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Mode-Coupling Theory for Purely Diffusive Systems

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A mode-coupling formalism is developed for multicomponent systems of particles performing diffusive motion in a uniform host medium. The mode-coupling equations are derived from a set of nonlinear fluctuating diffusion equations by expanding the concentration-dependent diffusion constants about their equilibrium values. From the mode-coupling equations the dominant long time behavior of current–current and super-Burnett correlation functions is derived. As specific applications I consider the long time behaviors of these correlation functions for collective and tracer diffusion in a one-component lattice gas with particle-conserving stochastic dynamics. The results agree with those from exactly solvable models and computer simulations.

KEY WORDS: Mode-coupling equations; diffusion; long time tails; Kawasaki dynamics.

1. INTRODUCTION

Mode-coupling theories have proved their great value both in the description of dynamical critical phenomena(1) and in calculations of long time tails in time correlation functions such as the autocorrelation function of the velocity of a tagged particle.(2) Here I want to concentrate on the latter type of applications. For the current–current correlation functions related to transport coefficients in a fluid, mode-coupling theory predicts a long time decay proportional to $t^{-d/2}$, with coefficients that can be expressed explicitly in terms of transport coefficients and thermodynamic functions.(2,3) Agreement of these predictions with other theories(2,4–7) as well as with results of computer simulations(8) is good; real experiments so far have failed to provide reliable information on long time tails. Up until

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recently no comparable mode-coupling theory has been available for purely diffusive systems; for example, systems of noninteracting particles moving in a random potential, a specific example of which is the Lorentz gas.(9) At low scatterer density kinetic theory predicts for this model a $t^{-(d/2+1)}$ long time tail for the velocity autocorrelation function of the moving particles,(10) with a coefficient that can be expressed in terms of the diffusion coefficient. Computer simulations, however, show that this coefficient remains valid over a very restricted density range only,(11) hence it would be desirable to avail ourselves of a theory usable at general density. Ernst *et al.*(12) have developed such a theory for diffusive motion of mutually independent particles in a spatially fluctuating stationary medium, which can be applied to the Lorentz gas among other systems. Here I will develop a similar theory for the case of diffusive systems consisting of one or more species of interacting particles, moving in a uniform medium. Examples are lattice gas models with Kawasaki dynamics(13) and systems with interacting Brownian particles.

The scheme of the paper is as follows: In Section 2 fluctuating diffusion equations are introduced and formal relations between correlation functions are discussed. In Section 3 the mode-coupling equations are derived and in Section 4 some applications are presented. In a concluding section the results are summarized and commented upon.

2. FLUCTUATING DIFFUSION EQUATIONS. RELATIONS BETWEEN TIME CORRELATION FUNCTIONS

Consider a system at fixed temperature $T = (k_B \beta)^{-1}$, where k_B is Boltzmann's constant, and with n particle species, to be denoted by an index α. The equilibrium concentrations c_α are summarized into a vector $\mathbf{c}$, and the chemical potentials μ_α likewise into a vector $\boldsymbol{\mu}$. Local fluctuating concentrations and chemical potentials are denoted as $\mathbf{c}(\vec{r}, t)$ and $\boldsymbol{\mu}(\vec{r}, t)$, respectively. If energy (but not momentum) of the system is conserved this may be accounted for by identifying one of the c_α with energy density and one of the μ_α with temperature. Assume that $\mathbf{c}$ and $\boldsymbol{\mu}$ satisfy a set of fluctuating diffusion equations of the form

$$\frac{\partial \mathbf{c}(\vec{r}, t)}{\partial t} = \nabla \cdot \overline{\overline{L}}(\mathbf{c}(\vec{r}, t)) \circ \nabla(\beta \boldsymbol{\mu}(\vec{r}, t)) + \mathbf{F}^L(\vec{r}, t) \tag{1a}$$

$$= \nabla \cdot \overline{\overline{D}}(\mathbf{c}(\vec{r}, t)) \circ \nabla \mathbf{c}(\vec{r}, t) + \mathbf{F}^L(\vec{r}, t) \tag{1b}$$

Here the closed dot denotes a contraction in real space and the open dot a contraction in "concentration space."

A basic assumption to be made here is that in the systems under consideration concentrations will be the only independent conserved densities, this in contrast to the systems treated in Ref. 12. Then the matrix of Onsager coefficients $\overline{\overline{L}}$ will depend on time and position only through the local concentrations. In addition these coefficients will satisfy the Onsager symmetry relations

$$L_{\alpha\gamma} = L_{\gamma\alpha} \tag{2}$$

The matrix D of diffusion coefficients is related to $\overline{\overline{L}}$ as

$$\overline{\overline{D}} = \overline{\overline{L}} \circ \overline{\overline{\mathsf{C}}} \tag{3}$$

where the matrix $\overline{\overline{\mathsf{C}}}$ of direct correlation functions is defined by

$$\mathsf{C}_{\alpha\gamma} = \frac{\partial(\beta\mu)_\alpha}{\partial c_\gamma} \tag{4}$$

The random forces driving the fluctuations are contained in $\mathbf{F}^L(t)$ and are assumed, as usual, to be independent of the previous history.

Before introducing the mode-coupling formalism it seems useful summarizing briefly how correlation functions of currents and their long time tails are related to time correlation functions of concentrations. Suppose the fluctuating concentrations satisfy an effective nonlocal noninstantaneous linear diffusion equation of the form

$$\frac{\partial}{\partial t}\mathbf{c}(\vec{r},t) = -\nabla \cdot \int d\vec{\rho} \int_0^t d\tau\, \overline{\overline{d}}(\rho,\tau) \circ \nabla \mathbf{c}(\vec{r}-\vec{\rho}, t-\tau) \tag{5}$$

A Fourier transform with respect to space coordinates and a Laplace transform with respect to time yields

$$\left(z + \overline{\overline{D}}(k,z)\right) \circ \hat{\mathbf{c}}(\vec{k},z) = \hat{\mathbf{c}}(\vec{k}) \tag{6}$$

with $\overline{\overline{D}}(k,z)$ the Fourier and Laplace transform of $\overline{\overline{d}}(r,t)$, $\hat{\mathbf{c}}(\vec{k},z)$ that of $\mathbf{c}(\vec{r},t)$ and $\hat{\mathbf{c}}(\vec{k})$ the Fourier transform of $\mathbf{c}(\vec{r},0)$. Then the Fourier and Laplace transformed equilibrium time correlation functions between concentrations satisfy the relation

$$\langle \hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k},z)\rangle = \langle \hat{\mathbf{c}}(-\vec{k})\left(z + k^2\overline{\overline{D}}(k,z)\right)^{-1} \circ \hat{\mathbf{c}}(\vec{k})\rangle \tag{7a}$$

$$= \langle \hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle \circ \left(z + k^2\overline{\overline{D}}^\dagger(k,z)\right)^{-1} \tag{7b}$$

where the brackets denote an equilibrium average over the initial fluctuations and $\overline{\overline{D}}^\dagger$ is the $n \times n$ matrix adjoint to $\overline{\overline{D}}$. Next one may split up $\overline{\overline{D}}(k,z)$ as

$$\overline{\overline{D}}(k,z) = \overline{\overline{D}} + \Delta\overline{\overline{D}}(k,z) \tag{8}$$

where $\overline{\overline{D}} = \lim_{z\to 0}\lim_{k\to 0}\overline{\overline{D}}(k,z)$ should satisfy $\overline{\overline{D}} = \overline{\overline{D}}(\mathbf{c})$. Furthermore one has the compressibility equations

$$\lim_{k\to 0}\langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle = \frac{\partial\mathbf{n}}{\partial\beta\boldsymbol{\mu}} = \overline{\overline{\mathrm{C}}}^{-1} \tag{9}$$

Hence, by expanding (7) in powers of $\Delta\overline{\overline{D}}$ and using (2), (3), and (9) one finds

$$\begin{aligned}
&\langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k},z)\rangle \\
&= \langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle \circ \Big\{\big(z + k^2\overline{\overline{D}}{}^{\dagger}\big)^{-1} - \big(z + k^2\overline{\overline{D}}{}^{\dagger}\big)^{-1} \\
&\qquad \circ k^2\Delta\overline{\overline{D}}{}^{\dagger}(k,z)\circ\big(z + k^2\overline{\overline{D}}{}^{\dagger}\big)^{-1} + \cdots\Big\} \qquad (10a) \\
&= \langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle \circ \big(z + k^2\overline{\overline{D}}{}^{\dagger}\big)^{-1} - \big(z + k^2\overline{\overline{D}}\big)^{-1} \circ \langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle \\
&\quad \circ k^2\Delta\overline{\overline{D}}{}^{\dagger}(k,z)\circ\big(z + k^2\overline{\overline{D}}{}^{\dagger}\big)^{-1} \qquad (10b) \\
&= \langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle \circ \big(z + k^2\overline{\overline{D}}{}^{\dagger}\big)^{-1} \\
&\quad - \big(z + k^2\overline{\overline{D}}\big)^{-1} \circ k^2\Delta\overline{\overline{L}}(k,z)\circ\big(z + k^2\overline{\overline{D}}{}^{\dagger}\big)^{-1} \qquad (10c)
\end{aligned}$$

In (10b) and (10c) terms of $O(\Delta^2)$ were neglected. Furthermore for small k $\langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle$ was replaced by its limit as $k\to 0$, which is consistent with the assumption that $\overline{\overline{D}}(\vec{r})$ and $\overline{\overline{L}}(\vec{r})$ depend only locally on the concentrations. Finally $\Delta\overline{\overline{L}}$ is defined similarly as $\Delta\overline{\overline{D}}$.

The relation between concentration and current correlation functions may be established by starting from the local conservation laws

$$\frac{\partial}{\partial t}\mathbf{c}(\vec{r},t) = -\nabla\cdot\vec{\mathbf{j}}(\vec{r},t) \tag{11}$$

After Fourier transforming one obtains the following identity between correlation functions

$$\Big\langle\frac{\partial}{\partial t_0}\hat{\mathbf{c}}(-\vec{k},t_0)\frac{\partial}{\partial t}\hat{\mathbf{c}}(\vec{k},t_0+t) = k^2\Big\langle\Big(\hat{\vec{k}}\cdot\hat{\vec{\mathbf{j}}}(-\vec{k},t_0)\Big)\Big(\hat{\vec{k}}\cdot\hat{\vec{\mathbf{j}}}(\vec{k},t_0+t)\Big)\Big\rangle \tag{12}$$

with $\hat{\vec{k}} = \vec{k}/|\vec{k}|$. By virtue of time translation invariance the left-hand side may be transformed to

$$-\langle\hat{\mathbf{c}}(-\vec{k},t_0)\frac{\partial}{\partial t_0}\frac{\partial}{\partial t}\hat{\mathbf{c}}(\vec{k},t_0+t)\rangle = -\langle\hat{\mathbf{c}}(-\vec{k},t_0)\frac{\partial^2}{\partial t^2}\hat{\mathbf{c}}(\vec{k},t_0+t)\rangle$$

Then a Laplace transform yields

$$z^2\langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k},z)\rangle = \langle\hat{\mathbf{c}}(-\vec{k})i\vec{k}\cdot\hat{\vec{\mathbf{j}}}(\vec{k})\rangle + z\langle\hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle - k^2\langle\big(\hat{\vec{k}}\cdot\hat{\vec{\mathbf{j}}}(-\vec{k})\big)\big(\hat{\vec{k}}\cdot\hat{\vec{\mathbf{j}}}(\vec{k},z)\big)\rangle \tag{13}$$

The first term on the right-hand side of this equation vanishes[2] on behalf of the isotropy of the equilibrium current distribution. Inserting (7b) on the left-hand side and performing some algebra one finds with the aid of (3) and (9) the result

$$\bar{\bar{L}}(k,z) = \left\{1 - \frac{k^2}{z}\langle\big(\hat{\vec{k}}\cdot\hat{\vec{\mathbf{j}}}(-\vec{k})\big)\big(\hat{\vec{k}}\cdot\vec{\mathbf{j}}(\vec{k},z)\big)\rangle\circ\bar{\bar{\mathsf{C}}}\circ\right\} \langle\big(\hat{\vec{k}}\cdot\hat{\vec{\mathbf{j}}}(-\vec{k})\big)\big(\hat{\vec{k}}\cdot\vec{\mathbf{j}}(\vec{k},z)\big)\rangle \tag{14}$$

At fixed z, $\bar{\bar{L}}(k,z)$ may be expanded as

$$\bar{\bar{L}}(k,z) = \bar{\bar{L}}_0(z) - k^2\bar{\bar{L}}_2(z) + \cdots \tag{15}$$

with an inverse Laplace transform

$$\bar{\bar{\phi}}(k,t) = \bar{\bar{\phi}}^{(2)}(t) - k^2\bar{\bar{\phi}}^{(4)}(t) \tag{16}$$

Ths shift of indices compared to (15) is made to conform to the existing literature.(11) The coefficients $\bar{\bar{L}}_0$ and $\bar{\bar{L}}_2$ may be interpreted as z-dependent ordinary diffusion coefficients and super-Burnett coefficients, respectively. For large t, $\bar{\bar{\phi}}^{(2)}$ and $\bar{\bar{\phi}}^{(4)}$ describe the long time behavior of the corresponding correlation functions. The latter may be identified from (14). Set

$$\langle\big(\hat{\vec{k}}\cdot\hat{\vec{\mathbf{j}}}(-\vec{k})\big)\big(\hat{\vec{k}}\cdot\hat{\vec{\mathbf{j}}}(\vec{k},t)\big)\rangle = \bar{\bar{\Lambda}}_0(t) - k^2\bar{\bar{\Lambda}}_2(t) + \cdots \tag{17}$$

Then one has

$$\phi^{(2)}(t) = \bar{\bar{\Lambda}}_0(t) \tag{18}$$

$$\phi^{(4)}(t) = \bar{\bar{\Lambda}}_2(t) - \int_0^t dt'\int_0^t d\tau\,\bar{\bar{\Lambda}}_0(\tau)\circ\bar{\bar{\mathsf{C}}}\circ\bar{\bar{\Lambda}}_0(t'-\tau) \tag{19}$$

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[2] Strictly speaking this is only unambiguously true if no instantaneous jumps may occur. If such jumps are possible the density–current correlation function should be interpreted as

$$\langle\hat{\mathbf{c}}(-\vec{k})\vec{k}\cdot\hat{\vec{\mathbf{j}}}(\vec{k})\rangle = \lim_{t\to 0}\tfrac{1}{2}\langle\hat{\mathbf{c}}(-\vec{k})\vec{k}\cdot\big(\hat{\vec{\mathbf{j}}}(\vec{k},t) + \hat{\vec{\mathbf{j}}}(\vec{k},-t)\big)\rangle$$

This vanishes under time reversal symmetry. If in the limit $t\to 0$ a correlation between $\hat{\mathbf{c}}(-\vec{k})$ and $\vec{\mathbf{j}}(k,t)$ remains, this is included as a frequency-independent term in the current–current correlation function $\langle\hat{\vec{\mathbf{j}}}(-\vec{k})\hat{\vec{\mathbf{j}}}(\vec{k},z)\rangle$.

3. MODE-COUPLING EQUATIONS

After these preliminaries the mode-coupling formalism is developed from (1) by expanding $\overline{\overline{D}}(\vec{r}, t)$ in deviations from its equilibrium value $\overline{\overline{D}}$. In order to obtain the leading long time tail contributions to the current–current time correlation functions it suffices to consider the first deviation from equilibrium. Using this approximation in (1) and applying a spatial Fourier transform one obtains the result

$$\frac{\partial}{\partial t}\hat{\mathbf{c}}(\vec{\mathbf{k}}, t) = -k^2\overline{\overline{D}} \circ \hat{\mathbf{c}}(\vec{k}, t) + \frac{1}{V}\sum_{\vec{q}} \overline{\overline{\overline{A}}}(\vec{q}, \vec{k}) \mathbin{\overset{\circ}{\circ}} \hat{\mathbf{c}}(\vec{k} - \vec{q}, t)\hat{\mathbf{c}}(\vec{q}, t) + \hat{\mathbf{F}}^L(\vec{k}, t) \tag{20}$$

where

$$A_{\alpha\beta\gamma}(\vec{q}, \vec{k}) = -(\vec{k} \cdot \vec{q})\frac{\partial D_{\alpha\beta}}{\partial c_\gamma} \tag{21}$$

Further $(\overline{\overline{\overline{A}}} \mathbin{\overset{\circ}{\circ}} \overline{\overline{B}})_\alpha = A_{\alpha\beta\gamma}B_{\gamma\beta}$, with summation over repeated indices. Equation (20) can be transformed into an integral equation

$$\hat{\mathbf{c}}(\vec{k}, t) = e^{-\overline{\overline{D}}k^2 t} \circ \hat{\mathbf{c}}(\vec{k}, 0) + \int_0^t d\tau\, e^{-\overline{\overline{D}}k^2\tau} \circ \hat{\mathbf{F}}^L(\vec{k}, t - \tau)$$

$$+ \frac{1}{V}\sum_{\vec{q}} \int_0^t d\tau\, e^{-\overline{\overline{D}}k^2\tau} \circ \overline{\overline{\overline{A}}}(\vec{q}, \vec{k}) \mathbin{\overset{\circ}{\circ}} \hat{\mathbf{c}}(\vec{k} - \vec{q}, t - \tau)\hat{\mathbf{c}}(\vec{q}, t - \tau) \tag{22}$$

The first term on the right-hand side of this equation is the solution of the unperturbed diffusion equation, the other two terms result from fluctuations. Next, consider the concentration correlation functions, which can be obtained from (22) as

$$\langle\hat{\mathbf{c}}(-\vec{k}, 0)\hat{\mathbf{c}}(\vec{k}, t)\rangle = \langle\hat{\mathbf{c}}(-\vec{k})e^{-\overline{\overline{D}}k^2 t} \circ \hat{\mathbf{c}}(\vec{k})\rangle + \frac{1}{V}\sum_{\vec{q}} \int_0^t d\tau$$

$$\times \langle\hat{\mathbf{c}}(-\vec{k})e^{-\overline{\overline{D}}k^2\tau} \circ \overline{\overline{\overline{A}}}(\vec{q}, \vec{k}) \mathbin{\overset{\circ}{\circ}} \hat{\mathbf{c}}(\vec{k} - \vec{q}, t - \tau)\hat{\mathbf{c}}(\vec{q}, t - \tau)\rangle$$

$$+ \int_0^t d\tau\, \langle\hat{\mathbf{c}}(-\vec{k})e^{-\overline{\overline{D}}k^2\tau} \circ \hat{\mathbf{F}}^L(\vec{k}, t - \tau)\rangle \tag{23}$$

Now the equilibrium average runs both over all initial fluctuations $\hat{\mathbf{c}}(-\vec{k})$ and over all the values of the random forces. The last term in (23) vanishes due to the properties of the latter. For the second term on the right-hand side of this equation it is convenient to use time-reversal symmetry in order to recast it into the form

$$\begin{aligned}\langle \hat{\mathbf{c}}(-\vec{k},0)\hat{\mathbf{c}}(\vec{k},t)\rangle &= \langle \hat{\mathbf{c}}(-\vec{k})e^{-\overline{\overline{D}}k^2t} \circ \hat{\mathbf{c}}(\vec{k})\rangle \\ &\quad + \frac{1}{V}\sum_{\vec{q}}\int_0^t d\tau\,\langle \hat{c}(-\vec{k},t-\tau)e^{-\overline{\overline{D}}k^2\tau} \\ &\quad \circ \overset{\equiv}{A}(\vec{q},\vec{k}) \overset{\circ}{\underset{\circ}{}} \hat{\mathbf{c}}(\vec{k}-q)\hat{\mathbf{c}}(\vec{q})\rangle \end{aligned} \tag{24}$$

Inserting (4) into this equation for $\hat{\mathbf{c}}(-\vec{k},t-\tau)$ one obtains

$$\begin{aligned}\langle \hat{\mathbf{c}}(-\vec{k},0)\hat{\mathbf{c}}(\vec{\mathbf{k}},t)\rangle &= \langle \hat{\mathbf{c}}(-\vec{k})e^{-\overline{\overline{D}}k^2t} \circ \hat{\mathbf{c}}(\vec{k})\rangle + \frac{1}{V}\sum_{\vec{q}}\int_0^t d\tau \\ &\quad \left\langle \left(e^{-\overline{\overline{D}}k^2(t-\tau)} \circ \hat{\mathbf{c}}(-\vec{k})\right)e^{-\overline{\overline{D}}k^2\tau} \circ \overset{\equiv}{A}(\vec{q},\vec{k}) \overset{\circ}{\underset{\circ}{}} \hat{\mathbf{c}}(\vec{k}-\vec{q})\hat{\mathbf{c}}(\vec{q})\right\rangle \\ &\quad + \frac{1}{V^2}\sum_{\vec{q}}\sum_{\vec{l}}\int_0^t d\tau\int_0^{t-\tau} d\tau' \\ &\quad \left\langle \left(e^{-\overline{\overline{D}}k^2\tau'} \circ \overset{\equiv}{A}(\vec{l},-\vec{k}) \overset{\circ}{\underset{\circ}{}} \hat{\mathbf{c}}(-\vec{k}-\vec{l},t-\tau-\tau')\hat{\mathbf{c}}(\vec{l},t-\tau-\tau')\right)\right. \\ &\quad \left. \times e^{-\overline{\overline{D}}k^2\tau} \circ \overset{\equiv}{A}(\vec{q},\vec{k}) \overset{\circ}{\underset{\circ}{}} \hat{c}(\vec{k}-\vec{q})\hat{c}(\vec{q})\right\rangle \end{aligned} \tag{25}$$

The dominant contribution to this expression is obtained by inserting for the time-dependent concentrations the leading order approximations, $\hat{\mathbf{c}}(\vec{l},t-\tau-\tau') = \exp(-\overline{\overline{D}}l^2(t-\tau-\tau')) \circ \hat{\mathbf{c}}(\vec{l})$, etc. Furthermore one has to use the well-known property$^{(1)}$ that in the thermodynamic limit the dominant contributions to static four-point correlation functions are those that can be factorized into two-point correlation functions, viz.,

$$\begin{aligned}&\langle \hat{c}_\alpha(\vec{q})\hat{c}_\beta(\vec{k}-\vec{q})\hat{c}_\gamma(\vec{l}\,)\hat{c}_\delta(-\vec{k}-\vec{l}\,)\rangle \\ &\quad = V\big[\delta_{\vec{q},-\vec{l}}\langle \hat{c}_\alpha(\vec{q})\hat{c}_\gamma(-\vec{q})\rangle\langle \hat{c}_\beta(\vec{k}-\vec{q})\hat{c}_\delta(\vec{q}-\vec{k})\rangle \\ &\qquad + \delta_{\vec{q}-\vec{k},\vec{l}}\langle \hat{c}_\alpha(\vec{q})\hat{c}_\delta(-\vec{q})\rangle\langle \hat{c}_\beta(\vec{k}-\vec{q})\hat{c}_\gamma(\vec{q}-\vec{k})\rangle \\ &\qquad + \delta_{\vec{k},\vec{0}}\langle \hat{c}_\alpha(\vec{q})\hat{c}_\beta(-\vec{q})\rangle\langle \hat{c}_\gamma(\vec{l}\,)\hat{c}_\delta(-\vec{l}\,)\rangle\big] + O(1)\end{aligned} \tag{26}$$

The last term between the square brackets is unimportant to us, because $\overset{\equiv}{A}(\vec{q},0) = 0$, according to (21). I further introduce the symbols $\overset{\equiv}{\widehat{A}}$ with $\widehat{A}_{\alpha\beta\gamma} = A_{\alpha\gamma\beta}$; $\overset{\equiv}{A}{}^\dagger$, with $A^\dagger_{\alpha\beta\gamma} = A_{\gamma\beta\alpha}$ and $\overset{\equiv}{\widehat{A}}{}^\dagger$, with $\widehat{A}^\dagger_{\alpha\beta\gamma} = A_{\beta\gamma\alpha}$. Then, applying a Laplace transform to (25) one obtain as dominant contributions

$$
\begin{aligned}
&\langle \hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k},z)\rangle \\
&\quad = \langle \hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle \circ \left(z + k^2\overline{\overline{D}}^{\dagger}\right)^{-1} + \left(z + k^2\overline{\overline{D}}\right)^{-1} \\
&\qquad \circ \frac{1}{V}\sum_{\vec{q}} \langle \hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{q})\hat{\mathbf{c}}(\vec{k}-\vec{q})\rangle \mathbin{\overset{\circ}{\circ}} \overline{\overline{\overline{A}}}^{\dagger}(\vec{q},\vec{k}) \circ \left(z + k^2\overline{\overline{D}}^{\dagger}\right)^{-1} \\
&\qquad + \left(z + k^2\overline{\overline{D}}\right)^{-1} \circ \frac{1}{V^2}\sum_{\vec{q}} \frac{1}{2}\left\{\overline{\overline{\overline{A}}}(-\vec{q},-\vec{k}) + \overline{\overline{\overline{\widehat{A}}}}(\vec{q}-\vec{k},-\vec{k})\right\} \\
&\qquad \mathbin{\overset{\circ}{\circ}} \left(z + q^2\overline{\overline{D}}^{(1)} + |\vec{k}-\vec{q}|^2\overline{\overline{D}}^{(2)}\right)^{-1} \mathbin{\overset{\circ}{\circ}} \langle \hat{\mathbf{c}}^{(1)}(-\vec{q})\hat{\mathbf{c}}^{(2)}(\vec{q}-\vec{k})\hat{\mathbf{c}}(\vec{q})\hat{\mathbf{c}}(\vec{k}-\vec{q})\rangle \\
&\qquad \mathbin{\overset{\circ}{\circ}} \left\{\overline{\overline{\overline{A}}}^{\dagger}(\vec{q},\vec{k}) + \overline{\overline{\overline{\widehat{A}}}}^{\dagger}(\vec{k}-\vec{q},\vec{k})\right\} \circ \left(z - k^2\overline{\overline{D}}^{\dagger}\right)^{-1}
\end{aligned}
\tag{27}
$$

Here the superscripts (1) and (2) serve to indicate that $\overline{\overline{D}}^{(1)}$ acts upon $\hat{\mathbf{c}}^{(1)}$ and $\overline{\overline{D}}^{(2)}$ acts upon $\hat{\mathbf{c}}^{(2)}$ only.[3]

On comparing (27) to (10c) one sees that the second term on the right-hand side of (27) at most contributes a term that is independent of z to $\Delta\overline{\overline{L}}$, therefore is unimportant for the long time tails. The dominant small-z behavior of $\Delta\overline{\overline{L}}$ is entirely due to the last term in (27) and is to be obtained from

$$
\begin{aligned}
\Delta\overline{\overline{L}}(k,z) = \frac{1}{2V^2k^2}\sum_{\vec{q}} &\left\{\overline{\overline{\overline{A}}}(-\vec{q},-\vec{k}) + \overline{\overline{\overline{\widehat{A}}}}(\vec{q}-\vec{k},-\vec{k})\right\} \\
&\mathbin{\overset{\circ}{\circ}} \left(z + q^2\overline{\overline{D}}^{(1)} + |\vec{k}-\vec{q}|^2\overline{\overline{D}}^{(2)}\right)^{-1} \\
&\mathbin{\overset{\circ}{\circ}} \langle \hat{\mathbf{c}}^{(1)}(-\vec{q})\hat{\mathbf{c}}^{(2)}(\vec{q}-\vec{k})\hat{\mathbf{c}}(\vec{q})\hat{\mathbf{c}}(\vec{k}-\vec{q})\rangle \\
&\mathbin{\overset{\circ}{\circ}} \left\{\overline{\overline{\overline{A}}}^{\dagger}(\vec{q},\vec{k}) + \overline{\overline{\overline{\widehat{A}}}}^{\dagger}(\vec{k}-\vec{q},\vec{k})\right\}
\end{aligned}
\tag{28}
$$

This is the central result of this paper. In the limit $k \to 0$ (28) generally assumes the form of an integral of type

$$
\int d\vec{q}\, \frac{-\left\{a(\vec{q}\cdot\vec{k})^2 + bk^2\right\}}{z + cq^2}
$$

which, after an inverse Laplace transform is proportional to

$$
-\left\{\frac{a}{2c}t^{-(d/2+1)} + bk^2t^{-d/2}\right\}
$$

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[3] In (27) the factorization given in (26) is left implicit in order to preserve the proper sequence of symbols in the double dot products.

This implies that the current–current correlation functions $\phi^{(2)}(t)$ in general decay as $t^{-(d/2+1)}$ and the super-Burnett correlation functions $\phi^{(4)}(t)$ decay as $t^{-d/2}$ in d dimensions. It is possible, however, that a or b vanish for certain specific reasons.

4. APPLICATIONS

The simplest system to which to apply (28) probably is the one-component lattice gas. For collective diffusion all matrices reduce to scalars and one has $D = D(c)$ and $A(\vec{q}, \vec{k}) = -(\vec{k} \cdot \vec{q})(\partial D/\partial c)$. Switching from $\vec{q}$ to $\vec{q} + \frac{1}{2}\vec{k}$ for the integration variable in (28) and using (21) for A, one immediately sees that $\phi^{(2)}(t)$ vanishes. By similar arguments one can show that also all higher-order mode-coupling contributions to $\phi^{(2)}(t)$ vanish for a one-component system.[4] The dominant long time contribution to $\phi^{(4)}(t)$ takes the form

$$\begin{aligned}\phi^{(4)}(t) &= \frac{\left\{(\partial D/\partial c)\lim_{k\to 0}\langle \hat{c}(-\vec{k})\hat{c}(\vec{k})\rangle\right\}^2}{2(2\pi)^d}\int d\vec{q}\, e^{-2Dq^2t}\\ &= 2^{-(d+1)}\left(\frac{\partial D}{\partial \beta\mu}\right)^2 (2\pi D t)^{-d/2}\end{aligned} \tag{29}$$

Next consider tracer diffusion in a one-component system of N particles in a volume V, N_t of which are tracer particles, identical in properties to the other particles. Now one has to introduce a two-component concentration vector $\mathbf{c}(\vec{r}, t)$. I will set $c_1 = c$, and $c_2 = c_t$, the concentration of tracer particles. The Onsager coefficients form a 2×2 matrix. The equilibrium values of its matrix elements are given as

$$L_{11} = \frac{1}{V}\left\langle \int_0^\infty dt \sum_{i=1}^{N}\sum_{j=1}^{N}\left(\hat{\vec{k}}\cdot\vec{v}_i(0)\right)\left(\hat{\vec{k}}\cdot\vec{v}_j(t)\right)\right\rangle \equiv L \tag{30}$$

$$\begin{aligned}L_{22} &= \frac{1}{V}\left\langle \int_0^\infty dt \sum_{i=1}^{N_t}\sum_{j=1}^{N_t}\left(\hat{\vec{k}}\cdot\vec{v}_i(0)\right)\left(\hat{\vec{k}}\cdot\vec{v}_j(t)\right)\right\rangle\\ &= (c_t/c)^2 L + c_t(1 - c_t/c)D_s\end{aligned} \tag{31}$$

$$L_{12} = L_{21} = \frac{1}{V}\left\langle \int_0^\infty dt \sum_{i=1}^{N}\sum_{j=1}^{N_t}\left(\hat{\vec{k}}\cdot\vec{v}_i(0)\right)\left(\hat{\vec{k}}\cdot\vec{v}_j(t)\right)\right\rangle = (c_t/c)L \tag{32}$$

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[4] This conclusion has to be relaxed in case the diffusion coefficient depends nonlocally on density. However, in order to obtain a nonvanishing long time tail, one has to couple the density fluctuations to products of at least three modes with a nonlocal vertex function. This gives rise to a long time behavior not slower than a t^{-d-3} power.

with $\vec{k}$ chosen in an arbitrary direction and the self-diffusion coefficient given as usual by

$$D_s = \int_0^\infty dt \left\langle \left(\hat{\vec{k}} \cdot \vec{v}_1(0)\right)\left(\hat{\vec{k}} \cdot \vec{v}_1(t)\right)\right\rangle \tag{33}$$

The matrix of correlation functions is given as

$$\lim_{k\to 0} \frac{1}{V} \langle \hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle = \frac{\partial \mathbf{c}}{\partial \beta \boldsymbol{\mu}} = \begin{vmatrix} \langle \hat{c}\hat{c}\rangle & \frac{c_t}{c}\langle \hat{c}\hat{c}\rangle \\ \frac{c_t}{c}\langle \hat{c}\hat{c}\rangle & \left(\frac{c_t}{c}\right)^2 \langle \hat{c}\hat{c}\rangle + c_t\left(1 - \frac{c_t}{c}\right) \end{vmatrix} \tag{34}$$

where $\langle \hat{c}\hat{c}\rangle = \lim_{k\to 0}(1/V)\langle \hat{\mathbf{c}}(-\vec{k})\hat{\mathbf{c}}(\vec{k})\rangle$. After inversion of this matrix one obtains the diffusion matrix $\overline{\overline{D}}$ through

$$\overline{\overline{D}} = \overline{\overline{L}} \circ \frac{\partial \beta \boldsymbol{\mu}}{\partial \mathbf{c}} = \begin{vmatrix} D & 0 \\ \frac{c_t}{c}(D - D_s) & D_s \end{vmatrix} \tag{35}$$

The eigenvalues of $\overline{\overline{D}}$ are D, with right eigenvector $\boldsymbol{\psi}_{\mathrm{I}} = \left|\begin{smallmatrix} 1 \\ c_t/c \end{smallmatrix}\right)$ and the left eigenvector $\boldsymbol{\phi}_{\mathrm{I}} = \left(\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}\right|$; and D_s, with right eigenvector $\boldsymbol{\psi}_{\mathrm{II}} = \left|\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}\right)$ and left eigenvector $\boldsymbol{\phi}_{\mathrm{II}} = \left(\begin{smallmatrix} -c_t/c \\ 1 \end{smallmatrix}\right|$.

Noteworthy relations between these are

$$\partial \boldsymbol{\phi}_{\mathrm{II}}/\partial \mathbf{c} = -c^{-1}\boldsymbol{\phi}_{\mathrm{I}}\boldsymbol{\phi}_{\mathrm{II}}, \qquad \partial \boldsymbol{\psi}_{\mathrm{I}}/\partial \mathbf{c} = c^{-1}\boldsymbol{\psi}_{\mathrm{II}}\boldsymbol{\phi}_{\mathrm{II}} \tag{36}$$

It is useful to expand $\overline{\overline{\overline{A}}}$ in terms of matrix elements

$$\overline{\overline{\overline{A}}}(\vec{q},\vec{k}) = \sum_{ijl} A_{ijl}(\vec{q},\vec{k})\boldsymbol{\psi}_i\boldsymbol{\phi}_j\boldsymbol{\phi}_l \tag{37}$$

with

$$\begin{aligned} A_{ijl}(\vec{q},\vec{k}) &= -(\vec{q}\cdot\vec{k})\boldsymbol{\phi}_i \circ \frac{\partial \overline{\overline{D}}}{\partial \mathbf{c}} \mathbin{\substack{\circ\\ \circ}} \boldsymbol{\psi}_j\boldsymbol{\psi}_l \\ &= -(\vec{q}\cdot\vec{k})\left\{ \frac{\partial}{\partial \mathbf{c}}\left(\boldsymbol{\phi}_i \circ \overline{\overline{D}} \circ \boldsymbol{\psi}_l\right) - \left(\frac{\partial}{\partial \mathbf{c}}\boldsymbol{\phi}_i\right)\right. \\ &\qquad\qquad \left. \circ\, \overline{\overline{D}} \circ \boldsymbol{\psi}_l - \boldsymbol{\phi}_i \circ \overline{\overline{D}} \circ \frac{\partial \boldsymbol{\psi}_l}{\partial \mathbf{c}} \right\} \circ \boldsymbol{\psi}_j \end{aligned} \tag{39}$$

The explicit forms for A_{ijl} are given by

$$\begin{gathered} A_{222} = A_{112} = 0, \qquad A_{211} = -(\vec{q}\cdot\vec{k})\frac{c_t}{c}\frac{\partial D}{\partial c} \\ A_{212} = (-\vec{q}\cdot\vec{k})\frac{\partial D_s}{\partial c}, \qquad A_{221} = \frac{-(\vec{q}\cdot\vec{k})(D - D_s)}{c} \\ A_{111} = -(\vec{q}\cdot\vec{k})\frac{\partial D}{\partial c} \end{gathered} \tag{40}$$

Inserting these results into (37) and substituting back into (28) using (26), (34), (41) and the transformation $\vec{q} \to \vec{q} + (D_l/(D_l + D_m)\vec{k}$, and passing to the limit $V \to \infty$, one obtains

$$\begin{aligned}
\Delta L_{ij}(k,z) &= \psi_i \circ \Delta \bar{\bar{L}}(k,z) \circ \psi_j \\
&= \frac{1}{2k^2(2\pi)^d} \int d\vec{q} \sum_{l,m} \left\{ A_{jlm}\left(\vec{q} + \frac{D_l}{D_l + D_m} \vec{k}, \vec{k} \right) \right. \\
&\qquad\qquad \left. + A_{jml}\left(-\vec{q} + \frac{D_m}{D_l + D_m} \vec{k}, \vec{k} \right) \right\} \\
&\quad \times \left\{ A_{ilm}\left(-\vec{q} - \frac{D_l}{D_l + D_m} \vec{k}, -\vec{k} \right) \right. \\
&\quad \left. + A_{iml}\left(\vec{q} - \frac{D_m}{D_l + D_m} \vec{k}, -\vec{k} \right) \right\} \\
&\quad \times \frac{\langle \hat{c}_l \hat{c}_l \rangle \langle \hat{c}_m \hat{c}_m \rangle}{z + (D_l + D_m) q^2 + (D_l D_m/(D_l + D_m)) k^2}
\end{aligned} \tag{41}$$

Especially interesting is $\Delta L_{\text{II II}}$ containing the long time behavior of the tracer diffusion coefficient. Since the coefficient of self-diffusion generally satisfies the relation $D_s(k,z) = L_{\text{II II}}(k,z)/[c_t(1 - c_t)]$, as follows from (30)–(32) and (41), one can define a time correlation function $\phi_s(k,t)$ as $\phi_s(k,t) = \phi_{\text{II II}}(k,t)/[c_t(1 - c_t)]$, with $\phi_{\text{II II}}$ the inverse Laplace transform of $L_{\text{II II}}$. Then, performing the usual expansion in powers of k^2 one obtains from (41) the following types of long time behavior:

$$\phi_s^{(2)}(t) = -2^{-(d+1)}\pi \{\pi(D + D_s)t\}^{-(d+2)/2} \langle \hat{c}\hat{c} \rangle \left\{ \frac{D - D_s}{c} - \frac{\partial D_s}{\partial c} \right\}^2 \tag{42}$$

$$\begin{aligned}
\phi_s^{(4)}(t) &= +2^{-d}\{\pi(D + D_s)t\}^{-d/2} \langle \hat{c}\hat{c} \rangle \\
&\quad \times \left[\left\{ \frac{D}{D + D_s} \frac{\partial D_s}{\partial c} + \frac{D_s}{D + D_s} \frac{D - D_s}{c} \right\}^2 \right. \\
&\qquad \left. - \frac{D D_s}{2(D + D_s)^2} \left\{ \frac{\partial D_s}{\partial c} - \frac{D - D_s}{c} \right\}^2 \right]
\end{aligned} \tag{43}$$

The results obtained above can be tested against a number of models for which explicit results are available. For several lattice gas models with dynamics of the Kawasaki type, the collective current correlation function is known exactly to be proportional to a δ function $\delta(t)$.(14) This is consistent with the prediction that long time tails will be absent from this function, or at most be very weak. Furthermore, even for lattice gas models not having this property computer simulations do not seem to give evidence for the occurrence of long time tails in the collective current correlation function.(15)

The long time tail in the velocity autocorrelation function can be calculated theoretically for certain models. For one-dimensional systems subject to a single filing constraint (particles cannot pass each other), causing D_s to be zero,(16) a simple argument given by Alexander and Pincus(17,18) can be used to prove (42). Computer simulations(19) indicate that for these systems $\phi_s^{(4)}(t)$ is proportional to $t^{-3/2}$, consistent with the vanishing of the coefficient of $t^{-1/2}$ on the right-hand side of (43). For lattice gases with Kawasaki dynamics at very high concentration (which implies very low concentration of vacancies) $\phi_s^{(2)}(t)$ and $\phi_s^{(4)}(t)$ can be calculated at arbitrary dimensionality.(20) The results are in agreement with mode-coupling predictions. Kutner(21) has performed computer simulations on two-dimensional models at different concentrations. He found that for long times the velocity autocorrelation function decays as t^{-2}, as predicted by (42). A comparison of the coefficients is presently under way.

5. CONCLUSION

In this paper mode-coupling equations were derived that are valid for purely diffusive systems. The starting point was a set of fluctuation diffusion equations and the basic assumptions made were (i) diffusion coefficients depend on space and time through the local concentrations of the diffusing species only and (ii) time-reversal symmetry holds. The mode-coupling equations are of the general form to be expected for a mode-coupling expansion,(22) but the occurrence of density derivatives of transport coefficients in the vertex functions to my knowledge is a new feature, originated in Ref. 12. The predictions of the mode-coupling theory could be checked against some models for which exact results are available and against some Monte Carlo results. So far in all cases agreement was found.

I want to conclude with a few small remarks: Firstly for anisotropic systems all diffusion coefficients have to be generalized to spatial tensors, which, at least in principle, can be done without any great problems. Secondly the use of time-reversal symmetry to evaluate (23) seemingly can be avoided by using an iterative solution for the time-dependent concentrations. In that case, however, one has to use higher-order dissipation fluctuation theorems to evaluate averages involving two random forces. To construct those theorems one has to invoke time-reversal symmetry again, but then the application of this to (23) as it stands is by far simpler and more direct. In addition the value of these higher-order fluctuation dissipation theorems beyond their restoration of time-reversal invariance seems questionable. The trouble is that one does not know how good it is to approximate the time evolution of a pair fluctuation by factorization. No doubt in most cases there occur interactions, which are not necessarily described correctly by the correlations of random forces as derived from time-reversal invariance.

Finally I want to mention that the possible relevance of the mode-coupling formalism developed here in the neighborhood of critical points is presently under consideration.

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