Journal of Statistical Physics, Vol. 35, Nos. 3/4, 1984

Long Time Tails in Stationary Random Media II: Applications

J. Machta,[1] M. H. Ernst,[2] H. van Beijeren,[3] and J. R. Dorfman[4]

Received October 18, 1983

In a previous paper we developed a mode-coupling theory to describe the long time properties of diffusion in stationary, statistically homogeneous, random media. Here the general theory is applied to deterministic and stochastic Lorentz models and several hopping models. The mode-coupling theory predicts that the amplitudes of the long time tails for these systems are determined by spatial fluctuations in a coarse-grained diffusion coefficient and a coarse-grained free volume. For one-dimensional models these amplitudes can be evaluated, and the mode-coupling theory is shown to agree with exact solutions obtained for these models. For higher-dimensional Lorentz models the formal theory yields expressions which are difficult to evaluate. For these models we develop an approximation scheme based upon projecting fluctuations in the diffusion coefficient and free volume onto fluctuations in the density of scatterers.

KEY WORDS: Long time tails; random media; mode-coupling theory; Lorentz models; random walks.

1. INTRODUCTION

In the previous paper (Paper I)[1] we developed a mode-coupling theory to describe the long time properties of diffusion in a stationary, statistically

Work supported by grant No. CHE 77-16308 from the National Science Foundation and by a Nato Travel Grant.

[1] Department of Physics and Astronomy, University of Massachusetts, Amherst, Massachusetts 01003.

[2] Institute for Theoretical Physics, State University, P.O.B. 80.006, 2508 TA Utrecht, The Netherlands.

[3] Institute for Theoretical Physics, Rhein-Westf. Techn. Hochschule, 5100 Aachen, West Germany.

[4] Institute for Physical Science and Technology and Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742.

0022-4715/84/0500-0413$03.50/0

homogeneous, random medium. In the present paper this general theory will be applied to a number of systems, including deterministic and stochastic Lorentz models and hopping models. The results obtained will be compared with results available from other methods—exact solutions, systematic and approximate kinetic theories, and computer simulations.

We begin with a review of the mode-coupling theory and a summary of the results obtained from it. The starting point of the theory is a phenomenological diffusion equation with spatially varying parameters:

$$\partial c(\mathbf{r},t)/\partial t = -\nabla \cdot \mathbf{j}(\mathbf{r},t) \tag{1.1a}$$

$$\mathbf{j}(\mathbf{r},t) = -\mathbf{K}(\mathbf{r},X) \cdot \nabla\big(c(\mathbf{r},t)/\psi(\mathbf{r},X)\big) \tag{1.1b}$$

where $c(\mathbf{r},t)$ is the concentration and $\mathbf{j}(\mathbf{r},t)$ the current density of (noninteracting) diffusing particles. The functions $\mathbf{K}(\mathbf{r},X)$ and $\psi(\mathbf{r},X)$ are fixed in time, but vary with position to account for the static disorder in the medium in which the diffusion is occurring; X is a set of parameters describing the particular configuration of the medium. For example, in a hopping problem X might refer to the set of random locations of the hopping centers or to the random transition rates between them. $\mathbf{K}(\mathbf{r},X)$ is the local Onsager coefficient and $\nabla(c/\psi)$ is the appropriate driving force for the diffusion according to the linear laws of irreversible thermodynamics, as shown in Paper I. Since there is no driving force when the concentration attains its equilibrium value, it is clear that $\psi(\mathbf{r},X)$ must be proportional to the equilibrium concentration of diffusing particles, where the constant of proportionality may still depend on the configuration X. In the *Lorentz models* we fix this constant by requiring that $\psi(\mathbf{r},X)$ has the value unity whenever $\mathbf{r}$ is outside of the scatterers. This means that $\psi(\mathbf{r},X)$ equals the overlap function $W(\mathbf{r},X)$, which vanishes whenever the moving particle is interacting with a scatterer, and equals unity elsewhere. Thus, the integral of $\psi(\mathbf{r},X)$ over the whole volume V of the system, i.e.,

$$\psi_0(X) = \int d\mathbf{r}\, W(\mathbf{r},X) \tag{1.2}$$

is the free volume available to a moving particle in configuration X. In *hopping models* on a regular lattice with N sites, labeled $\mathbf{n}$, it is not meaningful to define configurations, where the moving particle can be considered "free," and $\psi_{\mathbf{n}}(X)$ can only be determined up to an arbitrary constant, which does not depend on the configuration X. This constant is fixed by the normalization

$$\frac{1}{N}\sum_{\mathbf{n}} \psi_{\mathbf{n}}(X) = 1 \tag{1.3}$$

where the sum extends over all sites of the lattice.

The functions $c(\mathbf{r},t)$, $\mathbf{K}(\mathbf{r},X)$, and $\psi(\mathbf{r},X)$ in (1.1) are all to be considered coarse grained. The coarse graining is performed by averaging over cells in configuration space of volume $V_c = L_c^d$ (d is the dimensionality). The coarse-graining length L_c must be much larger than the correlation length of the static fluctuations. Finally we note that our mode-coupling theory is only applicable when the mean square fluctuations in $\mathbf{K}(\mathbf{r},X)$ and $\psi(\mathbf{r},X)$ are small compared to the average values $\langle \mathbf{K}(\mathbf{r},X)\rangle^2$ and $\langle \psi(\mathbf{r},X)\rangle^2$, respectively.

Assuming that (1.1) correctly describes the decay of concentration fluctuations in equilibrium, we can use it to calculate the intermediate scattering function

$$F(\mathbf{k},t) = \frac{\langle \hat{c}_{-\mathbf{k}}(0)\hat{c}_{\mathbf{k}}(t)\rangle}{\langle \hat{c}_{-\mathbf{k}}(0)\hat{c}_{\mathbf{k}}(0)\rangle} \tag{1.4a}$$

The average $\langle \cdots \rangle = \int dX\, \rho(X)\langle \cdots \rangle_X$ represents a double average: the last one is an average over the configurations X with a weight function $\rho(X)$, that will be specified for each of the models to be discussed; the first one, $\langle \cdots \rangle_X$, is a grand canonical average (fugacity ζ) over the phases of M noninteracting particles, moving in a frozen configuration X of the random medium. The Fourier transform is defined in the usual fashion and the carets represent a deviation from the equilibrium value in a frozen configuration, i.e., $\hat{c}_{\mathbf{k}} = c_{\mathbf{k}} - \langle c_{\mathbf{k}}\rangle_X$. Since the moving particles are noninteracting and Poisson distributed, the average in (1.4a) can be reduced to a symmetrical average over a single moving particle and a subsequent average over the configurations X, i.e.,

$$F(\mathbf{k},t) = \frac{1}{\langle M\rangle}\left\langle \sum_{i=1}^{M} e^{ik\Delta x_i(t)} \right\rangle \equiv \langle e^{ik\Delta x(t)}\rangle_s \tag{1.4b}$$

where the relation $\langle \hat{c}_{-\mathbf{k}}\hat{c}_{\mathbf{k}}\rangle = \langle M\rangle$ has been used.

The function $F(\mathbf{k},t)$ generates the moments $\langle[\Delta x(t)]^l\rangle$ of displacement in the x direction with $\Delta x(t) = x(t) - x(0)$, where the x axis is taken parallel to $\mathbf{k}$. The first derivative of the mean square displacement is the time-dependent diffusion coefficient $D(t)$, and its second derivative is (the analog of) the velocity autocorrelation function $\phi_2(t)$, whenever a "velocity" can be defined, i.e.,

$$\begin{aligned} D(t) &= (d/dt)\tfrac{1}{2}\langle[\Delta x(t)]^2\rangle_s \\ \phi_2(t) &= dD(t)/dt = \langle v_x(0)v_x(t)\rangle_s \end{aligned} \tag{1.5}$$

where $v_x(t)$ is the x component of the "velocity" at time t of a single particle. The first derivative of the fourth cumulant of the x displacment is the super-Burnett coefficient $B(t)$; its second derivative is related to the

Burnett correlation function $\phi_4(t)$, i.e.,

$$B(t) = (d/dt)\left\{\langle[\Delta x(t)]^4\rangle_s - 3\langle[\Delta x(t)]^2\rangle_s^2\right\}/4!$$
$$= D_4(t) - \int_0^t d\tau \{D(t) - D(\tau)\} D(t-\tau) \tag{1.6}$$

with

$$\phi_4(t) = dD_4(t)/dt$$
$$= \int_0^t d\tau \int_\tau^t d\tau' \left[\langle v_x(0)v_x(\tau)v_x(\tau')v_x(t)\rangle_s \right.$$
$$\left. - \langle v_x(0)v_x(\tau)\rangle_s \langle v_x(\tau')v_x(t)\rangle_s\right] \tag{1.7}$$

If the correlation functions $\phi_2(t)$ and $\phi_4(t)$ decay sufficiently fast, $D(t)$, $B(t)$, and $D_4(t)$ approach, respectively, the ordinary diffusion coefficient D, the super-Burnett coefficient B, and the modified super-Burnett coefficient D_4. As shown in Paper I, the mode-coupling theory yields the following long time results for arbitrary dimensionality; viz., for the correlation functions:

$$\phi_2(t) \simeq -2\pi D^2 \Delta_K (4\pi D t)^{-(d+2)/2} \tag{1.8a}$$

$$\phi_4(t) \simeq D^2 \Delta_\psi (4\pi D t)^{-d/2} \tag{1.8b}$$

and for the transport coefficients:

$$D_4(t) \simeq D_4 - \frac{D\Delta_\psi}{2\pi(d-2)} (4\pi D t)^{-(d-2)/2} \tag{1.9a}$$

$$B(t) \simeq B - \frac{D(2\Delta_\psi + \Delta_K)}{4\pi(d-2)} (4\pi D t)^{-(d-2)/2} \tag{1.9b}$$

For the special case $d = 2$ the last two equations reduce to

$$D_4(t) \simeq (D\Delta_\psi/4\pi)\log t \tag{1.9c}$$

$$B(t) \simeq \left[D(2\Delta_\psi + \Delta_K)/8\pi\right]\log t \tag{1.9d}$$

These expressions contain the mean square fluctuations

$$\Delta_K = \langle \delta \mathbf{K}_0(X) : \delta \mathbf{K}_0(X)\rangle / \left[dV(D\psi)^2\right]$$
$$\Delta_\psi = \langle [\delta\psi_0(X)]^2\rangle / (V\psi^2) \tag{1.10}$$

where $\delta A(X) = A(X) - \langle A(X)\rangle$ refers to the deviation from the average over the configuration X, and the subscript zero refers to a spatial average

of some local quantity, i.e., $A_0 = \int d\mathbf{r} A(\mathbf{r})$. We further introduced

$$\begin{aligned} \langle \psi_0(X) \rangle &= V \langle \psi(\mathbf{r}, X) \rangle = V\psi \\ \langle K_0^{\alpha\beta}(X) \rangle &= V < K_{\alpha\beta}(\mathbf{r}, X) \rangle = VD\psi\, \delta_{\alpha\beta} \end{aligned} \tag{1.11}$$

so that the fluctuations are given by

$$\begin{aligned} \delta K_0^{\alpha\beta}(X) &= \int d\mathbf{r} \left[K_{\alpha\beta}(\mathbf{r}, X) - D\psi\, \delta_{\alpha\beta} \right] \\ \delta\psi_0(X) &= \int d\mathbf{r} \left[\psi(\mathbf{r}, X) - \psi \right] \end{aligned} \tag{1.12}$$

In the next section of the paper the mode-coupling results are compared with exact results for several stochastic Lorentz models and hopping models, whereas in Appendix A.1 the corresponding expressions for the coarse-grained Onsager coefficient $\mathbf{K}(\mathbf{r}, X)$ are calculated. In Section 3 we apply the mode-coupling theory to the overlapping and nonoverlapping Lorentz gases. A comparison of the mode-coupling results with other theoretical and numerical results for the Lorentz gas is given in Section 4, and Section 5 presents our conclusions.

2. STOCHASTIC MODELS OF DIFFUSION

2.1. One-Dimensional Stochastic Lorentz Model

In this section we discuss several models of diffusion for which exact results are known. The first of these is the one-dimensional stochastic Lorentz model which is analyzed in Refs. 2–4.

In this model noninteracting point particles move with a constant speed v on a line. Fixed, pointlike scatterers are located at random on the line. When a moving particle meets a scatterer it has probability p of being reflected and $(1 - p)$ of being transmitted. The distances l_n between neighboring scatterers are independent random variables, sampled from an interval distribution which has a mean $l = \langle l_n \rangle$ (here $l^{-1} = n$ is the average density of scatterers) and a variance $\Delta_l = \langle (l_n - l)^2 \rangle / l^2$. The exact diffusion coefficient[3,4] is known to be $D = (1 - p)vl/2p$.

In our mode-coupling calculation we need the statistics of the coarse-grained Onsager coefficient $K(r, X)$ and free volume fraction $\psi(r, X)$. The free volume fraction $\psi(r, X)$, defined above (1.2), does not depend on r, since neither the number of scatterers nor their positions influence the equilibrium distribution of moving particles. Thus, spatial fluctuations in $\psi(r, X)$ are absent, so that $\psi = 1$ and $\Delta_\psi = 0$.

Next, we consider the local density of scatterers $n(r,X)$ or local volume per scatterer $l(r,X) = 1/n(r,X)$ in a coarse-graining cell of given size V_c, centered around position r with a fluctuating number of scatterers $N_c(r)$. Hence

$$l(r,X) = 1/n(r,X) = V_c/N_c(r) \tag{2.1a}$$

with

$$\begin{aligned} N_c(r) &= \sum_{n \in V_c(r)} 1 \\ V_c &= \sum_{n \in V_c(r)} l_n = \text{fixed} \end{aligned} \tag{2.1b}$$

As shown in Appendix A.1, the spatial fluctuations $\delta K(r,X)$ in the coarse-grained Onsager coefficient are completely determined by the fluctuation in $n(r,X)$ or $l(r,X)$, and we have from (A.6) in Appendix A.1

$$\delta K(r,X) = \frac{\partial \langle K(r,X)\rangle}{\partial \langle l(r,X)\rangle}\,\delta l(r,X) = \frac{\partial D}{\partial l}\,\delta l(r,X) \tag{2.2a}$$

where $\langle K(r,X)\rangle = D$. Hence, the fluctuation in the zeroth-order Fourier component $\delta K_0(X)$, defined in (1.12), is

$$\delta K_0(X) = \left(\frac{\partial D}{\partial l}\right) \sum_{\alpha}^{\text{cells}} V_c\big[\, l(r_\alpha, X) - l\big] \tag{2.2b}$$

Its mean square fluctuation follows from (1.10) and (2.2b) as

$$\Delta_K = (VD^2)^{-1}(\partial D/\partial l)^2 (V/V_c) V_c^2 \langle \big[\, l(r_\alpha, X) - l\big]^2 \rangle \tag{2.3}$$

The factor V/V_c represents the total number of coarse-graining cells. We further used the property that fluctuations in different coarse-graining cells are uncorrelated. The l fluctuations in (2.3) yield to dominant order in $1/V_c$

$$\begin{aligned} \langle \big[\, l(r,X) - l\big]^2 \rangle &= \left(1/\overline{N}_c\right)^2 \sum_{n,m \in V_c(r)} \langle (l_n - l)(l_m - l)\rangle \\ &= \left(1/\overline{N}_c\right) \langle (l_n - l)^2 \rangle = l^3 \Delta_l / V_c \end{aligned} \tag{2.4a}$$

where $\overline{N}_c$ is the average number of particles in a coarse-graining cell. Thus, our final result for Δ_K is

$$\Delta_K = l \Delta_l \tag{2.4b}$$

Using these results in combination with (1.8) and (1.9) yields the following

results for the time correlation functions at large t:

$$\phi_2(t) \simeq -\tfrac{1}{4} l\Delta_l (D/\pi)^{1/2} t^{-3/2} \tag{2.5a}$$

$$\phi_4(t) \simeq o(t^{-1/2}) \tag{2.5b}$$

and for the Burnett functions:

$$D_4(t) \simeq o(t^{1/2}) \tag{2.6a}$$

$$B(t) \simeq \tfrac{1}{2} l\Delta_l D^{3/2} (t/\pi)^{1/2} \tag{2.6b}$$

where $l = 1/n$. The symbol $o(t^\alpha)$ indicates that $t^{-\alpha} o(t^\alpha) \to 0$ as $t \to \infty$. The exact long time results for $\phi_2(t)$ and $B(t)$, found in Ref. 3, agree with the mode-coupling predictions in the previous equations, whereas the exact results $\phi_4(t) \sim t^{-3/2}$ and $D_4(t) \simeq D_4 + o(t^0)$ are consistent with the above predictions.

2.2. One-Dimensional Waiting Time Lorentz Model

In the previous model, the simple topology of one dimension permitted us to express fluctuations in the Onsager coefficient in terms of density fluctuations. In the present subsection, we discuss the one-dimensional waiting Lorentz model[3,5] which shares this simplification but also has fluctuations in $\psi(r, X)$. In this model the moving particle makes instantaneous jumps between neighboring sites with stochastically distributed waiting times between the jumps. There are site-independent waiting time distributions $\tilde{p}(t)$ for backward jumps—jumps in the direction opposite to that of the preceding jump—and $\tilde{q}(t)$ for forward jumps—jumps in the same direction as the preceding one. The sum of these distributions is normalized, hence

$$\int_0^\infty dt \left[\tilde{p}(t) + \tilde{q}(t) \right] = 1 \tag{2.7a}$$

and

$$\int_0^\infty dt \left[\tilde{p}(t) + \tilde{q}(t) \right] t = \tau < \infty \tag{2.7b}$$

where τ is the mean total waiting time. The intervals l_n between neighboring sites are independent random variables with the same properties as for the stochastic Lorentz model, viz., $\langle l_n \rangle = l = 1/n$ and $\langle (l_n - l)^2 \rangle = l^2 \Delta_l$.

Van Beijeren[3] has found an exact solution to this model from which one can derive both the diffusion coefficient and the long time behavior of the correlation functions of interest here. The diffusion coefficient satisfies

$$D = (1 - p) l^2 / 2p\tau \tag{2.8}$$

where

$$p = \int_0^\infty dt\, \tilde{p}(t) \tag{2.9}$$

In the waiting time Lorentz model the free volume $\psi(r,X)$ has spatial fluctuations, since moving particles can sit only on sites. Thus, the coarse-grained $\psi(r,X)$ is proportional to the coarse-grained density of scatterers $n(r,X) = 1/l(r,X)$, and its fluctuation $\delta\psi(r,X) = a\delta l(r,X)$ where a is a constant independent of the configuration of sites. A derivation similar to (2.2)–(2.4) yields $\Delta_\psi = l\Delta_l$.

As discussed in Appendix A.2, the coarse-grained value of the local Onsager coefficient depends on the local density of scatterers, i.e.,

$$K(r,X) = D(r,X)\psi(r,X) = l(r,X)(1-p)/2p\tau \tag{2.10a}$$

By following steps similar to (2.2)–(2.4) one finds

$$\delta K(r,X) = \left(\frac{\partial D\psi}{\partial l}\right)\delta l(r,X) \tag{2.10b}$$

which leads again to the equality $\Delta_K = l\Delta_l$.

From the above results for ψ, D and Δ_ψ and Δ_K in combination with (1.8) and (1.9) we obtain the mode-coupling results for the correlation functions:

$$\begin{aligned} \phi_2(t) &\simeq -\tfrac{1}{4} l\Delta_l (D/\pi)^{1/2} t^{-3/2} \\ \phi_4(t) &\simeq \tfrac{1}{2} l\Delta_l D^{3/2} (\pi t)^{-1/2} \end{aligned} \tag{2.11}$$

and for the Burnett functions:

$$\begin{aligned} D_4(t) &\simeq l\Delta_l D^{3/2} (t/\pi)^{1/2} \\ B(t) &\simeq (3/2) l\Delta_l D^{3/2} (t/\pi)^{1/2} \end{aligned} \tag{2.12}$$

These mode-coupling results are in full agreement with the results from the exact calculations.[3,5]

2.3. One-Dimensional Random Barrier Model

In this model[6–14] the diffusing particles make instantaneous jumps between neighboring sites on a line with a constant spacing l, according to the master equation:

$$\dot{P}_n = \nu_{n-1}(P_{n-1} - P_n) + \nu_n(P_{n+1} - P_n) = (1 - E_n^{-1})\nu_n(E_n - 1)P_n \tag{2.13}$$

where $E_n f_n = f_{n+1}$ and $(E_n - 1)/l$ and $(1 - E_n^{-1})/l$ are the analogs of a derivative in finite difference calculus, $P_n(t)$ is the probability of finding a particle at site n at time t. The jump rates ν_n are positive random variables,

sampled from a site-independent distribution for which $\langle 1/\nu_n \rangle = \tau$ and $\langle (1/\nu_n - \tau)^2 \rangle = \tau^2 \Delta_\tau$ are both finite. The quantity τ is the average waiting time for either a jump to the right or a jump to the left. The exact value of the diffusion coefficient is $D = l^2/\tau$. The equilibrium solution ψ_n to (2.13) is a constant, independent of the set $\{\nu_n\}$. Thus $\psi_n = 1$ on account of the normalization (1.3), so that $\psi(r, X) = 1$ does not have spatial fluctuations, and $\Delta_\psi = 0$.

Next we consider the coarse-graining procedure, in which the system is divided into coarse-graining cells, each containing N_c scatterers. The coarse-grained version of (2.13) reads

$$\partial c(r,t)/\partial t = \nabla K(r, X) \nabla c(r,t) \tag{2.14}$$

where $(E_n - 1)$ and $(1 - E_n^{-1})$ have been replaced by $l\nabla$, and the coarse-grained Onsager coefficient $K(r, X)$ has been calculated in Appendix A.3 with the result

$$K(r, X) = l^2/\tau(r, X) \tag{2.15a}$$

where the local waiting time is

$$\tau(r, X) = \frac{1}{N_c} \sum_{n \in V_c(r)} \frac{1}{\nu_n} \tag{2.15b}$$

The fluctuations in $K(r, X)$ are completely determined by the fluctuations in the local waiting time $\tau(r, X)$. Hence, by following the steps taken in the derivation of (2.2)–(2.4) we find

$$\begin{aligned} \delta K(r, X) &= \left(\frac{\partial D}{\partial \tau} \right) \delta\tau(r, X) \\ \delta K_0(X) &= \left(\frac{\partial D}{\partial \tau} \right) l \sum_i \delta\tau_i \end{aligned} \tag{2.16}$$

where we used the relation $V_c = N_c l$, so that Δ_K in (1.10) becomes $\Delta_K = l\Delta_\tau$. The mode-coupling equations lead now to the following results:

$$\phi_2(t) \simeq -\tfrac{1}{4} l \Delta_\tau (D/\pi)^{1/2} t^{-3/2} \tag{2.17a}$$

$$\phi_4(t) \simeq o(t^{-1/2}) \tag{2.17b}$$

$$D_4(t) \simeq o(t^{1/2}) \tag{2.17c}$$

$$B(t) \simeq \tfrac{1}{2} l \Delta_\tau D^{3/2} (t/\pi)^{1/2} \tag{2.17d}$$

The result for $\phi_2(t)$ is in agreement with the previously obtained exact results for the long time tail in the velocity autocorrelation function.[7–10]. Denteneer and Ernst[14] have shown that $\phi_4(t) \simeq bt^{-3/2}$ and $D_4(t) \simeq D_4 + O(t^{-1/2})$ for long times, where D_4 contains fluctuations up to $\langle (\delta l)^4 \rangle$ included, and b to $\langle (\delta l)^6 \rangle$ included.

2.4. Isotropic Random Jump Rate Model

The previous model included disorder in the rate for jumping between sites. An alternative form of disorder can be introduced[10,14–16] by assigning a random waiting time $\tau_{\mathbf{n}}$ to the nth site, and by letting the particle jump with equal probability from a given site to any of its nearest-neighbor sites. Thus the jump rate from site $\mathbf{n}$ in a given lattice direction is $\nu_{\mathbf{n}} = (c\tau_{\mathbf{n}})^{-1}$ (where C is the coordination number of the lattice). For simplicity we restrict ourselves to d-dimensional hypercubic lattices with lattice spacing l where $C = 2d$. The isotropic jump rate model incorporates this kind of disorder via the following master equation:

$$\dot{P}_{\mathbf{n}} = \sum_{\alpha=1}^{d} \left(E_{\mathbf{n}\alpha} + E_{\mathbf{n}\alpha}^{-1} - 2\right)\nu_{\mathbf{n}} P_{\mathbf{n}} \tag{2.18}$$

Here $E_{\mathbf{n}\alpha} f(\mathbf{n}) = f(\mathbf{n} + \mathbf{e}_\alpha)$, where $\mathbf{e}_\alpha$ ($\alpha = 1, 2, \ldots, d$) is a set of orthogonal unit vectors along the lattice directions. $(E_{\mathbf{n}\alpha} - 1)/l$ and $(1 - E_{\mathbf{n}\alpha}^{-1})/l$ are again the finite difference analogs of a derivative ∇_α in the α direction. The random variables $\tau_{\mathbf{n}}$ are sampled from a site-independent distribution function with a mean $\tau = \langle \tau_{\mathbf{n}} \rangle$ and variance $\Delta_\tau = \langle (\tau_{\mathbf{n}} - \tau)^2 \rangle / \tau^2$. Haus *et al.*[15] have found the exact diffusion coefficient for this model as $D = l^2/C\langle \tau_{\mathbf{n}} \rangle = l^2/2d\tau$. The stationary solution of (2.18) is nonuniform, i.e., $\psi_{\mathbf{n}} = c\tau_{\mathbf{n}}$. We fix the constant by the normalization (1.3), so that $c^{-1} = N^{-1}\sum_{\mathbf{n}} \tau_{\mathbf{n}} = \langle \tau_{\mathbf{n}} \rangle = \tau$. Hence $\psi_{\mathbf{n}} = \tau_{\mathbf{n}}/\tau$. The coarse-grained $\psi(\mathbf{r}, X)$ is therefore

$$\psi(\mathbf{r}, X) = \frac{1}{N_c} \sum_{\mathbf{n} \in V_c(\mathbf{r})} (\tau_{\mathbf{n}}/\tau) \tag{2.19}$$

Hence

$$\delta\psi_0 = l^d \sum_{\mathbf{n}} (\tau_{\mathbf{n}}/\tau) \tag{2.20}$$

and

$$\Delta_\psi = l^d \Delta_\tau \tag{2.21}$$

Coarse graining of (2.18) is seen to lead to a form analogous to (1.1), i.e.,

$$\partial c(\mathbf{r}, t)/\partial t = D\nabla^2 \left[c(\mathbf{r}, t)/\psi(\mathbf{r}, X) \right] \tag{2.22}$$

where the second finite difference (2.18) is replaced by ∇^2. Equation (2.22) shows that $K(\mathbf{r}, X) = D$ is constant in this model as explained in Appendix A.4, and hence $\Delta_K = 0$.

The physical reason why the Onsager coefficient is independent of the fluctuations in $\nu_{\mathbf{n}}$ is the following. Suppose that $1/\nu_{\mathbf{n}}$ is larger than $\langle 1/\nu_{\mathbf{n}} \rangle$; the jump rate per particle from site $\mathbf{n}$ is then less than the average but the steady state number of particles at site $\mathbf{n}$ is greater than average. The two

effects exactly cancel and the steady current, for a given driving force, is independent of v_n. Combination of these results with (1.8) and (1.9) yields the following long time behavior:

$$\begin{aligned}
\phi_2(t) &\simeq o(t^{-(d+2)/2}) \\
\phi_4(t) &\simeq l^d D^2 \Delta_\tau (4\pi D t)^{-d/2} \\
D_4(t) &\simeq D_4 - \frac{l^d D \Delta_\tau}{2\pi(d-2)} (4\pi D t)^{-(d-2)/2} \\
B_4(t) &\simeq B - \frac{l^d D \Delta_\tau}{2\pi(d-2)} (4\pi D t)^{-(d-2)/2}
\end{aligned} \tag{2.23}$$

For the special two-dimensional case the last two equations reduce to

$$D_4(t) \simeq B(t) \simeq (4\pi)^{-1} l^2 D \Delta_\tau \log t \tag{2.24}$$

As was pointed out by Haus, Kehr, and Lyklema[15] the fact that there is no long time tail in $\phi_2(t)$ is a rigorous result of the isotropy of the jump rates. Indeed, a simple argument shows that $\phi_2(t) = D\delta_+(t)$, where $\delta_+(t)$ is a delta function on the positive time interval. At each jump there is an equal probability of going in any of the possible lattice directions. Thus, after one jump, all memory of the direction of motion is lost and the only contribution to $\phi_2(t)$ comes from the correlation of the velocity with itself during a single jump. For the case $\phi_4(t)$, Machta[10] has obtained a result for one dimension using a microscopic renormalization group procedure. This result agrees with Eq. (2.24). For the d-dimensional case Denteneer and Ernst[17] have given a systematic expansion in powers of the fluctuation $\delta\tau_n$, and have calculated the long time behavior of the fourth moment of x displacement:

$$\frac{1}{4!}\left(\frac{d}{dt}\right)^2 \langle (\Delta x)^4 \rangle \simeq D^2 + \phi_4(t) \tag{2.25}$$

as follows from (1.5)–(1.7) with $\phi_2(t) = D\delta_+(t)$ and $\phi_4(t)$ as given in (2.23).

3. LORENTZ MODELS

3.1. Lorentz Gas with Nonoverlapping Scatterers

In this section we apply the general theory to the Lorentz gas with nonoverlapping scatterers.[18] In this model a noninteracting point particle moves with constant speed in a two- or three-dimensional random array of scatterers which are hard disks or spheres, respectively. We suppose that the moving particle and a scatterer interact as hard disks or spheres and

that the radius of the scatterers is σ. The intermediate scattering function is usually defined as an average over a grand canonical ensemble of static scatterers and one moving particle:

$$F(\mathbf{k},t) = \langle e^{ik\Delta x(t)} \rangle_{\text{eq}} = \frac{\sum_{N=0} \frac{Z^N}{N!} \int dX^N \, d\hat{\mathbf{v}} \, d\mathbf{r} \, W(X) W(\mathbf{r},X) \exp[ik\Delta x(t)]}{\sum_{N=0} \frac{Z^N}{N!} \int dX^N \, d\hat{\mathbf{v}} \, d\mathbf{r} \, W(X) W(\mathbf{r},X)} \tag{3.1}$$

Here the configuration X denotes the positions of the N scatterers and their number N; $\mathbf{r}$ and $\hat{\mathbf{v}}$ denote the position and velocity ($|\hat{\mathbf{v}}| = 1$) of the moving particle; Z is the fugacity of the scatterers; their overlap function $W(X)$ vanishes whenever two scatterers overlap and equals unity otherwise; $W(\mathbf{r},X) \equiv \psi(\mathbf{r},X)$ is the overlap function for the moving particle, which equals unity when $\mathbf{r}$ is outside all scatterers and vanishes when it is inside a scatterer; $\Omega_d = \int d\hat{\mathbf{v}}$ is a d-dimensional solid angle.

In order to make contact with the function $F(\mathbf{k},t)$ defined in (1.4), we consider the normalized stationary probability distribution,

$$P(\mathbf{r},\hat{\mathbf{v}},X) = W(\mathbf{r},X)/[\Omega_d \psi_0(X)] \tag{3.2}$$

for finding a single moving particle at position $\mathbf{r}$ with velocity $\hat{\mathbf{v}}$ in a frozen configuration X. The total free volume available to a moving particle is

$$\psi_0(X) = \int d\mathbf{r} \, W(\mathbf{r},X) \tag{3.3}$$

For the nonoverlapping Lorentz gas it equals

$$\psi_0(X) = V - Nv_0 \tag{3.4}$$

where v_0 is the volume of a single scatterer.

The probability distribution for the nonoverlapping scatterers is described by the grand canonical ensemble for the hard-sphere fluid:

$$\rho(X) = Z^N W(X)/N! \, \mathcal{Z}_{\text{gr}}(Z) \tag{3.5}$$

where $\mathcal{Z}_{\text{gr}}(Z)$ is the grand canonical partition function. Using the above equations we may rewrite (3.1) as

$$F(\mathbf{k},t) = \langle \psi_0(X) \langle e^{ik\Delta x(t)} \rangle_{X,1} \rangle / \langle \psi_0(X) \rangle \tag{3.6}$$

where $\langle \cdots \rangle$ is an average over the scatterers, calculated with (3.5) and

$$\langle \cdots \rangle_{X,1} = \int d\mathbf{r} \, d\hat{\mathbf{v}} \, P(\mathbf{r},\hat{\mathbf{v}},X) \cdots \tag{3.7}$$

is an equilibrium average over one moving particle in the frozen configuration X. Next, consider the explicit form of the double average appearing in

(1.4b), where $a(\mathbf{r}_i) = \exp[ik\Delta x_i(t)]$ is used as a shorthand notation. Then

$$\left\langle \sum_{i=1}^{M} a(\mathbf{r}_i) \right\rangle = \int dX\, \rho(X) \left\langle \sum_{i=1}^{M} a(\mathbf{r}_i) \right\rangle_X \tag{3.8}$$

with

$$\left\langle \sum_{i=1}^{M} a(\mathbf{r}_i) \right\rangle_X = \frac{\displaystyle\sum_{M=0} \frac{(\zeta/\Omega_d)^M}{M!} \int \left[\prod_{i=0}^{M} d\mathbf{r}_i\, d\hat{\mathbf{v}}_i\, W(\mathbf{r}_i, X) \right] \sum_{i=1}^{M} a(\mathbf{r}_i)}{\displaystyle\sum_{M=0} \frac{(\zeta/\Omega_d)^M}{M!} \int \left[\prod_{i=1}^{M} d\mathbf{r}_i\, d\hat{\mathbf{v}}_i\, W(\mathbf{r}_i, X) \right]} \tag{3.9a}$$

where ζ is the fugacity of the moving particles, and where the denominator equals $\exp[\zeta\psi_0(X)]$ by virtue of (3.3). With the help of (3.2), (3.3), and (3.7) we can reduce (3.9a) to

$$\left\langle \sum_{i=1}^{M} a(\mathbf{r}_i) \right\rangle_X = \langle M \rangle_X \langle A(\mathbf{r}) \rangle_{X,1} = \zeta\psi_0(X) \langle a(\mathbf{r}) \rangle_{X,1} \tag{3.9b}$$

Combination of (3.8) and (3.9) with (1.4b) shows that both definitions (1.4) and (3.1) of the intermediate scattering function are identical.

In order to apply the mode-coupling theory to the overlapping Lorentz gas we need to know the diffusion coefficient D of the moving particles as a function of the density of scatterers $n = \langle N \rangle / V$ and specify the fluctuating quantities $K_0(X)$ and $\psi_0(X)$. To do this we first note that an expression for $D(n)$ is given by the time correlation function method, i.e.,

$$\begin{aligned} D(n) &= \lim_{z \to 0} \left[d\langle \psi_0(X) \rangle \right]^{-1} \left\langle \int \frac{d\mathbf{r}\, d\hat{\mathbf{v}}}{\Omega_d} W(\mathbf{r}, X) \hat{\mathbf{v}} \cdot G_z(\mathbf{r}, \hat{\mathbf{v}}, X) \hat{\mathbf{v}} \right\rangle \\ &= \lim_{z \to 0} \left(d\langle \psi_0(X) \rangle \right)^{-1} \langle \psi_0(X) \langle \hat{\mathbf{v}} \cdot G_z(\mathbf{r}, \hat{\mathbf{v}}, X) \hat{\mathbf{v}} \rangle_{X,1} \rangle \end{aligned} \tag{3.10}$$

Here the resolvent $G_z(\mathbf{r}, \hat{\mathbf{v}}, X)$ is the Laplace transform of $S_t(\mathbf{r}, \hat{\mathbf{v}}, X)$, which is the time displacement operator replacing the position and velocity $(\mathbf{r}, \hat{\mathbf{v}})$ of the moving particle by their value $(\mathbf{r}(t), \hat{\mathbf{v}}(t))$ at a time t later. The density dependence of the diffusion coefficient is not completely known, but a few terms of its low-density expansion have been calculated for two and three dimensions, and it is found that $D(n)$ is nonanalytic at $n = 0$.[25] Furthermore, $D(n)$ has been calculated by means of computer-simulated molecular dynamics.[28–35]

To specify $\mathbf{K}_0(X)$ we need only note the relation (1.11) as well as the time correlation expression (3.10) for $D(n)$. They lead to the following result:

$$\mathbf{K}_0(X) = \lim_{z \to 0} \psi_0(X) \langle \hat{\mathbf{v}} G_z \hat{\mathbf{v}} \rangle_{X,1} \tag{3.11}$$

Having specified all relevant quantities for the application of the general mode-coupling theory to the nonoverlapping Lorentz gas, we can begin to compute the explicit expressions for the various long time tail coefficients. We start with Δ_ψ, defined in (1.10), and $\psi_0(X)$, given in (3.4), using the average with weight function (3.5):

$$\Delta_\psi = \frac{v_0^2}{\psi^2} \frac{\langle (\delta N)^2 \rangle}{V} = \left(\frac{v_0}{1 - nv_0} \right)^2 S_0(n) \tag{3.12}$$

The equilibrium fluctuation,

$$S_0(n) = V^{-1} \langle (\delta N)^2 \rangle = nk_B T (\partial n / \partial p)_T \tag{3.13}$$

has been expressed in terms of the compressibility of a gas of hard disks or spheres with a temperature T (k_B is Boltzmann's constant). We further calculated the average free volume

$$\langle \psi_0(X) \rangle \equiv V\psi = V(1 - nv_0) \tag{3.14}$$

with the help of (3.4).

Next, we turn to a consideration of Δ_K, defined through (1.10) and (3.11) as

$$\Delta_K = \lim_{z,z' \to 0} \left[\frac{\langle \psi_0(X) \langle \hat{\mathbf{v}} G_z \hat{\mathbf{v}} \rangle_{X,1} : \psi_0(X) \langle \hat{\mathbf{v}} G_z \hat{\mathbf{v}} \rangle_{X,1} \rangle}{dV (D\psi)^2} \right] - V \tag{3.15}$$

This fluctuation in $\langle \hat{\mathbf{v}} G_z \hat{\mathbf{v}} \rangle_{X,1}$ is of a form similar to Sinai's fluctuation, discussed by van Beijeren.[3]

In order to evaluate this expression for Δ_K we would need to carry out a kinetic theory analysis of the fluctuations in $\langle \hat{\mathbf{v}} G_z \hat{\mathbf{v}} \rangle_{X,1}$ in the Lorentz gas, produced by collisions of a moving particle with the scatterers. The amount of calculation needed to carry out this program is extensive, and would be the subject of another paper. Hence, we will only present an approximate method for computing Δ_K.

One cause for fluctuation in $K_0(X)$ will certainly be fluctuations in the density of scatterers, but unlike in the one-dimensional case (discussed in Section 2.1) it will not account for all fluctuations in $K_0(X)$. This follows from the observation that it is the arrangement of scatterers in a coarse-graining cell and not just the number of scatterers in the cell which determines the transport of particles across the cell.

We therefore split a fluctuation $\delta A_0(X)$ of some quantity $A_0(X)$ [here either $K_0(X)$ or $\psi_0(X)$] into a part caused by fluctuations in the number of scatterers δN, and a remainder or orthogonal part:

$$\delta A_0 = (\partial \langle A_0 \rangle / \partial \langle N \rangle) \delta N + \delta_\perp A_0 \tag{3.16}$$

where $\langle \delta N \delta_\perp A_0 \rangle = 0$ and where the $\langle N \rangle$ derivative is taken at constant temperature. The mean square fluctuation yields then[5]

$$\langle (\delta A_0)^2 \rangle = (\partial \langle A_0 \rangle / \partial \langle N \rangle)^2 \langle (\delta N)^2 \rangle + \langle (\delta_\perp A_0)^2 \rangle \tag{3.17}$$

Therefore, taking $A_0(X)$ equal to $\mathbf{K}_0(X)$ and combining (1.10), (3.11), and (3.17) we find

$$\Delta_K = \left(\frac{1}{D\psi} \frac{dD\psi}{dn} \right)^2 S_0(n) + \frac{1}{V(D\psi)^2 d} \langle \delta_\perp \mathbf{K}_0 : \delta_\perp \mathbf{K}_0 \rangle \tag{3.18}$$

On the other hand, the fluctuations in $\psi_0(X)$ are entirely determined by fluctuations in N, as can be seen from (3.4). Thus, the remainder in (3.17) does not give a contribution to Δ_ψ.

In view of the fact that a calculation of Δ_K is not yet available, a simple approximation is to replace Δ_K by the first term on the right-hand side of (3.18). This approximation yields the following results for the long time behavior of the time correlation functions, as given in (1.8):

$$\begin{aligned} \phi_2(t) &\simeq -2\pi \frac{D^2}{n^2} S_0(n) \left(\frac{n}{D} \frac{dD}{dn} - \frac{nv_0}{1 - nv_0} \right)^2 (4\pi Dt)^{-(d+2)/2} \\ \phi_4(t) &\simeq \left(\frac{nv_0}{1 - nv_0} \right)^2 \frac{D^2}{n^2} S_0(n) (4\pi Dt)^{-d/2} \end{aligned} \tag{3.19}$$

For the Burnett functions, given in (1.9), one has for $d \neq 2$

$$\begin{aligned} D_4(t) &\simeq D_4 - \frac{\left[nv_0/(1 - nv_0) \right]^2 D S_0(n)}{2\pi (d-2) n^2 (4\pi Dt)^{(d-2)/2}} \\ B(t) &\simeq B - \frac{\left[\left(\frac{n}{D} \frac{dD}{dn} - \frac{nv_0}{1 - nv_0} \right)^2 + 2 \left(\frac{nv_0}{1 - nv_0} \right)^2 \right] D S_0(n)}{4\pi (d-2) n^2 (4\pi Dt)^{(d-2)/2}} \end{aligned} \tag{3.20a}$$

[5] Note that we are dealing with fluctuations in a grand canonical ensemble. With the help of (3.16) one verifies immediately that $\langle (\delta_\perp A_0)^2 \rangle$ equal the mean square fluctuation in δA_0 in a canonical ensemble, where the total number of particles N is kept fixed. With this interpretation of the second term on the right-hand side of (3.17) the fluctuation formula (3.17) relates the fluctuation of some quantity A_0 in the grand canonical ensemble to the fluctuations of the same quantity A_0 in a canonical ensemble, and is simply a special case of a general formula, derived by Lebowitz, Percus, and Verlet[19] relating fluctuation formulas in different equilibrium ensembles.

and for $d = 2$

$$D_4(t) \simeq \left(\frac{nv_0}{1 - nv_0} \right)^2 \left[\frac{DS_0(n)}{4\pi n^2} \right] \log t$$
$$B(t) \simeq \left[\left(\frac{n}{D} \frac{dD}{dn} - \frac{nv_0}{1 - nv_0} \right)^2 + 2 \left(\frac{nv_0}{1 - nv_0} \right)^2 \right] \left(\frac{DS_0(n)}{8\pi n^2} \right) \log t \tag{3.20b}$$

Since the coefficients of the long time tails in $\phi_4(t)$ and $D_4(t)$ contain only Δ_ψ, they are expected to be exact. The coefficient of the tail in $\phi_2(t)$ and $B(t)$, containing Δ_K, are only approximate, since we have neglected the fluctuation $\delta_\perp K_0$ in (3.18). One would expect that the latter approximation is only exact to the lowest order in the density, where the diffusing particle never collides with the same scatterer twice, so that $\langle \hat{\mathbf{v}} G_z \hat{\mathbf{v}} \rangle_{X,1}$ will depend only on the mean free path in configuration X, i.e., on the local density. At higher density correlated collision sequences contribute to $\langle \hat{\mathbf{v}} G_z \hat{\mathbf{v}} \rangle_{X,1}$ in a way which depends on the microscopic arrangement of the scatterers and not just on the local density of scatterers and the second term on the left-hand side of (3.18) becomes important.

3.2. Lorentz Gas with Overlapping Scatterers

In the overlapping Lorentz gas[18] the scatterers do not interact with each other, and hence two or more of them may form overlapping clusters. The distribution of scatterers is given by the grand canonical distribution for an ideal gas with $W(X)$ in (3.5) replaced by unity. This is the Poisson distribution

$$\rho(X) = \frac{n^N e^{-nV}}{N!} \tag{3.21}$$

where the fugacity Z equals the average density of scatterers n. For the overlapping case the situation is complicated by the fact that the diffusive medium is not simply connected; there exist, even at low scatterer density, trapping regions from which moving particles cannot escape and into which they cannot penetrate. In addition there exists in the thermodynamic limit exactly one "diffusive" region of infinite extent, provided the density of scatterers is smaller than the percolation density[20–23] for the free volume.

Since the mode-coupling theory assumes that the moving particles obey a coarse-grained diffusion equation it is applicable only to particles in the percolating part of the free volume. Thus, for the overlapping Lorentz gas ψ refers only to the fraction of free volume in the infinite cluster and the average in (1.4), leading to the long time tails (1.8) and (1.9), represents an average in which *the moving particle is required to be on the infinite cluster.*

On the other hand, the averages introduced in (3.1) and (3.8) and (3.9) of Subsection 3.1, as well as those computed in molecular dynamics simulations or kinetic theory, generally include both trapped and untrapped particles. Let us denote these conventional averages $\langle \cdots \rangle^*$. To see the difference between the two averages, consider the intermediate scattering function $F^*(k,t)$, defined using the conventional averaging procedure [see (3.1)],

$$F^*(k,t) = \langle e^{ik\Delta x(t)} \rangle^*_{\text{eq}} \tag{3.22}$$

Since the displacement of the trapped particles is bounded, for sufficiently small k these particles simply contribute unity to the argument of the average in (3.22). Thus the relation between F and F^* is, for small k,

$$F^*(k,t) \simeq \xi F(k,t) + (1-\xi) \tag{3.23}$$

where ξ is the probability in the $\langle \cdots \rangle^*$ ensemble that the particle is on the infinite cluster.

The physical situation corresponding to the mode-coupling average can be realized by freezing an equilibrium configuration of scatterers and feeding the moving particles in afterwards, so that the density of moving particles in the trapping regions remains equal to zero. The ensemble average in (3.9a) has to be modified by setting ζ equal to zero within the trapping regions. As a function of the density n of scatterers the average free volume fraction ψ exhibits a phase transition at the percolation density.[23,24] In fact, ψ is the order parameter for this transition and vanishes above the percolation threshold.

We are unable to calculate ξ, ψ, or Δ_ψ at arbitrary scatterer density. Thus, for the remainder of this subsection we will make the approximation that the particle can diffuse in and out of the trapping regions. (Since at least three scatterers are required for $d=2$ to form a trapping region, we estimate the errors made to be of relative order n^3.[6] In this approxiation $\xi = 1$ and the average density is constant throughout the total free volume. Thus, the ensemble (3.9a) with a uniform ζ applies and $\psi(\mathbf{r}, X)$ is defined in the same way as for nonoverlapping Lorentz gas.

Accordingly, we take $\psi(\mathbf{r}, X)$ to be the overlap function

$$\psi(\mathbf{r}, X) = W(\mathbf{r}, X) = \prod_{i=1}^{N} \left[1 + f(\mathbf{r}, \mathbf{R}_i)\right] \tag{3.24}$$

where $\mathbf{R}_i$ is the position of the ith scatterer and

$$f(\mathbf{r}, \mathbf{R}) = \begin{cases} -1 & \text{for } |\mathbf{r}-\mathbf{R}| < \sigma \\ 0 & \text{for } |\mathbf{r}-\mathbf{R}| > \sigma \end{cases} \tag{3.25}$$

[6] In d dimensions the error is $O(n^{d+1})$.

Thus

$$\psi_0(X) = \int d\mathbf{r}\, W(\mathbf{r}, X) \tag{3.26}$$

and $\mathbf{K}_0(X)$ is given by (3.11). We calculate first the average free volume $\langle \psi_0(X) \rangle$, in which we interchange the $\mathbf{r}$ integration in (3.8) and (3.9) with the $\mathbf{R}_i$ integrations. The latter yield $\int dX^N W(\mathbf{r}, X) = (V - v_0)^N$, where v_0 is the volume of a scatterer; the former yields an additional factor V with the result

$$\langle \psi_0(X) \rangle \equiv V\psi = e^{-nv_0} \tag{3.27}$$

Next, we consider the fluctuations Δ_ψ, defined through (3.24) and (1.10)–(1.12) as

$$\Delta_\psi = (V\psi^2)^{-1} \int d\mathbf{r} \int d\mathbf{r}' \left[\langle W(\mathbf{r}, X) W(\mathbf{r}', X) \rangle - \psi^2 \right] \tag{3.28}$$

By first performing the integrations over the positions of the scatterers, using the relations

$$\int dX\, W(\mathbf{r}, X) W(\mathbf{r}', X) = \left[V - 2v_0 + g(|\mathbf{r} - \mathbf{r}'|) \right]^N \tag{3.29}$$

with

$$g(|\mathbf{r} - \mathbf{r}'|) = \int d\mathbf{R}\, f(\mathbf{r}, \mathbf{R}) f(\mathbf{r}', \mathbf{R}) \tag{3.30}$$

we find for the fluctuation in the free volume

$$\Delta_\psi = \int d\mathbf{r} \left(e^{ng(r)} - 1 \right) \tag{3.31}$$

Thus we can give an expression for Δ_ψ in terms of an integral that depends on the volume excluded by two overlapping scatterers. This can be evaluated numerically, and the results for hard disks are listed in Table I. One should keep in mind, however, that the free volume and its fluctuations, as calculated in (3.27) and (3.31), include not only the diffusive region but also the trapping regions.

Although we have just obtained an expression for Δ_ψ (presumed to be correct to second order in the density), we can also write Δ_ψ in terms of fluctuations in the density, using (3.17) and (3.27):

$$\Delta_\psi = nv_0^2 + \langle (\delta_\perp \psi_0)^2 \rangle / (V\psi^2) \tag{3.32}$$

In view of the fact that the free volume fluctuations of the *diffusive* regions are not known, a simple and consistent approximation is to neglect the second term in (3.32). (The range of its validity will be discussed later on.) We, then, find for the fluctuations

$$\Delta_\psi \simeq nv_0^2 \tag{3.33}$$

Table I. Free Volume Fluctuations of Hard Disks

$n\sigma^2$	$\Delta_\psi v_0^{-1}$	$\Delta_\psi(\pi n\sigma^2 v_0)^{-1}$
0.02	0.06	1.02
0.03	0.10	1.02
0.05	0.16	1.04
0.10	0.34	1.08
0.14	0.50	1.11
0.18	0.65	1.14
0.20	0.73	1.16
0.24	0.91	1.20
0.30	1.19	1.26
0.32	1.28	1.28
0.65	3.59	1.75
0.74	4.39	1.90

Next, we turn to a consideration of Δ_K, defined in (3.15), which may also be written in the form (3.18) with the density fluctuations (3.13) for an ideal gas, $S_0(n) = n$. Consistency requires again to neglect the second term in (3.18). Thus using (3.23) we obtain

$$\Delta_K \simeq n\left(\frac{1}{D}\frac{dD}{dn} - v_0\right)^2 \tag{3.34}$$

With these approximations we find that the long time behavior of the correlation functions $\phi_2(t)$ and $\phi_4(t)$ is given by

$$\phi_2(t) \simeq -\frac{2\pi D^2}{n}\left(\frac{n}{D}\frac{dD}{dn} - nv_0\right)^2 (4\pi Dt)^{-(d+2)/2} \tag{3.35a}$$

$$\phi_4(t) \simeq nv_0^2 D^2 (4\pi Dt)^{-(d+2)/2} \tag{3.35b}$$

For the Burnett coefficient we find for dimensionality $d \neq 2$

$$D_4(t) \simeq D_4 - \frac{(nv_0)^2 D}{2\pi(d-2)n}(4\pi Dt)^{(d-2)/2} \tag{3.36a}$$

$$B(t) \simeq B - \frac{\left[\left(\frac{n}{D}\frac{dD}{dn} - nv_0\right)^2 + 2(nv_0)^2\right]}{4\pi(d-2)n}(4\pi Dt)^{(d-2)/2} \tag{3.36b}$$

while for $d = 2$

$$D_4 \simeq (nv_0)^2 (D/4\pi n)\log t \tag{3.36c}$$

$$B(t) \simeq \left[\left(\frac{n}{D}\frac{dD}{dn} - nv_0\right)^2 + 2(nv_0)^2\right](D/8\pi n)\log t \tag{3.36d}$$

In order to assess the range of validity of these results, it is useful to compare the value $\Delta\psi$ in (3.33), with the value given by (3.31). A density expansion of the latter yields

$$\Delta\psi = nv_0^2 + \tfrac{1}{2}n^2 \int d\mathbf{r}\, g^2(\mathbf{r}) + O(n^3) \tag{3.37}$$

where we have used the relation $\int d\mathbf{r}\, f(\mathbf{r}, \mathbf{R}) = -v_0$. According to the arguments, presented above (3.24), the fluctuations (3.31) and (3.37) in the *total free volume* agree with the fluctuations in the *volume of the diffusive region* to terms of $O(n^3)$ excluded. Hence, the result (3.33) is correct only to lowest order in the density. The estimate (3.34) for Δ_K is also correct only to lowest-order in the density, as discussed at the end of Subsection 3.1. One would therefore expect that the results given by (3.35) and (3.36) are correct only to lowest order in the density. The higher density corrections would come from using better expressions for Δ_ψ and Δ_K.

4. COMPARISON FOR THE LORENTZ GAS

4.1. Systematic Kinetic Theory

For the d-dimensional Lorentz gas at general densities no exact results are known. However, the Lorentz gas has been studied extensively by kinetic theory and by computer simulations. In the present section we want to compare the mode-coupling predictions with results obtained from these other methods, starting with the most fundamental one: kinetic theory. It is derived from the microscopic equations of motion, and therefore is in principle exact. The first prediction of a long time tail in the velocity autocorrelation function (VACF) for the Lorentz gas was made by Ernst and Weyland.[24] They used low-density kinetic theory, including the so-called ring terms to predict a long time behavior for $d \geqslant 2$:

$$\phi_2^{(0)}(t) \simeq -\left(2\pi D_0^2/n\right)(4\pi D_0 t)^{-(d+2)/2} \tag{4.1}$$

where D_0 is the Lorentz–Boltzmann diffusion coefficient in d dimensions,[5] i.e.,

$$D_0 = \left[\Gamma\left(\tfrac{1}{2}(d+3)\right)/2v\sigma^{d-1}\pi^{(d-1)/2}\right]/n \tag{4.2}$$

The mode-coupling results (3.19) and (3.35a) agree with this in the limit $n \to 0$ indeed.

To compare results obtained from different methods, it is convenient to introduce the ratio a of the long tail in the VACF $\phi_2(t)$ to its low-density value $\phi_2^{(0)}(t)$ n (4.1), i.e.,

$$\phi_2(t) \simeq a\phi_2^{(0)}(t) \tag{4.3}$$

where the mode-coupling theory predicts

$$a = (n\Delta_K / D_0^2)(D_0/D)^{(d+2)/2} \tag{4.4}$$

In a systematic comparison one should consider the kinetic theory prediction for the first density correction to the coefficient a in (4.3). For the diffusion coefficient D systematic higher-order density corrections are available, calculated by van Leeuwen and Weyland,[25] but not for the long time tail.

A determination of the long time tail from the mode-coupling theory would require an extensive kinetic analysis to calculate Δ_K in (3.15). Such analysis remains to be carried out. An approximate result for Δ_K, in which only density fluctuations are taken into account, was given in (3.19) for nonoverlapping scatterers and in (3.35) for overlapping scatterers, i.e.,

$$\begin{aligned} a^{(\mathrm{nov})} &= \frac{S_0(n)}{n}\left(\frac{n}{D}\frac{dD}{dn} - \frac{nv_0}{1-nv_0}\right)^2\left(\frac{D_0}{D}\right)^{(d-2)/2} \\ a^{(\mathrm{ov})} &= \left\{\frac{n}{D}\frac{dD}{dn} - nv_0\right\}^2\left(\frac{D_0}{D}\right)^{(d-2)/2} \end{aligned} \tag{4.5}$$

Note that both expressions approach 1 as $n \to 0$, since D approaches its Boltzmann value (4.2). A careful examination of the linear density correction shows that there are additional contributions from kinetic theory of $O(n)$, not accounted for in the approximate result (4.5), but presumably present in Δ_K. Numerical values are presented in Table II. For the Burnett correlation functions $D_4(t)$ and $\phi_4(t)$, introduced in (1.6) and (1.7), the situation is more satisfactory. The long time tails of these functions depend only on Δ_ψ and not on Δ_K, as can be seen by inspection of (1.8) and (1.9). For the nonoverlapping Lorentz gas Δ_ψ is given *exactly* by (3.12). For the overlapping Lorentz gas Δ_ψ can be calculated exactly to terms of relative order n^2 included, shown in (3.37) and Table I. The Burnett coefficient $B(t)$, defined in (1.6), involves both Δ_ψ and Δ_K, where Δ_K has not yet been

Table II. Amplitude of the Long Time Tail in the VACF for the Two-Dimensional Lorentz Gas[a]

$n\sigma^2$	$d\log D/d\log n$	a_{comp}	a_{MC}	a_{GLY}	a_{KM}
0.03 (O)	1.13 ± 0.05	2.7 ± 0.6	1.5 ± 0.1	1.08	1.20
0.05 (O)	1.18 ± 0.05	3.7 ± 1	1.8 ± 0.1	1.15	1.34
0.05 (N)	1.4	2	1.2		

[a]The coefficient a measures the strength of the long time tail in the VACF for the two-dimensional Lorentz gas. Compared are computer results (a_{comp}) with mode-coupling results (a_{MC}) and other results ($a_{\mathrm{GLY}}, a_{\mathrm{KM}}$), defined in (4.9) and (4.10), respectively. Units are chosen so that $a = 1$ for the low-density result. (O) refers to overlapping and (N) to nonoverlapping. The logarithmic derivative of the diffusion coefficient is also given.

Table III. Long Time Tail in the Modified Burnett Coefficient[a]

$n\sigma^2$	D/D_0	b_{comp}	b_{MC}
0.03 (O)	0.88 ± 0.01	3.9 ± 1.5	1.3 ± 0.1
0.05 (O)	0.81 ± 0.01	4.2 ± 1.5	1.5 ± 0.1

[a] Comparison of mode-coupling results with the computer results for the coefficient, b, of the long time tail of the correlation function $\rho_B(\tau)$ whose integral is the modified Burnett coefficient, $B(t)$. The ratio of the diffusion coefficient to its Boltzman value is also given.

calculated exactly. Its long time behavior has been calculated by Ernst and van Beijeren,[5] using *low-density* kinetic theory, including the ring terms. Their low-density result

$$\frac{dB^{(0)}(t)}{dt} \simeq -\left(\frac{1}{2n}\right)^2 D_0^2 (4\pi D_0 t)^{-d/2} \tag{4.6}$$

is in agreement with the mode-coupling results (3.19), (3.20) and (3.35), (3.36) for the Lorentz gas with nonoverlapping and overlapping scatterers in the limit as $n \to 0$.

At general densities the mode-coupling results may be represented as

$$\frac{dB(t)}{dt} \simeq b \frac{dB^{(0)}(t)}{dt} \tag{4.7}$$

In the same approximation as used in (4.5), the ratio b follows for the nonoverlapping and overlapping case, respectively, from (3.20) and (3.36) as

$$\begin{aligned} b^{(\text{nov})} &= \frac{S_0(n)}{n}\left[\left(\frac{n}{D}\frac{dD}{dn} - \frac{dv_0}{1-nv_0}\right)^2 + 2\left(\frac{nv_0}{1-nv_0}\right)^2\right]\left(\frac{D}{D_0}\right)^{2-d/2} \\ b^{(\text{ov})} &= \left[\left(\frac{n}{D}\frac{dD}{dn} - nv_0\right)^2 + 2(nv_0)^2\right]\left(\frac{D}{D_0}\right)^{2-d/2} \end{aligned} \tag{4.8}$$

Numerical estimates of b in the two-dimensional Lorentz gas are given in Table III.

4.2. Approximate Kinetic Theories

The behavior of correlation functions in the Lorentz gas with overlapping scatterers at general density has also been studied in a series of papers by Götze *et al.*[26] Their method starts from the Zwanzig–Mori projection operator technique to obtain an equation of motion for the microscopic

phase space density of the moving particle. By means of a number of approximations a closed equation for the memory function is then obtained. From this equation the behavior of the correlation functions can be determined in the limit of large t and small k. Their result for the long time tail of the velocity correlation function $\phi_2(t)$ for arbitrary dimensionality d is of the form (4.3), but with a given by

$$a_{\mathrm{GLY}}^{(\mathrm{ov})} = \left(\frac{D}{D_0} + nv_0 \right)^2 \left(\frac{D_0}{D} \right)^{d/2} \tag{4.9}$$

Numerical estimates of a in (4.9) for the two-dimensional overlapping Lorentz gas are shown in Table II.

Excluded volume corrections, present in (4.5), have been taken into account by Keyes and Mercer,[27] who quote for arbitrary dimensionality

$$a_{\mathrm{KM}} = (1 + nv_0)^2 \tag{4.10}$$

(for numerical values see Table II).

4.3. Computer Simulations

There are several computer simulations of time correlation functions over a long time range in the two-dimensional Lorentz gas. In the case of *overlapping scatterers* the first simulations for the VACF have been performed by Bruin.[28] More recently Alder and Alley[29–33] have repeated these simulations with much greater precision, for larger systems over a larger range of times and scatterer densities. In addition they have investigated the super-Burnett correlation functions, and performed simulation for Lorentz models with stochastic scattering laws. For the Lorentz gas with nonoverlapping hard disks Tjon and Lewis[34] have computed the VACF.

In order to compare our mode-coupling results with those from computer simulations it is convenient to represent the correlation functions in dimensionless units. The dimensionless density is $n^* = n\sigma^2$ and the dimensionless time is $\tau = t/t_0 = 2n^* vt/\sigma$, where $t_0 = 1/2n\sigma v$ is the mean free between collisions. Our long time results (4.3) for the VACF in the two-dimensional Lorentz gas may then be represented as

$$\rho_D(\tau) = \phi_2(t)/\phi_2(0) \simeq -n^* a/\pi\tau^2 \tag{4.11}$$

where $\phi_2(0) = \frac{1}{2}v^2$ is the initial value, and a is given in (4.4). This result follows directly from (4.1) and (4.2), where $a \to 1$ as $n \to 0$. In order to calculate a at general densities one needs D as a function of n. Unfortunately only a few terms in the nonanalytic expansion of D in powers of n and $\log n$ have been calculated.[25] For the range of densities at which the computer simulations were performed, several more terms would be

needed. Therefore we used Bruin's computer values for the diffusion coefficient to calculate the derivative dD/dn. Bruin gives D at intervals of 0.01 in n^*, from which we estimated derivatives by taking differences. At the densities, where Alder and Alley have computed D, their results are in close agreement with those of Bruin.

For the nonoverlapping Lorentz gas we used Lewis' curve fitting[35] to his published data to evaluate the derivative of the diffusion coefficient with respect to n. We used Ree and Hoover's[36] equation of state for hard disks to calculate the isothermal compressibility $(\partial p/\partial n)_T$. In Table II the approximate results (4.8) for both the nonoverlapping and the overlapping Lorentz gas are presented and compared with the computer results of Alder and Alley, and of Tjon and Lewis, respectively, at densities $n^* = 0.03$ and $n^* = 0.05$. At these densities the computer results take the form (4.11) at long times, and the coefficient can be compared to the mode-coupling prediction. The agreement is in general rather poor as can be seen from Fig. 1 and Table II. However, Alder and Alley[29] have plotted the computer simulation values of a in (4.11) as a function of n, and extrapolated this function linearly to zero density. The extrapolated value of a is very close to unity, in good agreement with the kinetic theory calculations

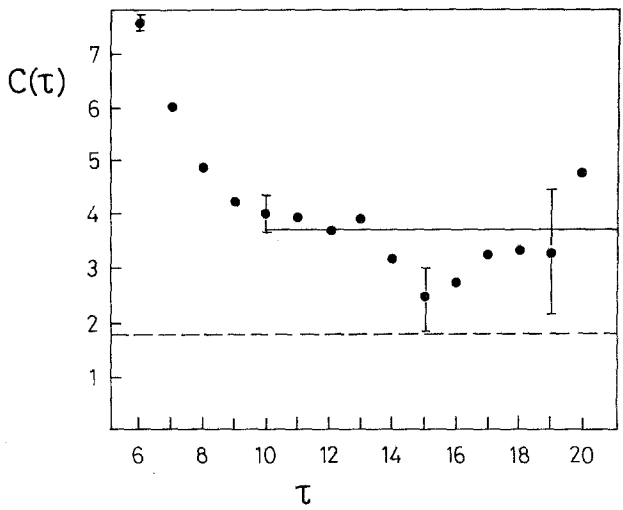

Fig. 1. Computer results[29,30] for the velocity autocorrelation function $C(\tau) = -(\pi\tau^2/n\sigma^2)[\rho_D(\tau) - \exp(-4\tau/3)]$ at a density $n\sigma^2 = 0.05$ as a function of the dimensionless time $\tau = 2n\sigma vt$, where $C(\tau) \simeq a$ for large τ on account of (4.11). Here $\rho_D(\tau)$ is defined in (4.11) and $\exp(-4\tau/3)$ represents its behavior as calculated from the Boltzmann equation. The dotted line is an evaluation of the approximate mode-coupling prediction for the long time tail; the solid line is the arithmetic mean of the points between $\tau = 10$ and $\tau = 20$ collision times.

for low densities. However, the coefficient a, obtained from computer simulations, increases much faster with increasing density than predicted by the approximate results for Δ_K and Δ_ψ. Alder and Alley have also computed the time dependence of the Burnett function $B(t)$ for the overlapping Lorentz gas.[30] They expressed this function in dimensionless variables by introducing[7]

$$\rho_B(\tau) = D_0^{-2}\, dB(t)/dt \tag{4.12}$$

In the mode-coupling theory for the overlapping case this function assumes for long times the form

$$\rho_B(\tau) \simeq 4n^* b/3\pi\tau \tag{4.13}$$

as follows from (4.8) and (4.9). Numerical values of b are given in Table II, and compared with computer results. A similar extrapolation to zero density of the computer values for b at $n^* = 0.03$ and $n^* = 0.05$ is not inconsistent with the theoretical value 1, but the uncertainties in the data are so large that no stronger conclusions can be drawn.

5. CONCLUSION

The mode-coupling theory predicts long time effects in diffusion phenomena in random media. We have investigated in particular the VACF $\phi_2(t)$ and the four-point velocity correlation function $\phi_4(t)$, related to the super-Burnett coefficient, for several models. The strength of the long time tails in these correlation functions is proportional to the variance Δ_K of the fluctuations in the local coefficient $\mathbf{K}(\mathbf{r}, X)$. Randomness in the scattering medium is necessary for the appearance of the long time effects discussed here. For instance, if the random lattice in the models of Sections 2.1 and 2.2 becomes strictly periodic, i.e., the interval distributions become sharp, the long time effects disappear as in ordinary random walks on regular lattices. In the random walk models of Sections 2.3 and 2.4 on regular lattices the strict periodicity is broken since the jump rates vary stochastically per lattice bond or site. If the jump rate distribution becomes sharp and site independent, strict periodicity is restored and the long time tails disappear. In Section 2 we were able to verify that the mode-coupling theory is *exact* for several one-dimensional models and one d-dimensional hopping model. For these systems we found a single variable which entirely determines the fluctuations in Δ_K and Δ_ψ. For the stochastic Lorentz gases this variable is the step length, and for the random hopping models it is the waiting time, as has been shown in Appendix A.1.

[7] In the literature[30] $\rho_B(\tau)$ has also been defined as $\rho_B(\tau) = D_0^{-2}(d/dt)^2[tB(t)]$. As $B(t) \sim \log t$ for long times, the dominant behavior for both functions is the same.

For the deterministic Lorentz gases the situation is much more complicated because fluctuations in Δ_K are not controlled by fluctuations in any simple variable such as density. In Section 3 we made an approximate calculation of the mode-coupling coefficients of Section 1 by finding the contribution of density fluctuations to Δ_K and Δ_ψ. Unfortunately, the results of this approximation are in poor agreement with the computer simulations except at the lowest densities. This fact leads us to believe that there are important contributions to the full expression for Δ_K, given in (3.15), from fluctuations which are more complicated than density fluctuations, perhaps fluctuations in the arrangement of the scatterers. Because of the simple geometry of one dimension these arrangement fluctuations do not contribute to Δ_K or Δ_ψ for the models discussed in Section 2. In order to test the formal validity of the mode-coupling theory for the Lorentz gas and related higher-dimensional models it will be necessary to develop a kinetic theory of similar microscopic methods to evaluate the expression in (3.15).

It is interesting to contrast the mode-coupling theory presented here for disordered diffusive systems with the mode-coupling theory for long time tails in fluids. Although the hydrodynamic equations are more complicated than the fluctuating diffusion equation, the resulting amplitudes for the leading long time tails are much easier to evaluate for fluids. The reason is that, for fluids, the amplitudes contain only thermodynamic fluctuations which can be reduced to specific heats and compressibilities. For disordered media the amplitudes depend on fluctuations in nonthermodynamic quantities.

ACKNOWLEDGMENTS

The authors would like to thank B. J. Alder, W. E. Alley, T. R. Kirkpatrick, R. Zwanzig, and J. C. Lewis for helpful dicussions and correspondence, and W. Hoogeveen for performing the calculations for Table I. M.H.E. Wishes to express his thanks to the Institute for Physical Science and Technology of the University of Maryland for its hospitality in the fall of 1981 and spring of 1983.

NOTE ADDED IN PROOF

We have been informed that P. Visscher has recently obtained similar results by an independent method.[37]

APPENDIX

A.1. One-Dimensional Stochastic Lorentz Model

We first consider the one-dimensional stochastic Lorentz model described in Section 2.1, and compute the coarse-grained Onsager coefficient

$K(r, X)$. To do this we imagine a current-carrying steady state and use the basic property of such one-dimensional systems, namely, that the current across each scatterer has the same value, say, j. To compute $K(r, X)$ we first relate j to the microscopic concentration of particles to the left and right of each scatterer, and then relate j to K.

We focus our attention on a single scatterer and define c_R and c_L as the concentration of moving particles immediately to the right and to the left of the scatterer, respectively. Of the c_R particles $c_R^{(+)}$ will be moving to the right and $c_R^{(-)}$ will be moving to the left. Similarly, c_L is composed of $c_L^{(+)}$ particles moving to the right and $c_L^{(-)}$ moving to the left. The current j across a scatterer can then be written in three equivalent ways as

$$j = v\left(c_R^{(+)} - c_R^{(-)}\right) = v\left(c_L^{(+)} - c_L^{(-)}\right) \tag{A.1a}$$

$$= v(1-p)\left(c_L^{(+)} - c_R^{(-)}\right) \tag{A.1b}$$

Here v and p are defined in Section 2.1. The expressions in (A.1a) are simply the microscopic expressions for the current in terms of the concentration of the moving particles, while (A.1b) expresses the microscopic dynamics of the moving particles, i.e., $c_R^{(+)} = (1-p)c_R^{(-)} + pc_L^{(+)}$. If we combine these equations with the relations $c_R = c_R^{(+)} + c_R^{(-)}$ and $c_L = c_L^{(+)} + c_L^{(-)}$ we obtain

$$j = \left[v(1-p)/2p\right]\Delta c \tag{A.2a}$$

where

$$\Delta c = c_L - c_R \tag{A.2b}$$

Since in the steady state the current j has the same value across each scatterer, it follows from (A.2a) that the concentration jump Δc is the same across each scatterer also.

Next, we use (A.2a) to relate j to the coarse-grained concentration gradient at position r. To do this we consider the number $N_c(r)$ of scatterers in the coarse-graining cell of length V_c, centered around r. The total change in the concentration of moving particles across a coarse-graining cell is then equal to the number of scatterers in the cell, multiplied by the change in concentration across one scatterer. Then, if we divide this value by the length V_c, we obtain the coarse-grained concentration gradient, i.e.,

$$\nabla c(r) = -\Delta c N_c(r)/V_c = -\Delta c/l(r, X) \tag{A.3}$$

and we have introduced the coarse-grained local volume per scatterer

$$V_c/N_c(r) = l(r, X) = 1/n(r, X) \tag{A.4}$$

Combination of (A.2a) and (A.3) yield a coarse-grained description for the current in the steady state

$$j(r) = -\left[v(1-p)/2p\right]l(r, X)\nabla c(r) \tag{A.5}$$

By comparing (A.4) with the expression for the current in (1.1b), and using the relation $\psi = 1$ for this model, we obtain

$$K(r,X) = \left[v(1-p)/2p\right] l(r,X) \tag{A.6}$$

A.2. One-Dimensional Waiting Time Lorentz Model

Next we consider the one-dimensional waiting time Lorentz model of Section 2.2. and compute the coarse-grained Onsager coefficient, using the *symmetric* model with $p = 1/2$ as an example. This is done again by considering current-carrying steady states, which can be set up by introducing appropriate boundary conditions with emitting and absorbing walls, as described by van Beijeren.[3]

For this model the probability $P_n(t)$ of finding a particle at site n satisfies[3] a master equation of the form (2.13) with a fixed jump rate $\nu_n = 1/2\tau$. This equation allows a solution with a steady current

$$j = (1/2\tau)\,\Delta P = \text{const} \tag{A.7}$$

where $\Delta P = P_{n+1} - P_n$.

In order to relate the coarse-grained $P(r)$ to the coarse-grained concentration $c(r)$ we observe that $V_c c(r) = N_c(r)P(r)$. In addition we have for this model (see Section 2.2) an equilibrium solution of the form $\psi(r,X) = n(r,X) = 1/l(r,X) = N_c(r)/V_c$. Hence we have the relation

$$\begin{aligned} \Delta P &= \Delta(c/\psi) = \text{const} \\ &= -l(r,X)\nabla(c/\psi) \end{aligned} \tag{A.8}$$

By combining (A.7) and (A.8) and comparing with (1.1) we obtain for the coarse-grained Onsager coefficient

$$K(r,X) = l(r,X)/2\tau \tag{A.9}$$

For the asymmetric waiting time Lorentz model (where $p \neq 1/2$) we will use the following relation without further arguments:

$$K(r,X) = \left[(1-p)/2p\tau\right] l(r,X) \tag{A.10}$$

A.3. One-Dimensional Random Barrier Model

The arguments in this section closely parallel those in the previous subsection. The steady-state current through the bond between the sites n and $(n+1)$ is according to (2.13)

$$j = \nu_n(P_{n+1} - P_n) = \text{const} \tag{A.11}$$

The coarse graining is performed by dividing the system into cells of a given size $V_c = N_c l$, where l is the lattice distance and N_c the number of particles in a cell. Since the coarse-grained value of P/l equals the concentration of moving particles, we compute from (A.11) the jump, $\Delta c(r)$, across the coarse-graining cell $V_c(r)$, centered at r, i.e.,

$$\Delta c(r) = \sum_{n \in V_c(r)} (P_{n+1} - P_n) \Big/ l = (j/l) \sum_{n \in V_c(r)} (1/\nu_n) \tag{A.12}$$

The coarse-grained gradient $\nabla c(r) = \Delta c(r)/N_c l$ is obtained by dividing (A.12) by the length $N_c l$ of the coarse-graining cell.

Since $\psi(r, X) = 1$ for this model (see Section 2.3) we can deduce from (1.1) that the coarse-grained Onsager coefficient $K(r, X)$ is given by

$$l^2/K(r, X) = \tau(r, X) = N_c^{-1} \sum_{n \in V_c(r)} \frac{1}{\nu_n} \tag{A.13}$$

where $\tau(r, X)$ is the local waiting time.

Note that the arguments used in (A.12) for calculating the gradient in $c(r)$ can only be applied in one-dimensional systems.

A.4. d-Dimensional Jump Rate Model

The steady-state solutions of the master equation (2.18) are given by

$$\nu_{\mathbf{n}} P_{\mathbf{n}} = a + \mathbf{b} \cdot \mathbf{n} \tag{A.14}$$

where a and $\mathbf{b}$ are constants, and $\mathbf{n} = (n_\alpha, n_\beta, \ldots)$ is a lattice vector. Hence the jump $\Delta_\alpha(\nu_{\mathbf{n}} P_{\mathbf{n}})$ across a bond in the α direction is given by the constant $b_\alpha = l j_\alpha$, where j_α is the α component of the steady state current density. The coarse-grained value of $\nu_{\mathbf{n}} P_{\mathbf{n}} l^{-d}$ is according to (2.14) given by Dc/ψ, so that

$$j_\alpha = \frac{1}{l} \Delta_\alpha \left(\nu_{\mathbf{n}} P_{\mathbf{n}} l^{-d} \right) = \frac{D}{l} \Delta_\alpha \frac{c}{l} = D \nabla_\alpha \frac{c}{\psi} \tag{A.15}$$

Hence, the coarse-grained Onsager coefficient,

$$K(r, X) = D \tag{A.16}$$

is not fluctuating.

REFERENCES

1. M. H. Ernst, J. Machta, J. R. Dorfman, and H. van Beijeren, *J. Stat. Phys.* (1984).
2. P. Grassberger, *Physica* **103A**:558 (1980).
3. H. van Beijeren, *Rev. Mod. Phys.* **54**:195 (1982).
4. H. Spohn and H. van Beijeren, *J. Stat. Phys.* **31**:231 (1983).
5. M. H. Ernst and H. van Beijeren, *J. Stat. Phys.* **26**:1 (1981).
6. P. M. Richards and R. L. Renken, *Phys. Rev. B* **21**:3740 (1981).

7. S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, *Rev. Mod. Phys.* **53**:175 (1981).
8. J. Machta, *Phys. Rev. B* **24**:5260 (1981).
9. R. Zwanzig, *J. Stat. Phys.* **28**:127 (1982).
10. J. Machta, *J. Stat. Phys.* **30**:305 (1983).
11. J. W. Haus, K. W. Kehr, and K. Kitahara, *Phys. Rev. B* **25**:4918 (1982); *Z. Phys.* **B50**:161 (1983).
12. I. Webman and J. Klafter, *Phys. Rev. B* **26**:5950 (1982).
13. M. J. Stephen and R. Kariotis, *Phys. Rev. B* **26**:2917 (1982).
14. P. J. H. Denteneer and M. H. Ernst, *J. Phys. C* **16**:L961 (1983).
15. J. W. Haus, K. W. Kehr, and J. Lyklema, *Phys. Rev. B* **25**:2905 (1982).
16. V. Halpern, *J. Phys. C* **15**:L827 (1982).
17. P. J. H. Denteneer and M. H. Ernst, *Phys. Rev. B* **29**:1755 (1984).
18. E. H. Hauge, *Lecture Notes in Physics*, G. Kirczenow and J. Marro, eds. (Springer Verlag, Berlin, 1974), Vol. 31.
19. J. L. Lebowitz, J. K. Percus, and L. Verlet, *Phys. Rev.* **153**:250 (1967); D. C. Wallace and G. K. Straub, *Phys. Rev. A* **27**:2201 (1983).
20. J. Kertesz, *J. Phys. (Paris) Lett.* **42**:L395 (1981).
21. S. W. Haan and R. Zwanzig, *J. Phys. A. Math. Gen.* **10**:1547 (1977).
22. E. T. Gawlinski and H. E. Stanley, *J. Phys. A. Math. Gen.* **14**:L291 (1981).
23. A. Masters and T. Keyes, *Phys. Rev. A* **25**:1010 (1982); **26**:2129 (1982); T. Keyes, *Physica* **118A**:395 (1983).
24. M. H. Ernst and A. Weyland, *Phys. Lett.* **34A**:39 (1971).
25. J. M. J. van Leeuwen and A. Weyland, *Physica* **36**:457 (1967); **38**:35 (1968).
26. W. Götze, E. Leutheuser, and S. Yip, *Phys. Rev. A* **23**:2634 (1981); **24**:100 (1981); **25**:533 (1982).
27. T. Keyes and J. Mercer, *Physica* **95A**:473 (1979).
28. C. Bruin, *Phys. Rev. Lett.* **29**:1670 (1972); *Physica* **72**:261 (1974).
29. W. E. Alley, Ph.D. thesis, Univ. Calif. Davis (1979).
30. B. J. Alder and W. E. Alley, *J. Stat. Phys.* **19**:341 (1978).
31. B. J. Alder in *Lecture Notes in Physics*, Vol. 84, L. Carrido, P. Seglar, and P. J. Shepherd, eds. (Springer, Berlin, 1978).
32. B. J. Alder and W. E. Alley, preprint, November (1981).
33. B. J. Alder and W. E. Alley, *Phys. Rev. Lett.* **43**:653 (1979).
34. J. C. Lewis and J. A. Tjon, *Phys. Lett.* **66A**:349 (1978).
35. J. C. Lewis, private communication.
36. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**:939 (1964).
37. P. Visscher, private communication and *Phys. Rev. B*, to appear.