of transverse currents. Other possibilities can be envisaged, but are of less direct physical interest. Apart from the brief discussion of mixtures given in Section 3.3, we limit the discussion to the case of one-component systems.

3.1. Longitudinal Particle Current

We consider first the case of an external field which couples to the particle density $n(\mathbf{r})$, the Fourier components of which are defined by

$$\hat{n}(\mathbf{k}) = (1/V) \sum_{i=1}^{N} \exp(-i\mathbf{k}\cdot\mathbf{r}_i) \tag{3.1}$$

The corresponding conservation law is given by

$$\dot{\hat{n}}(\mathbf{k}, t) + i\mathbf{k}\cdot\hat{\mathbf{J}}^n(\mathbf{k}, t) = 0 \tag{3.2}$$

where

$$\hat{\mathbf{J}}^n(\mathbf{k}) = (1/V) \sum_{i=1}^{N} \dot{\mathbf{r}}_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) \tag{3.3}$$

is the particle current; from Eq. (3.2) we see that density fluctuations are linked only to the longitudinal component of the current.

The perturbation in this example is of the form

$$\mathscr{H}_l(t) = -\int d\mathbf{r}\, n(\mathbf{r})\phi(\mathbf{r}, t) = -V\sum_{k} \hat{n}(-\mathbf{k})\phi(\mathbf{k}, t) \tag{3.4}$$

where $\phi(\mathbf{r}, t)$ is a scalar field (with dimensions of energy) and the sum on $\mathbf{k}$ runs over all wave vectors allowed by the periodic boundary conditions used in the molecular dynamics calculations. In practice, given the assumption of linearity, we are concerned only with the response to a single Fourier component of the external field, $\mathbf{k}$ say, which we shall assume to be of the form $\mathbf{k} = (k, 0, 0)$. The external field can therefore be written as

$$\phi(\mathbf{r}, t) = \Phi \exp(ikx)\, \delta(t) \tag{3.5}$$

and Eq. (3.4) simplifies to

$$\mathscr{H}_I(t) = -V\hat{n}(-\mathbf{k})\phi(\mathbf{k}, t) = -V\hat{n}(-\mathbf{k})\Phi\,\delta(t) \tag{3.6}$$

By identifying α with n we see from Eq. (2.9) that

$$\begin{aligned}\langle\hat{O}(\mathbf{k})\rangle_t &= \beta V\sum_{\nu}\langle\hat{O}(\mathbf{k}, t)\hat{J}_\nu^{\,n}(-\mathbf{k}, 0)\rangle_0 ik_\nu\Phi \\ &= \beta V\langle\hat{O}(\mathbf{k}, t)\hat{J}_x^{\,n}(-\mathbf{k}, 0)\rangle_0 ik\Phi \end{aligned} \tag{3.7}$$

In particular, the longitudinal particle current induced by a field of unit strength is given by

$$\frac{1}{\Phi}\langle\hat{J}_x^{\,n}(\mathbf{k})\rangle_t = \beta V\langle\hat{J}_x^{\,n}(\mathbf{k}, t)\hat{J}_x^{\,n}(-\mathbf{k}, 0)\rangle_0 ik = \frac{i\beta V}{k}C_l(k, t) \tag{3.8}$$

where

$$C_l(k, t) = k^2\langle\hat{J}_x^{\,n}(\mathbf{k}, t)\hat{J}_x^{\,n}(-\mathbf{k}, 0)\rangle_0 \tag{3.9}$$

is the equilibrium longitudinal current autocorrelation function.

Equation (3.8) shows that the response in **k** space to the field (3.5) is purely imaginary. This means only that the induced current is out of phase with the driving field by exactly $\frac{1}{2}\pi$ and it is easy to show that the response in **r** space to a real applied field is purely real. Taking the inverse transform of Eq. (3.8) for the case when only one Fourier component is excited, we see that

$$(1/\Phi)\langle J_x^{\,n}(\mathbf{r})\rangle_t = (i\beta V/k)C_l(\mathbf{k}, t)\exp(ikx) \tag{3.10}$$

so the response to a real field of the form

$$\phi(\mathbf{r}, t) = \tfrac{1}{2}\phi\{\exp(ikx) + \exp(-ikx)\}\,\delta(t) = \Phi\,\delta(t)\cos kx \tag{3.11}$$

is given by

$$\begin{aligned}\frac{1}{\Phi}\langle J_x^{\,n}(\mathbf{r})\rangle_t &= \frac{i\beta V}{2k}C_l(\mathbf{k}, t)\{\exp(ikx) + \exp(-ikx)\} \\ &= \frac{-\beta V}{k}C_l(k, t)\sin kx \end{aligned} \tag{3.12}$$

But from Eq. (3.8) we see that the real part of the corresponding Fourier component of the induced current is zero. Thus

$$\frac{1}{\Phi}\left\langle\sum_{i=1}^{N}\dot{x}_i\sin kx_i\right\rangle_t = -\frac{V^2}{k}C_l(k, t) \tag{3.13}$$

where the left-hand side gives the response to a field varying as cos kx. If, on the other hand, we choose to perturb the system with a field varying as sin kx, we must look for the response in the real part of the current.

From the general result given by Eq. (3.7) we see that a perturbation of the form of (3.5) will also induce change in other dynamical variables, the stress tensor (momentum current) **T** and the energy current $\mathbf{J}^e$, for example. However, the stress tensor is linked to the particle current by the conservation law

$$m\dot{\hat{\mathbf{J}}}^n(\mathbf{k}, t) + i\mathbf{k}\cdot\hat{\mathbf{T}}(\mathbf{k}, t) = 0 \tag{3.14}$$

Thus observation of the response in the diagonal element $\hat{T}_{xx}$ yields only the time derivative of $C_l(k, t)$. This particular type of cross effect is therefore rather uninteresting. Observations of the thermal response, given by

$$(1/\Phi)\langle \hat{J}_x{}^e(\mathbf{k})\rangle_t = -\beta V\langle \hat{J}_x{}^e(\mathbf{k}, t)\hat{J}_x{}^n(-\mathbf{k}, 0)\rangle_0 ik \tag{3.15}$$

provides a measure of the coupling between the particle current and the flow of energy.

3.2. Transverse Particle Current

In the case of the transverse component of the particle current the required perturbation is of the general form of Eq. (2.22) with the restrictions imposed by (2.15). Typically, therefore, choosing again the vector $\mathbf{k} = (k, 0, 0)$ and setting $\gamma_i = 1$ for all i, the applied force field takes the form

$$\xi_y(\mathbf{r}, t) = \Xi \exp(ikx)\,\delta(t), \qquad \xi_x(\mathbf{r}, t) = \xi_z(\mathbf{r}, t) = 0 \tag{3.16}$$

On substituting in Eq. (2.17), we obtain

$$\langle \hat{O}(\mathbf{k})\rangle_t = \beta V\langle \hat{O}(\mathbf{k}, t)\hat{J}_y{}^n(-\mathbf{k}, 0)\rangle_0\Xi \tag{3.17}$$

which is the transverse analog of Eq. (3.7). In particular, the response seen in the transverse current itself is

$$\frac{1}{\Xi}\langle \hat{J}_y{}^n(\mathbf{k})\rangle_t = \beta V\langle \hat{J}_y{}^n(\mathbf{k}, t)\hat{J}_y{}^n(-\mathbf{k}, 0)\rangle_0 = \frac{\beta V}{k^2}C_t(k, t) \tag{3.18}$$

where

$$C_t(k, t) = k^2\langle \hat{J}_y{}^n(\mathbf{k}, t)\hat{J}_y{}^n(-\mathbf{k}, 0)\rangle_0 \tag{3.19}$$

is the transverse current autocorrelation function. The response is in this case purely real, showing that the induced current is now in phase with the driving force. The response to a real force

$$\boldsymbol{\xi}(r) = (0, \Xi\cos kx, 0) \tag{3.20}$$

is therefore

$$\frac{1}{\Xi}\left\langle \sum_{i=1}^{N} \dot{y}_i \cos kx_i \right\rangle_t = \frac{\beta V^2}{k^2}C_t(k, t) \tag{3.21}$$

The possibility of studying cross-correlation effects again exists, but these are likely to be small, since in the hydrodynamic limit the transverse current is decoupled from all other fluctuating variables.

3.3. Binary Mixtures

The arguments of the two preceding sections are easily generalized to multicomponent systems. Consider, for example, the case of a binary mixture. If N_s is the number of particles of species s, with $N = N_1 + N_2$, then the Fourier components of the partial densities may be defined as

$$\hat{n}_s(\mathbf{k}) = \frac{1}{V}\sum_{i=1}^{N_s} \exp(-i\mathbf{k}\cdot\mathbf{r}_{is}), \qquad s = 1, 2 \tag{3.22}$$

where $\mathbf{r}_{is}$ denotes the coordinates of particle i of species s. The total number density is then given by

$$\hat{n}(\mathbf{k}) = \hat{n}_1(\mathbf{k}) + \hat{n}_2(\mathbf{k}) \tag{3.23}$$

but in addition we may introduce the mass density

$$\hat{m}(\mathbf{k}) = m_1\hat{n}_1(\mathbf{k}) + m_2\hat{n}_2(\mathbf{k}) \tag{3.24}$$

and, for uncharged systems, the concentration

$$\hat{c}(\mathbf{k}) = c_2\hat{n}_1(\mathbf{k}) - c_1\hat{n}_2(\mathbf{k}) \tag{3.25}$$

where m_s is the mass of a particle of species s and $c_s = N_s/N$. In the case of charged fluids the analog of (3.25) is the charge density

$$\hat{q}(\mathbf{k}) = q_1\hat{n}_1(\mathbf{k}) + q_2\hat{n}_2(\mathbf{k}) \tag{3.26}$$

where q_s is the charge carried by particles of species s.

Each of the densities (3.24)–(3.26) obeys a conservation law similar to Eq. (3.2) and both the longitudinal and transverse components of the corresponding currents can be induced by the methods already discussed. The only extra step required is to identify α_i (or γ_i) with the appropriate scalar quantity—mass, concentration, or charge—appearing in the definitions of the densities. This makes it straightforward to study a wide variety of cross effects: the coupling of concentration currents with the flow of energy, the mixing of modes of optical and acoustic character, and so on. Of greater importance, perhaps, is the fact that transverse currents of concentration or charge can be studied even in the limit $k = 0$. This offers a practical means of measuring electrical conductivity. By way of illustration, consider the case of a monovalent molten salt, for which we may use the notation $s = +, -$, with $q_+ = e$ and $q_- = -e$. If a homogeneous force field of the form

$$\boldsymbol{\xi} = (0, \Xi, 0) \tag{3.27}$$

is applied and if γ_i is set equal to the charge on particle i, we find as a special case of Eq. (2.16) that the response in the y component of the microscopic electric current $\mathbf{I}$ defined by

$$\mathbf{I} = e \sum_{i=1}^{N_+} \dot{\mathbf{r}}_{i+} - e \sum_{j=1}^{N_-} \dot{\mathbf{r}}_{j-} \tag{3.28}$$

is

$$(e/\Xi)\langle I_y \rangle_t = \beta \langle I_y(t) I_y(0) \rangle_0 \tag{3.29}$$

It follows immediately from the well-known formula of Kubo(1) that the electrical conductivity σ is given in terms of the response by

$$\sigma = (e/V\Xi) \int_0^\infty dt\, \langle I_y \rangle_t \tag{3.30}$$

A similar argument applied in the case of uncharged fluids leads to an expression for the interdiffusion coefficient.

3.4. Stress Tensor Fluctuations

The coefficient of shear viscosity η_s is related through a Kubo formula to the long-wavelength limit of the autocorrelation function of an off-diagonal element of the stress tensor and the longitudinal viscosity $\eta_l = \frac{4}{3}\eta_s + \xi$ (ξ being the bulk viscosity) is similarly linked to the autocorrelation function of a diagonal element of T. Specifically(2,9)

$$\eta_s = \beta V \int_0^\infty dt\, \langle \hat{T}_{xy}(0, t) \hat{T}_{xy}(0, 0) \rangle_0 \tag{3.31}$$

$$\eta_l = \beta V \int_0^\infty dt\, \langle \{\hat{T}_{xx}(0, t) - P\}\{\hat{T}_{xx}(0, 0) - P\} \rangle_0 \tag{3.32}$$

In writing Eq. (3.32) we have taken account of the fact that $\langle \hat{T}_{xx}(0) \rangle_0$ is equal to the pressure P. In the case of pairwise additive forces the microscopic stress tensor is given by

$$\mathbf{T}(\mathbf{k}) = \frac{1}{V} \sum_{i=1}^{N} m \dot{\mathbf{r}}_i \dot{\mathbf{r}}_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) + \frac{1}{2V} \sum_{i \neq j}^{N} \sum^{N} \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}} v'(r_{ij}) Q_{ij}(\mathbf{k}) \tag{3.33}$$

where $v(r)$ is the pair potential, $v'(r) = dv(r)/dr$, $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, and

$$Q_{ij}(\mathbf{k}) = [\exp(-i\mathbf{k}\cdot\mathbf{r}_j) - \exp(-i\mathbf{k}\cdot\mathbf{r}_i)]/i\mathbf{k}\cdot\mathbf{r}_{ij} \tag{3.34}$$

In studying the viscous modes of the system it is clear from the earlier discussion that the most suitable form of applied field is one which couples to the momentum density and consequently must be a *vector* field. In this case the perturbation is velocity dependent, having the form

$$\mathscr{H}_I = -\int d\mathbf{r}\, \mathbf{J}^n(\mathbf{r})\cdot\boldsymbol{\phi}(\mathbf{r}, t) = -V\sum_{\mathbf{k}} \hat{\mathbf{J}}^n(\mathbf{k})\cdot\hat{\boldsymbol{\phi}}(\mathbf{k}, t) \tag{3.35}$$

which corresponds to identifying α_i with $\dot{\mathbf{r}}_i$. If we write $\boldsymbol{\phi}(\mathbf{r}, t)$ (which has the dimensions of momentum) as

$$\boldsymbol{\phi}(\mathbf{r}, t) = \boldsymbol{\phi}(\mathbf{r})\,\delta(t) \tag{3.36}$$

we see from the conservation law (3.14) that the response in the general case is given by

$$\langle\hat{O}(\mathbf{k})\rangle_t = \frac{\beta V}{m}\sum_{\mu}\sum_{\nu}\langle\hat{O}(\mathbf{k}, t)\hat{T}_{\mu\nu}(-\mathbf{k}, 0)\rangle_0 ik_\mu\hat{\phi}_\nu(k) \tag{3.37}$$

It is clear from Eq. (3.37) that by varying the form of $\boldsymbol{\phi}(\mathbf{r})$ we can couple the field to a diagonal element of $\hat{\mathbf{T}}$, an off-diagonal element, or some combination of the two. Choosing

$$\boldsymbol{\phi}(\mathbf{r}) = (0, \phi\exp(ikx), 0) \tag{3.38}$$

and assuming, as always, that $\mathbf{k}$ is parallel to the x axis, we find that Eq. (3.37) reduces to

$$\langle\hat{O}(\mathbf{k})\rangle_t = (\beta V/m)\langle\hat{O}(\mathbf{k}, t)\hat{T}_{xy}(-\mathbf{k}, 0)\rangle_0 ik\Phi \tag{3.39}$$

In particular, choosing for $\hat{O}$ the xy component of $\hat{T}(\mathbf{k})$, we see that the response is given by

$$\langle\hat{T}_{xy}(\mathbf{k})\rangle_t = (\beta V/m)\langle\hat{T}_{xy}(\mathbf{k}, t)\hat{T}_{xy}(-\mathbf{k}, 0)\rangle_0 ik\Phi \tag{3.40}$$

As in the case of the longitudinal particle currents, it follows from Eq. (3.40) that the response to a field varying as $\cos kx$ is in the imaginary part of $\hat{T}_{xy}(\mathbf{k}, t)$. Thus in the limit $k \to 0$ we find that

$$\eta_s = (m/k\Phi)\int_0^\infty dt\, \lim_{k\to 0}\langle\mathrm{Im}\,\hat{T}_{xy}(\mathbf{k})\rangle_t \tag{3.41}$$

In practice, in contrast to the case of the electrical conductivity, we are unable to take the $k \to 0$ limit, and it is well known that we cannot interchange the limiting operation and the integration, since the integral then vanishes. The second of these difficulties can be avoided by replacing the upper limit of integration by a time τ which is finite but sufficiently large for the response to be essentially zero. However, the result thereby obtained for η_s will be useful only if the smallest value of k consistent with the periodic boundary conditions is sufficiently small to give an adequate estimate of the integrand in Eq. (3.41). For $k > 0$ we can study both the stress–stress autocorrelation itself and cross-correlations such as that between the stress tensor and the energy current. The latter quantity plays a role in generalized hydrodynamic descriptions of density fluctuations in liquids.(10,11)

In Fig. 1 we show some results obtained for the wavelength dependence of the function $C(t) = \langle \mathrm{Im}\, \hat{T}_{xy}(k)\rangle_t$ for the case of a Lennard-Jones fluid at a reduced number density $n\sigma^3 = 0.75$ and mean reduced temperature $k_{\mathrm{B}}T/\epsilon = 1.15$; the calculations were made on a system of 256 particles in a cubic box. It is clear from the figure that the response is a rapidly varying function of k. In particular, the marked growth with increasing k of the region of negative autocorrelation means that the apparent shear viscosity obtained from Eq. (3.31) decreases rapidly with k. Choosing values of σ and ϵ appropriate to argon,(12) we find that for the smallest accessible wave vector the apparent shear viscosity is $\eta_s = 0.44 \times 10^{-3}\,\mathrm{g\,cm^{-1}\,sec^{-1}}$. This is approximately three times smaller than the experimental value(13) and it is clear that the major part of the discrepancy is due to the fact that the wavelength associated with the perturbation is too small for Eq. (3.41) to be useful. Improvement could be sought by, for example, extending the length of the molecular dynamics box in one direction. On the other hand, the shear viscosity can also be related to the response in transverse current to a shearing field, which was discussed in Section 3.2. A simple hydrodynamic(3,13) argument shows that the shear viscosity can be expressed as

$$\eta_s^{-1} = \int_0^\infty dt \lim_{k\to 0}(k^2/n^2\Xi)\langle \hat{J}_y{}^n(\mathbf{k})\rangle_t \tag{3.42}$$

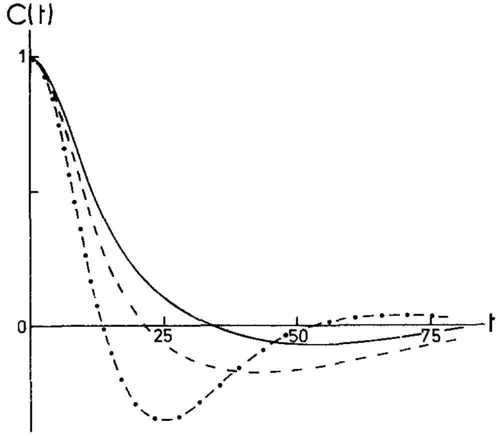

Fig. 1. The wave number-dependent function $C(t)$ for the Lennard-Jones fluid at $n\sigma^3 = 0.75$, $k_{\mathrm{B}}T/\epsilon = 1.15$, normalized to unity at $t = 0$. Full curve: $k\sigma = 0.899$; dashed curve: $k\sigma = 1.798$; dash-dotted curve: $k\sigma = 4.495$. The unit of time is $h = 0.032(m\sigma^2/48\epsilon)^{1/2}$, equal to 10^{-14} sec in the case of argon.

where $\langle \hat{J}_y{}^n(\mathbf{k})\rangle_t$ is the response defined by Eq. (3.18). We are now much more favourably placed for taking the $k = 0$ limit, since the work of Levesque *et al.*(14) on the Lennard-Jones fluid and our own calculations for molten salts(6,15) show that the integral in (3.42) is only weakly k dependent at small k. Typically the extrapolation from the smallest accessible wavenumber to the limit $k = 0$ involves a correction of approximately 20–30%.

If, in place of (3.38), we choose

$$\boldsymbol{\phi}(\mathbf{r}) = (\Phi \exp(ikx), 0, 0) \tag{3.43}$$

Eq. (3.39) becomes

$$\langle \hat{O}(\mathbf{k})\rangle_t = (\beta V/m)\langle \hat{O}(\mathbf{k}, t)\hat{T}_{xx}(-\mathbf{k}, 0)\rangle_0 ik\Phi \tag{3.44}$$

and substitution of $\hat{T}_{xx}$ for $\hat{O}$ leads to an equation analogous to (3.40). This can be treated in the same way to yield an expression for the longitudinal viscosity. The constant term appearing in Eq. (3.32) does not enter the equation analogous to (3.41), since $\langle \hat{T}_{xx}(\mathbf{k})\rangle_0 = 0$ for $k \neq 0$.

3.5. Energy Fluctuations

The formula analogous to (3.31) [or (3.32)] for the thermal conductivity is

$$\lambda T = \beta V \int_0^\infty dt\, \langle \hat{J}_x{}^e(0, t)\hat{J}_x{}^e(0, 0)\rangle_0 \tag{3.45}$$

where $\hat{\mathbf{J}}^e$ is the energy current, defined as

$$\hat{\mathbf{J}}^e(\mathbf{k}) = \frac{1}{V}\sum_{i=1}^{N} e_i \dot{\mathbf{r}}_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) + \frac{1}{2V}\sum_{i\neq j}^{N}\sum^{N} \mathbf{r}_{ij}\cdot\dot{\mathbf{r}}_{ij}\,\frac{v'(r_{ij})}{r_{ij}}\,\mathbf{r}_{ij}Q_{ij}(\mathbf{k}) \tag{3.46}$$

e_i is the energy of particle i

$$e_i = (|\mathbf{p}_i|^2/2m) + \sum_{j>i}^{N} v(r_{ij}) \tag{3.47}$$

and the local energy density

$$\hat{e}(\mathbf{k}) = (1/V)\sum_{i=1}^{N} e_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) \tag{3.48}$$

is linked to the energy current by the conservation law

$$\dot{\hat{e}}(\mathbf{k}, t) + i\mathbf{k}\cdot\hat{\mathbf{J}}^e(\mathbf{k}, t) = 0 \tag{3.49}$$

To study thermal fluctuations it is clearly appropriate to apply a field which couples to the energy density. In this case the interaction with the system is represented by the Hamiltonian

$$\mathscr{H}_I(t) = -\int d\mathbf{r}\, e(\mathbf{r})\phi(\mathbf{r}, t) = -V\sum_{\mathbf{k}} \hat{e}(-\mathbf{k})\hat{\phi}(\mathbf{k}, t) \tag{3.50}$$

where ϕ is a dimensionless scalar field. This corresponds to setting $\alpha_i = e_i$. Proceeding along the now familiar lines, we see that the response in a variable $\hat{O}$ is

$$\langle \hat{O}(\mathbf{k})\rangle_t = \beta V \sum_{\nu} \langle \hat{O}(\mathbf{k}, t)\hat{J}_\nu^e(-\mathbf{k}, 0)\rangle_0 ik_\nu \phi(\mathbf{k}) \tag{3.51}$$

In particular, taking $\mathbf{k} = (k, 0, 0)$ and $\hat{O} = \hat{J}_x^e$, we find that

$$\langle \hat{J}_x^e(\mathbf{k})\rangle_t = \beta V \langle \hat{J}_x^e(\mathbf{k}, t)\hat{J}_x^e(-\mathbf{k}, 0)\rangle_0 ik\Phi \tag{3.52}$$

Thus

$$\lambda T = \int_0^\infty dt \lim_{k\to 0}[\langle \operatorname{Im} \hat{J}_x^e(\mathbf{k})\rangle_t / k\Phi] \tag{3.53}$$

if the applied field varies as cos kx. The remarks following Eq. (3.41) are also relevant to the calculation of the thermal conductivity. As we have recently shown,(7) the apparent thermal conductivity is a rapidly varying function of k, but extrapolation to $k = 0$ yields a result for the Lennard-Jones fluid in fair agreement with experimental data on argon. As in the case of the shear viscosity, the calculation could again be improved by increasing the size of the molecular dynamics box in one dimension. It is also possible that the expression for the thermal conductivity in terms of the heat current (see Appendix B of Ref. 2) would yield a result which converges more rapidly to the $k = 0$ limit. By choosing $\hat{O} = \hat{J}_x^n$ or $\hat{O} = \hat{T}_{xy}$ in Eq. (3.51) we can again study the coupling between energy current and particle current or energy current and the stress tensor. On grounds of symmetry the cross-correlation functions determining the response must be identical to those introduced in earlier sections.

4. SOLUTION OF THE EQUATIONS OF MOTION AND MEASUREMENT OF THE RESPONSE

In solving the equations of motion of the particles we use for the most part the central-difference or "leap-frog" algorithm described by Verlet.(16) At $t = 0$, however, the perturbation appears as an impulsive force and some modification of the algorithm is needed.

Let h be the time step in the numerical integration. Making a Taylor expansion forward and backward in time about $t = 0$, we find

$$\mathbf{r}_i(h) = \mathbf{r}_i(0+) + \dot{\mathbf{r}}_i(0+)h + \tfrac{1}{2}\ddot{\mathbf{r}}_i(0+)h^2 + O(h^3) \tag{4.1}$$

$$\mathbf{r}_i(-h) = \mathbf{r}_i(0-) - \dot{\mathbf{r}}_i(0-)h + \tfrac{1}{2}\ddot{\mathbf{r}}_i(0-)h^2 + O(h^3) \tag{4.2}$$

Thus, to terms of order h^3, the predicted coordinates at $t = h$ are given by

$$\begin{aligned}\mathbf{r}_i(h) = 2\mathbf{r}_i(0-) - \mathbf{r}_i(-h) + \ddot{\mathbf{r}}_i(0-)h^2 + \{\mathbf{r}_i(0+) - \mathbf{r}_i(0-)\} \\ + \{\dot{\mathbf{r}}_i(0+) - \dot{\mathbf{r}}_i(0-)\}h + \tfrac{1}{2}\{\ddot{\mathbf{r}}_i(0+) - \ddot{\mathbf{r}}_i(0-)\}h^2 \qquad (4.3)\end{aligned}$$

The first three terms on the right-hand side are the customary ones: the three succeeding terms arise from discontinuities in (i) position, (ii) velocity, and (iii) acceleration. Not all the additional terms will contribute in every case. In particular, when the perturbing field acting on particle i is a function solely of its position $\mathbf{r}_i$, the only discontinuity which appears is that in $\dot{\mathbf{r}}_i$.

To see in detail what happens at $t = 0$ it is helpful to rewrite Eq. (2.13) in a form in which the singularity in time appears explicitly. This we achieve by writing

$$\ddot{\mathbf{r}}_i(t) = \mathbf{P}(t) + \mathbf{Q}(t)\,\delta(t) + (d/dt)\{\mathbf{R}(t)\,\delta(t)\} \qquad (4.4)$$

where $\mathbf{P}$, $\mathbf{Q}$, and $\mathbf{R}$ are the regular functions of t defined by

$$m\mathbf{P}(t) = -\partial\mathscr{H}_0/\partial\mathbf{r}_i \qquad (4.5)$$

$$m\mathbf{Q}(t) = \alpha_i\frac{\partial\phi(\mathbf{r}_i)}{\partial\mathbf{r}_i} + \sum_{j=1}^{N}\phi(\mathbf{r}_j)\frac{\partial\alpha_j}{\partial(\mathbf{r}_i)} \qquad (4.6)$$

$$\mathbf{R}(t) = -\phi(\mathbf{r}_i)\,\partial\alpha_i/\partial\mathbf{p}_i \qquad (4.7)$$

In the transverse case the function $\mathbf{P}(t)$ retains the same form, $\mathbf{R}(t)$ is zero, and

$$\mathbf{Q}(t) = \gamma_i\xi(\mathbf{r}_i) \qquad (4.8)$$

By integrating Eq. (4.4) we find that

$$\dot{\mathbf{r}}_i(0+) - \dot{\mathbf{r}}_i(0-) = \lim_{t\to 0+}\int_{0-}^{t}\ddot{\mathbf{r}}_i(t')\,dt' = \mathbf{Q}(0) + \mathbf{R}(0)\,\delta(t) \qquad (4.9)$$

The first term on the right-hand side of (4.9) is just the discontinuity in velocity appearing in Eq. (4.3) and the second term represents an impulsive change in velocity at $t = 0$. The latter gives rise to a discontinuity in coordinates of the form

$$\mathbf{r}_i(0+) - \mathbf{r}_i(0-) = \mathbf{R}(0) \qquad (4.10)$$

This last result follows immediately from integration of the delta-function term in Eq. (4.9).

From the discussion just given we see that if the perturbation is velocity independent, the effect of the applied field appears only as a discontinuity in $\dot{\mathbf{r}}_i$. In the more general case the function $\mathbf{R}(t)$ is nonzero [cf. Eq. (2.13)] and in consequence there is additionally a discontinuity in $\mathbf{r}_i$. This in turn implies a discontinuity in $\ddot{\mathbf{r}}_i$, since the total intermolecular force acting on particle i is a function of the coordinates of all interacting particles. Formulas giving the discontinuities in $\mathbf{r}_i$ and $\dot{\mathbf{r}}_i$ in particular cases can now be obtained by inserting in Eq. (4.6) and (4.7) the corresponding choices for α_i and the applied field, making the appropriate contraction of indices when the latter are vectorial quantities.

We now turn to the question of the computation of the response. The basic procedure we use is illustrated schematically in Fig. 2. The thick curve represents the trajectory in phase space which the system follows in the absence of any applied field. Branching off from this are the trajectories resulting from switching on a perturbation at times 1, 2, 3, 4,.... The response to the perturbation for $t > 0$ is given by

$$\begin{aligned}\langle \hat{O}(\mathbf{k})\rangle_t &= \langle \exp(-i\mathscr{L}t)\, \hat{O}(\mathbf{k})\rangle_0 \\ &= \lim_{\tau\to\infty} \tau^{-1} \int_0^\tau d\tau' \exp(i\mathscr{L}_0\tau') \exp(-i\mathscr{L}t)\, \hat{O}(\mathbf{k}) \qquad (4.11)\end{aligned}$$

It is important to note that the average appearing on the right-hand side of (4.11) is taken over the unperturbed trajectory; the Liouville operators $\mathscr{L}$ and $\mathscr{L}_0$ have the same meaning as in Eq. (1.5). In principle, Eq. (4.11) could be used to calculate directly the mean change in $\hat{O}$ due to the perturbation, since we can always formulate the problem in such a way that $\langle \hat{O}(\mathbf{k})\rangle_0 = 0$. In practice, because the unperturbed trajectory is not of infinite length, the mean value of $\hat{O}$ along that trajectory will invariably have some small but nonzero value. Furthermore, the perturbation used is very small; typically the parameter Φ (or Ξ) is chosen such that the changes in coordinates and momenta are of order one part in 10^6. Thus the systematic response is in general much smaller than the statistical fluctuations. We therefore choose to measure the response in the manner described by Eqs. (1.5) and (1.6), that is to say, by averaging the *difference* in the variable of interest in perturbed and

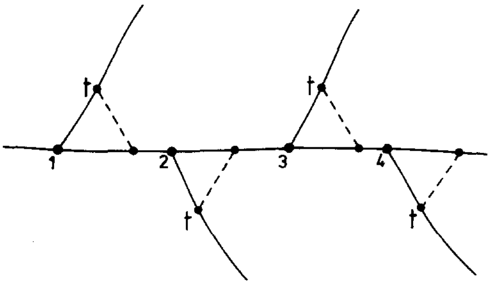

Fig. 2. Schematic illustration of the procedure used in calculating the response. The perturbation is assumed to be switched on at times 1, 2, 3, 4,..., and the broken lines link corresponding points on the perturbed and unperturbed trajectories. Calculation of the difference in the value of a given dynamical variable at two such points yields the mechanical response discussed in the text.

unperturbed trajectories at a time t after the field is switched on. For times which are not too long the improvement achieved is dramatic.

We come finally to a question of purely computational significance. Let us write the coordinates at time $t = h$ in the form

$$\mathbf{r}_i(h) = \mathbf{r}_{i0}(h) + \delta\mathbf{r}_i(h) \tag{4.12}$$

where $\mathbf{r}_{i0}(h)$ are the coordinates at time h in the absence of the perturbation and $\delta\mathbf{r}_i(h)$ is determined by the discontinuities on the right-hand side of (4.3). In principle, we must integrate $\mathbf{r}_i$ and $\mathbf{r}_{i0}$ separately. From the practical point of view this is the simplest way to proceed, but on the other hand it may be computationally more economical to solve instead an approximate differential equation for $\delta\mathbf{r}_i$ itself. The exact equation of motion for $\delta\mathbf{r}_i(t)$ is

$$\begin{aligned} m\,\delta\ddot{\mathbf{r}}_i(t) &= m\ddot{\mathbf{r}}_i(t) - m\ddot{\mathbf{r}}_{i0}(0) \\ &= \mathbf{F}_i(\{\mathbf{r}_j(t)\}) - \mathbf{F}_i(\{\mathbf{r}_{j0}(t)\}) \\ &\quad + \mathbf{Q}(t)\,\delta(t) + (d/dt)\{\mathbf{R}(t)\,\delta(t)\} \end{aligned} \tag{4.13}$$

where $\mathbf{F}_i$ is the force acting on particle i. We can now approximate the difference in internal forces by the first term in the Taylor expansion

$$\begin{aligned} \delta\mathbf{F}_i(t) &= \mathbf{F}_i(\{\mathbf{r}_j(t)\}) - \mathbf{F}_i(\{\mathbf{r}_{j0}(t)\}) \\ &\simeq \sum_{k=1}^{N} \frac{\partial}{\partial\mathbf{r}_{k0}(t)}\,\mathbf{F}_i(\{\mathbf{r}_{j0}(t)\})\cdot\delta\mathbf{r}_k(t) \end{aligned} \tag{4.14}$$

If the potential energy is pairwise additive, Eq. (4.14) may be rewritten as

$$\delta\mathbf{F}_i(t) = \sum_{j\neq i}^{N}\left\{\frac{\delta\mathbf{r}_{ij}}{\mathbf{r}_{ij}}\,v'(r_{ij}) - \frac{\mathbf{r}_{ij}}{r_{ij}}\frac{d}{dr_{ij}}\left(\frac{v'(r_{ij})}{r_{ij}}\right)\mathbf{r}_{ij}\cdot\delta\mathbf{r}_{ij}\right\} \tag{4.15}$$

where

$$\delta\mathbf{r}_{ij} = \delta\mathbf{r}_j(t) - \delta\mathbf{r}_i(t) \tag{4.16}$$

and $\mathbf{r}_{ij}$ is to be evaluated at time t. The justification for this linearization is the observation that the mechanical response is linear with respect to the applied force over an extremely wide range. The equation of motion for $\delta\mathbf{r}_i(t)$ for $t > 0$ is now solved in the usual way by writing

$$\delta\mathbf{r}_i(t+h) = -\delta\mathbf{r}_i(t-h) + 2\delta\mathbf{r}_i(t) + \delta\mathbf{F}_i(t)h^2 \tag{4.17}$$

where $\delta\mathbf{F}_i(t)$ is given by Eq. (4.14). Equation (4.17) is to be solved subject to the initial condition that

$$\delta\mathbf{r}_i(0) = \mathbf{r}_i(0+) - \mathbf{r}_i(0-) \tag{4.18}$$

with $\delta\mathbf{r}_i(h)$ given by Eq. (4.3). The advantage of proceeding in this fashion lies in the fact that $\delta\mathbf{F}_i(t)$ can be computed at rather small cost in the same loop as the calculation of $\mathbf{F}_i(t)$ along the equilibrium trajectory.

If this linearization is used, it is clearly appropriate to measure a response which is also linearized with respect to the phase space variables. This may be achieved by approximating the mechanical response in the form

$$\begin{aligned}&\exp(-i\mathscr{L}t)\,\hat{O}(\mathbf{k}) - \exp(-i\mathscr{L}_0 t)\,\hat{O}(\mathbf{k}) \\ &\quad\simeq \sum_{i=1}^{N} \frac{\partial}{\partial \mathbf{r}_i(t)}\,\hat{O}(\mathbf{k}, t)\cdot\delta\mathbf{r}_i(t) + \frac{\partial}{\partial \mathbf{p}_i(t)}\,\hat{O}(\mathbf{k}, t)\cdot\delta\mathbf{p}_i(t)\end{aligned} \tag{4.19}$$

from which the statistical response can be obtained in the manner already described. Proceeding in this way we find, for example, that the induced particle current [cf. Eq. (1.5)] is given in linearized form by

$$\Delta\hat{J}_x{}^n(\mathbf{k}, t) \simeq \frac{1}{V}\sum_{i=1}^{N} \{\delta\dot{x}_i(t) - ik\dot{x}_i(t)\,\delta x_i(t)\}\exp\{-ikx_i(t)\} \tag{4.20}$$

This linearization is consistent with the linearization of the equations of motion, and furthermore it is much the most sensible method available for computing the response when the equations of motion are solved in linearized form, since in that case the quantities known are not the perturbed coordinates and velocities themselves, but only the differences $\delta\mathbf{r}_i(t)$ and $\delta\dot{\mathbf{r}}_i(t)$. Reconstruction of the perturbed trajectory would obviously be very wasteful. Complete linearization also allows the computations to be carried out in single precision on, for example, IBM computers. Double-precision arithmetic is essential when the full equations of motion are solved along the perturbed trajectory. It must be said, however, that for the stress tensor and the energy current the calculation of the linearized response adds substantially to the length of the computation. When complete linearization is adopted the strength of the perturbing field enters only as a multiplicative factor.

5. DISCUSSION

The method we have described differs from other nonequilibrium molecular dynamics techniques(13,17–19) primarily insofar as the perturbation used is very small. This has two important consequences. First, the results obtained may legitimately be interpreted in the framework of linear response theory. Second, we avoid the systematic heating up of the system, energy drift, and other undesirable effects associated with the use of strong external fields. The method therefore represents a direct and economical means of studying the dynamical properties of liquids. Furthermore, again in contrast to other work, the method yields the complete, frequency-dependent response of the system as described by the corresponding time correlation function. The saving in cost which can be achieved is very considerable. In the calculation of electrical conductivity, for example, we find(6) a reduction in computing time by a factor of approximately five compared with that required with the conventional equilibrium technique.(20) Its main disadvantage is the fact that, except in special cases, it is limited to the study of the response to a disturbance having a finite wavelength. This creates difficulties when the quantity sought is the value of a transport coefficient. A less serious problem is the fact that it cannot be used for the study of very long-time (low-frequency) behavior, since in that case the correlation between perturbed and unperturbed trajectories is lost and the subtraction technique is no longer useful. In practical terms this limits its application to times which, for monatomic systems, are typically of order 200 integration steps. The accuracy of the algorithm which is used is here an important factor. In particular there is a strong case for adopting a more accurate scheme for calculating the velocities of the particles than that usually adopted with the leap-frog scheme. We should point out finally that though we have limited the discussion to the case of collective dynamical properties, the method is also very well suited to the study of single-particle motion. In general, of course, such phenomena are easily studied by the usual methods. However, in the case of molecules in solution, particularly very dilute solutions, there is obvious scope for application of a suitably modified form of the method we describe. By proceeding in this way it should be straightforward to compute quantities such as the mobility of an ion in a polar solvent, the reorientational correlation times of, say, a single molecule in an inert gas medium, the intrinsic viscosity of polyatomic molecules, and so on. We hope to return to some of these questions in a later publication.

REFERENCES

1. R. Kubo, *J. Phys. Soc. Jpn.* **12**:570 (1957).
2. J. M. Luttinger, *Phys. Rev.* **135**:A1505 (1964).
3. J. L. Jackson and P. Mazur, *Physica* **30**:2295 (1964).
4. R. Zwanzig, *Ann. Rev. Phys. Chem.* **16**:67 (1965).
5. G. Ciccotti and G. Jacucci, *Phys. Rev. Lett.* **35**:789 (1975).
6. G. Ciccotti, G. Jacucci, and I. R. McDonald, *Phys. Rev. A* **13**:426 (1976).
7. G. Ciccotti, G. Jacucci, and I. R. McDonald, *J. Phys. C: Solid State* **11**:L509 (1978).
8. R. Kubo, *Rep. Prog. Phys.* **29**:255 (1966).
9. E. Helfand, *Phys. Rev.* **119**:1 (1960).
10. J. R. D. Copley and S. W. Lovesey, *Rep. Prog. Phys.* **38**:461 (1975).
11. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1976).
12. A. Michels, H. Wijker, and Hk. Wijker, *Physica* **15**:627 (1949).
13. E. M. Gosling, I. R. McDonald, and K. Singer, *Mol. Phys.* **26**:1475 (1973).

14. D. Levesque, L. Verlet, and J. Kürkijarvi, *Phys. Rev. A* **7**:1690 (1973).
15. G. Jacucci, I. R. McDonald, and A. Rahman, *Phys. Rev. A* **13**:1581 (1976).
16. L. Verlet, *Phys. Rev.* **163**:201 (1968).
17. W. T. Ashurst and W. G. Hoover, *Phys. Rev. Lett.* **31**:206 (1973).
18. W. T. Ashurst and W. G. Hoover, in *Theoretical Chemistry: Advances and Perspectives*, H. Eyring and D. Henderson, eds. (Academic Press, New York, 1975), Vol. 1.
19. D. J. Evans, *Mol. Phys.*, to appear.
20. J. P. Hansen and I. R. McDonald, *Phys. Rev. A* **11**:2111 (1975).