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Superionic Conductors

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The so-called superionic conductors represent a class of solid materials showing an unusually high ionic conductivity. Their structure is characterized by strong disorder in the sublattice of conducting ions. We shall describe the dynamic properties of the partially disordered state on the basis of two classes of theoretical models. For stochastic lattice gases we discuss the behavior of various time-correlation functions relevant for inelastic neutron- and light-scattering experiments and for tracer-diffusion measurements. In addition we study a system of interacting Brownian particles in the presence of a periodic potential as a model for optimized (AgI-type) ionic conductors. A mean-field theory is developed which implies a relationship between the conductivity and structural properties.

KEY WORDS: Superionic conductors; stochastic lattice gas; Brownian motion.

1. INTRODUCTION

The so-called superionic conductors form a particular class of ionic solids characterized by ionic conductivities of an order of magnitude as usually found for molten salts.(1,2) This phenomenon of fast ionic transport in solids has been observed in a variety of materials with different kinds of structure. Well-known examples are the AgI-type materials, e.g., the Ag^+ conductors AgI, Ag_2S, Ag_3SI, or the Cu^+ conductors CuI, CuBr, etc., which have been studied extensively in the past. Another interesting group of substances includes anionic conductors like CaF_2 or PbF_2. Examples, where the conduction process is confined to a lower dimensionality are the β-alumina ($d=2$) or K-hollandite ($d=1$).

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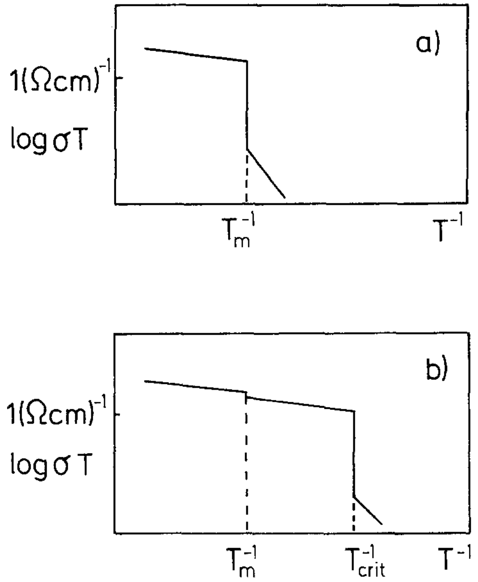

Fig. 1. Schematic behavior of the ionic conductivity σ as a function of temperature T for a 'normal' ionic material (*a*) and an AgI-type superionic conductor (*b*). T_m denotes the melting temperature and T_{crit} the critical temperature for sublattice disordering.

In Fig. 1 the conductivity of AgI-type compounds is shown schematically as a function of temperature. At low temperatures the behavior is similar to "normal" ionic solids, whose conductivity is due to a small concentration of thermally generated mobile defects. In the temperature range between a certain critical temperature T_c and the melting point T_m a highly conducting phase exists which is characterized by a high degree of disorder in the system of conducting ions and crystalline order in the counterion system. Detailed information on the structure of this phase has become available both from experiments(3) and from molecular dynamics studies.(4) For example, in AgI or Ag_2S the density distribution $\rho_{Ag}(\mathbf{r})$ of silverions reflects a network of paths connecting the tetrahedral interstitial sites in the bcc-lattice frame.(3) The Ag–Ag pair correlation function averaged over orientation shows liquidlike features with a correlation hole such that the occupation of first and second neighbor sites is excluded.(5) This shows that we are dealing with a highly correlated system and that the effect of interparticle interactions should play an important role in the diffusion process.

We shall give here a brief account of simple theoretical concepts which are useful for understanding the dynamic behavior of fast ionic conductors.(6) The motion of ions will be treated as a stochastic motion in a medium with a periodic structure. First we consider nondilute lattice gas models and review some of their main transport properties. Models of this type apply to the rather general situation of many-particle hopping encountered also in hydrogen–metal systems,$^{(7)}$ chemisorbed submonolayer films,$^{(8)}$ or intercalation compounds.$^{(9)}$

Secondly, noting the fact that in the equilibrium state of AgI-type compounds the mobile ions are considerably delocalized along the diffusion paths, we may regard the ions as a "fluid" of interacting Brownian particles moving in the periodic lattice potential. For this model we derive a nonlinear mean-field equation which gives an interrelation between the conductivity and structural properties. Our approach should provide a rather general description of the collective properties of ionic conductors.

2. STOCHASTIC LATTICE GAS

2.1. Master Equation

For a lattice of equivalent sites $\mathbf{l}$ we introduce occupation numbers n_l which are zero or unity depending on whether the site $\mathbf{l}$ is vacant or occupied. By $c = \langle n_l \rangle$ we denote the fraction of occupied sites. The configurations $\mathbf{n} = \{n_l\}$ of the system are allowed to change in time via consecutive particle hops from a site $\mathbf{l}$ to a nearest-neighbor site $\mathbf{l} + \boldsymbol{\delta}$. We describe the hopping process by a master equation of the form

$$\frac{dp(\mathbf{n}, t)}{dt} = \frac{1}{2} \sum_{l,\delta} \left[w_{l,l+\delta}(\mathbf{n}')\, p(\mathbf{n}', t) - w_{l,l+\delta}(\mathbf{n})\, p(\mathbf{n}, t) \right] \tag{2.1}$$

for the probability $p(\mathbf{n}, t)$ to find the configuration $\mathbf{n}$ at time t. $\mathbf{n}'$ denotes the configuration which results from $\mathbf{n}$ by the interchange of occupations n_l and $n_{l+\delta}$. $w_{l,l+\delta} = w_{l+\delta,l}$ is the corresponding transition rate, which is assumed to satisfy detailed balance,

$$w_{l,l+\delta}(\mathbf{n})\, e^{-\beta(\mathbf{n})} = w_{l,l+\delta}(\mathbf{n}')\, e^{-\beta H(\mathbf{n}')} \tag{2.2}$$

with $\beta = (k_B T)^{-1}$. The lattice gas Hamiltonian $H(\mathbf{n})$ is given by

$$H(\mathbf{n}) = \frac{1}{2} \sum_{l,l'} V_{l-l'} n_l n_{l'} \tag{2.3}$$

$V_{l-l'}$ denotes the pair interaction. Its form depends on the actual system considered. For superionic conductors the Coulomb interaction is most important, $V_{l-l'} = e^2/|\mathbf{l} - \mathbf{l}'|$, whereas in hydrogen–metal systems the dominant interaction between protons at large distances is the elastic interaction. Generally, for a lattice gas model to apply, typical hopping rates must be much smaller than the frequencies of vibrational degrees of freedom, which are not taken into account so far. In the following we discuss various dynamic correlation functions at equilibrium, which are relevant for inelastic neutron scattering, light scattering, or transport measurements.

2.2. "Ideal" Lattice Gas

Let us begin our discussion with the simplest case of an "ideal" lattice gas, where $V_{l-l'} \equiv 0$. This case already bears some interesting dynamics because in our general formulation double occupancy of sites is excluded, which amounts to a hard-core repulsion between the particles.

The transition rates are taken to be

$$w^0_{l,l+\delta}(\mathbf{n}) = \alpha(n_l - n_{l+\delta})^2 \tag{2.4}$$

with some rate constant α. Physically one may interpret α as the escape rate for the lattice potential wells. A thermally activated behavior may be assumed, $\alpha \propto \exp(-\beta V_0)$, where V_0 is the barrier between two sites.

Owing to the form (2.4), which describes the blocking of occupied sites, the particle hops are not purely random. Nevertheless, certain *collective properties* can be worked out exactly.

Consider as a first example the coherent dynamic structure factor which determines the cross section for inelastic neutron scattering. It is defined in terms of the dynamic correlation function for density fluctuations

$$n(\mathbf{q}) = \sum_l (n_l - c)\, e^{-iql} \tag{2.5}$$

by

$$S_{\mathrm{coh}}(\mathbf{q}, \omega) = \frac{1}{N} \int_{-\infty}^{+\infty} \frac{dt}{2\pi}\, e^{i\omega t} \langle n(\mathbf{q}, t)\, n(-\mathbf{q}, 0) \rangle \tag{2.6}$$

N is the total number of particles. To evaluate (2.6) one has to solve the equations of motion for the averaged occupation numbers $n_l(t)$ and then perform an equilibrium average over the initial configurations. From the master equation one can readily show that

$$\frac{dn_l(t)}{dt} = \alpha \sum_\delta [n_{l+\delta}(1 - n_l) - n_l(1 - n_{l+\delta})](t) \tag{2.7}$$

The bilinear terms in (2.7), which come from site blocking, obviously cancel. Therefore we are left with a linear set of rate equations which are identical with the independent particle case. This leads to the well-known quasielastic spectrum

$$S_{\mathrm{coh}}(\mathbf{q}, \omega) = \frac{1-c}{\pi} \frac{\gamma(\mathbf{q})}{\omega^2 + \gamma^2(\mathbf{q})} \tag{2.8}$$

with a half-width

$$\gamma(\mathbf{q}) = \alpha \sum_{\boldsymbol{\delta}} (1 - e^{i\mathbf{q}\boldsymbol{\delta}}) \tag{2.9}$$

The collective diffusion constant, determined by $\gamma(\mathbf{q} \to 0) \simeq D_{\mathrm{coll}} q^2$, is therefore simply given by the diffusion constant D_0 for infinite dilution.

Next we calculate the current in the presence of an external static bias field F. The rates for forward or backward jumps are assumed to be $\alpha_{\pm} = \alpha \exp(\pm \beta a F/2)$, where a is the lattice constant. From this the average current is found to be

$$\langle j \rangle = 2\alpha c(1-c) \sinh(\beta a F/2) \tag{2.10}$$

which shows particle–hole symmetry. We remark that the conductivity $\sigma = \langle j \rangle / F$ obtained in the linear response regime $F \to 0$ is consistent with the Nernst–Einstein relation

$$\sigma = \rho \beta D_{\mathrm{coll}} S(\mathbf{q} \to 0) \tag{2.11}$$

ρ is the average density and $S(\mathbf{q}) = 1 - c$ the static structure factor. The dynamic conductivity is simply constant, $\sigma(\omega) = \sigma(0)$. This, however, is no longer true for lattices with inequivalent sites.$^{(10)}$

As a further solvable case we consider the correlation function of the density of pairs with relative distance $\mathbf{l}$,

$$A_l(\mathbf{q}) = \sum_{l_1} n_{l_1} n_{l_1 + l} e^{-i\mathbf{q}l_1} \tag{2.12}$$

$$C_{l,l'}(\mathbf{q}, \omega) = \frac{1}{N} \int_{-\infty}^{+\infty} \frac{dt}{2\pi} e^{i\omega t} \langle A_l(\mathbf{q}, t) A_{l'}(-\mathbf{q}, 0) \rangle \tag{2.13}$$

It turns out that in the equation of motion for the pairs the three-particle contributions cancel, in analogy to the cancellation of two-particle terms in (2.7). The resulting system of equations for the quantities $A_l(\mathbf{q}, t)$ with arbitrary $\mathbf{l}$ can be solved by a defect matrix method.$^{(11)}$

Although the model used so far is highly idealized, it does allow us to make some comparison with experiments. The solution for (2.13), for example, can be applied to the inelastic scattering of light by the superionic conductor CuI.$^{(12)}$ The observed depolarized component $I_{\mathrm{depol}}(\omega)$ can be understood in terms of a pair mechanism, where each nearest-neighbor pair $n_l n_{l+\delta}$ gives rise to a certain anisotropic polarizability $\alpha_{\mu\nu}(\boldsymbol{\delta})$. One finds $I_{\mathrm{depol}}(\omega) \propto C_{\parallel}(\omega) - C_{\perp}(\omega)$, where the functions $C_{\parallel}$ and $C_{\perp}$ are given by (2.13) with $\mathbf{q}=0$, setting $\mathbf{l}=\mathbf{l}'=\boldsymbol{\delta}$ or $\mathbf{l}=\boldsymbol{\delta}\perp\mathbf{l}'=\boldsymbol{\delta}'$, respectively. Explicitly,$^{(11)}$

$$C_{\parallel}(\omega) - C_{\perp}(\omega) = \frac{1}{\pi}\,[c(1-c)]^2\,\mathrm{Re}\,\frac{f(\omega)}{1-2\alpha f(\omega)} \tag{2.14}$$

$f(\omega)$ denotes a lattice Green's function

$$f(\omega) = 2a^3 \int \frac{d^3\mathbf{q}}{(2\pi)^3}\,\frac{\cos aq_x(\cos aq_y - \cos aq_z)}{i\omega + 2\gamma(\mathbf{q})} \tag{2.15}$$

where $\gamma(\mathbf{q})$ is given by (2.9). The spectra obtained$^{(13)}$ are shown in Fig. 2. Taking the jump frequency α from conductivity data, the calculated half-width for the depolarized spectrum is in accord with experiment. The polarized scattering component $I_{\mathrm{pol}}(\omega)$ has a contribution proportional to $C_{\parallel}(\omega) + 2C_{\perp}(\omega)$. Note the $\omega^{1/2}$-dependence for $\omega \to 0$ of the individual functions $C_{\parallel}$ and $C_{\perp}$, which predicts that $I_{\mathrm{pol}}(0) - I_{\mathrm{pol}}(\omega) \propto \omega^{1/2}$ for sufficiently small frequencies.$^{(13)}$

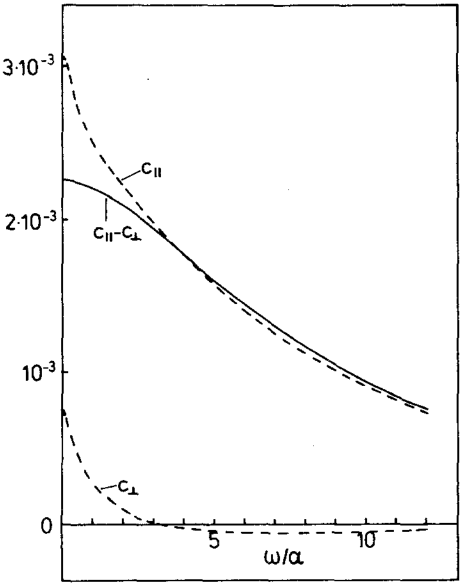

Fig. 2. Frequency-dependence of the pair-density-correlation functions $C_{\parallel}(\omega)$ and $C_{\perp}(\omega)$. The full curve is proportional to the depolarized light scattering spectrum obtained from the pair-mechanism.

Lattice gas models are particularly useful for discussing the motion of a test particle, e.g., a tracer atom. The starting master equation has now to be generalized somewhat in order to distinguish between the total occupation n_l of a site l and the tracer occupation p_l. The motion of the tracer is described by the incoherent dynamic structure factor $S_{\text{inc}}(\mathbf{q}, \omega)$, defined in terms of the tracer density $p(\mathbf{q})$,

$$S_{\text{inc}}(\mathbf{q}, \omega) = \frac{1}{N} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle p(\mathbf{q}, t)\, p(-\mathbf{q}, 0) \rangle \tag{2.16}$$

As $\mathbf{q} \to 0$, it behaves as

$$S_{\text{inc}}(\mathbf{q}, \omega) \simeq \frac{1}{\pi} \frac{D_t q^2}{\omega^2 + (D_t q^2)^2} \tag{2.17}$$

Here D_t denotes the tracer diffusion constant, which is usually written in the form(14)

$$D_t = D_0(1-c)\, f_t(c) \tag{2.18}$$

The term $D_0(1-c)$ represents the mean-field diffusion constant. The fact that the tracer actually performs a correlated random walk is taken into account by the tracer correlation factor $f_t(c)$. When the tracer performs a jump, it leaves a vacancy behind so that a backward jump is more likely than a forward jump, giving $f_t(c) \leqslant 1$.

In order to compute $f_t(c)$ one starts from the equation of motion [compare Eq. (2.07)],

$$\frac{dp_l(t)}{dt} = \alpha \sum_{\delta} [p_{l+\delta}(1-n_l) - p_l(1-n_{l+\delta})](t) \tag{2.19}$$

which shows the coupling of p_l to bilinear terms of the form $p_l n_{l'}$. Repeated differentiation with respect to time leads to an infinite hierarchy of equations. Several approximation schemes have been developed in order to deal with this problem.(15–18) We shall describe briefly a pair approximation which is equivalent to Tahir–Kheli's treatment in Ref. 17. Within the frame of the Mori–Zwanzig method(19) we introduce the infinite set of variables

$$B_0(\mathbf{q}) \equiv p(\mathbf{q}) = \sum_{l'} p_{l'} e^{-i\mathbf{q}l'} \tag{2.20}$$

$$B_l(\mathbf{q}) = \frac{1}{[c(1-c)]^{1/2}} \sum_{l'} p_{l'}(n_{l'+l} - c)\, e^{-i\mathbf{q}l'}, \qquad l \neq 0 \tag{2.21}$$

with

$$\langle B_l(\mathbf{q}) \mid B_{l'}(\mathbf{q}) \rangle = \delta_{l,l'} \tag{2.22}$$

using the conventional scalar product notation. Our approximation consists in projecting the tracer motion on this set of variables, i.e., in neglecting the memory function which would contain the influence of variables beyond pairs. For the Laplace transform of the tracer density-correlation function one arrives at

$$\hat{S}_{\mathrm{inc}}(\mathbf{q}, z) = (z \cdot \delta_{l,l'} - \langle B_l \mid dB_{l'}/dt \rangle_{t=0})^{-1}_{0,0} \tag{2.23}$$

where on the right-hand side the $\mathbf{l} = \mathbf{l}' = 0$ element of the inverse matrix $(\cdots)^{-1}$ is to be taken. This matrix inversion is performed again with the aid of the defect matrix method. One finally obtains$^{(17)}$

$$f_t(c) = \left[1 - \frac{2c\,\overline{\cos\theta}}{(2-c)(1+\overline{\cos\theta})} \right]^{-1} \tag{2.24}$$

Here θ denotes the angle between the orientations of consecutive jump vectors of the tracer. The quantity $\overline{\cos\theta}$ is an average with respect to the single-vacancy problem, which can be treated by random walk theory. At $c = 1$ the exact result $f_t(1) = (1 + \overline{\cos\theta})/(1 - \overline{\cos\theta})$ is recovered from (2.24). For intermediate concentration (2.24) agrees very well with Monte Carlo data.$^{(20-22)}$

The incoherent structure factor at finite $\mathbf{q}$ in an fcc lattice has been studied by Monte Carlo simulation.$^{(22)}$ The line shape is nearly Lorentzian with a half-width $(1-c)\,\gamma(\mathbf{q})\, f_t(\mathbf{q}, c)$. The $\mathbf{q}$-dependent correlation factor $f_t(\mathbf{q}, c)$ can be obtained from the approximation method described above.$^{(17)}$

2.3. Interacting Lattice Gas

Most of the work on transport properties of interacting lattice gases is based on the assumption of nearest-neighbor interactions. The dc conductivity and the tracer correlation factor as a function of both concentration and temperature have been studied by means of the path probability method$^{(23)}$ and by Monte Carlo calculations.$^{(21)}$ A review of these and related results obtained by simulation methods is found in Ref. 24. Properties of a current-carrying steady state have also been investigated recently.$^{(25)}$

In the following we refer to a charged lattice gas with $V_{l-l'} = e^2/|\mathbf{l} - \mathbf{l}'|$ as a more realistic model for ionic conductors. First we have to specify the transition rates $w_{l,l+\delta}(\mathbf{n})$ in the master equation (2.1). Generally, different choices of rates compatible with the detailed balance condition (2.2) are possible, giving different dynamic behavior.(26) Therefore, some additional physical input is required, when the model is applied to an actual material. In our case of Coulomb interactions we assume that the local barrier along a bond $(\mathbf{l}, \mathbf{l}+\boldsymbol{\delta})$ has a contribution proportional to the local electric field.(27) This leads to the expression

$$w_{l,l+\delta}(\mathbf{n}) = w^0_{l,l+\delta}(\mathbf{n}) \exp\{\beta[H(\mathbf{n}) - H(\mathbf{n}')]/2\} \tag{2.25}$$

where $w^0_{l,l+\delta}$ is given by (2.4). This form is actually used in many investigations.

A general result for a charged lattice gas consists in the following form of the coherent dynamic structure factor in the long-wavelength limit $\mathbf{q} \to 0$,

$$S_{\text{coh}}(\mathbf{q}, \omega) \simeq \frac{1}{\pi} S(\mathbf{q}) \operatorname{Re}[-i\omega + 4\pi\sigma(\omega)]^{-1} \tag{2.26}$$

with the static structure factor $S(\mathbf{q}) \simeq q^2/q_D^2$, $q_D = (4\pi e^2 \beta\rho)^{1/2}$ being the inverse Debye–Hückel screening length. The real part of the dynamic conducticity $\sigma(\omega)$ is an increasing function of frequency with the high-frequency limit $\sigma(\infty) = e^2\beta\langle w\rangle/2a$. Here $\langle w\rangle$ denotes the equilibrium average of (2.25). In contrast to neutral systems the spectrum (2.26) is not diffusive, but has a finite width as $\mathbf{q} \to 0$.(28)

Explicit calculations of the incoherent structure factor have been performed by mode-coupling techniques.(29,30) At $c = 0.5$ the tracer correlation factor shows a strong decrease near the transition of the lattice gas to a superstructure with the wave vector $\mathbf{q}_0 = (\pi/a)(1, 1, 1)$. This is to be expected because the ions surrounding the test particle form a cage which becomes more and more "rigid" as the transition is approached. In the dilute limit $c \to 0$ the tracer correlation factor shows a $c^{1/2}$ dependence, in analogy to the Debye–Hückel result for the tracer diffusion constant of the one-component plasma.(31)

Mode-coupling results for the half-width $\Gamma(\mathbf{q})$ of the incoherent structure factor are shown in Fig. 3. The lowering of $\Gamma(\mathbf{q})$ as compared with the mean-field prediction $\Gamma_{\text{MF}}(\mathbf{q}) = \langle w\rangle \gamma(\mathbf{q})/2c$ arises from the coupling to density-fluctuations which become slow in the vicinity of the critical wave vector $\mathbf{q}_0$.

3. FLUIDLIKE MODEL

As mentioned in the Introduction, the static properties of AgI-type superionic conductors show fluidlike features. This suggests a model where

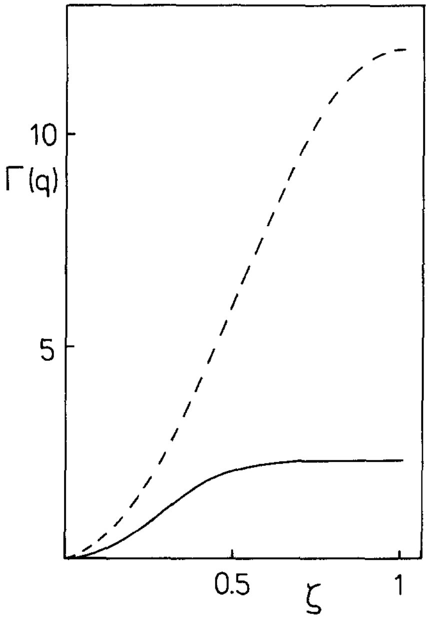

Fig. 3. Quasi-elastic width of the incoherent dynamic structure factor as a function of wavevector $\mathbf{q} = (\pi/a)(\zeta, \zeta, \zeta)$ for a simple cubic charged lattice gas. The parameters chosen are $c = 0.5$ and $e^2/a\, k_B T = 9$. The transition to a superstructure occurs at about $e^2/a\, k_B T \simeq 11$. The dashed curve shows the width $\Gamma_{\mathrm{MF}}(\mathbf{q})$ obtained from mean-field theory (after Ref. 30).

the ionic motion is described as a continuous process. One is therefore lead to investigate a system of interacting Brownian particles subjected to an external periodic potential.$^{(6,32-34)}$ The corresponding N-particle Fokker–Planck equation for the space- and velocity-dependent distribution function $p(\mathbf{r}_1, ..., \mathbf{r}_N, \mathbf{v}_1, ..., \mathbf{v}_N, t)$ takes the form

$$\frac{\partial p}{\partial t} = \sum_{i=1} \left[-v_i \frac{\partial}{\partial \mathbf{r}_i} - \frac{\mathbf{K}_i}{m} \frac{\partial}{\partial \mathbf{v}_i} + \gamma \frac{\partial}{\partial \mathbf{v}_i} \left(\mathbf{v}_i + \frac{k_B T}{m} \frac{\partial}{\partial \mathbf{v}_i} \right) \right] p \tag{3.1}$$

m denotes the particle mass and γ the friction constant. The total force $\mathbf{K}_i = -\partial v/\partial \mathbf{r}_i$ acting on particle i is derived from the potential

$$V = \sum_i V^{(1)}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} V^{(2)}(\mathbf{r}_i - \mathbf{r}_j) \tag{3.2}$$

which contains the lattice potential $V^{(1)}$ originating from the host ions and the pair interaction $V^{(2)}$.

Two special cases of (3.1) deserve special attention. For vanishing pair interaction one arrives at a single-particle Fokker–Planck equation including an external potential. A powerful tool to treat this problem is the matrix continued fraction method,(35–37) which yields accurate results for the experimentally relevant dynamic correlation functions and also for the nonequilibrium response. A second special case consists in setting $V^{(1)}(\mathbf{r}) \equiv 0$. The model of a homogeneous Brownian fluid obtained in this way is particularly important for understanding the dynamic properties of macromolecular solutions.(38)

The complete equation (3.1) is applicable to a general situation of many-particle diffusion in a periodic medium. Discrete hopping models as discussed in Section 2 are contained in (3.1) as the limiting case where the single-particle density becomes sharply peaked near the minima of the lattice potential $V^{(1)}(\mathbf{r})$.

In the following we shall outline a calculation of the dynamic conductivity and discuss its relation to structural properties. The calculation is based on mean-field theory. Details will be given elsewhere.(39) We apply an external driving force to our system by adding a term $-[\mathbf{K}^{\text{ext}}(t)/m] \sum_i \partial p/\partial \mathbf{v}_i$ to the right-hand side of (3.1). For the resulting nonequilibrium distribution we make an ansatz(40,41)

$$p(\mathbf{r}_1,\dots,\mathbf{v}_N,t) = p_{\text{eq}}(\mathbf{r}_1,\dots,\mathbf{v}_N) \prod_{i=1}^{N} h(\mathbf{r}_i,\mathbf{v}_i,t) \tag{3.3}$$

(3.3) can be interpreted as a local equilibrium approximation. The deviation from the equilibrium distribution p_{eq} is given by the action of the single-particle field $-k_B T \log h(\mathbf{r},\mathbf{v},t)$. The function h can be determined by requiring consistency with respect to the single-particle distribution function $p(\mathbf{r},\mathbf{v},t)$. In the linear response regime this leads to the following equation for $p(\mathbf{r},\mathbf{v},t)$:

$$\begin{aligned}\frac{\partial p(\mathbf{r},\mathbf{v},t)}{\partial t} &= L[U]\, p(\mathbf{r},\mathbf{v},t) - \frac{\mathbf{K}^{\text{ext}}(t)}{m}\frac{\partial}{\partial \mathbf{v}} p_{\text{eq}}(\mathbf{r},\mathbf{v}) \\ &\quad - \frac{1}{m\beta}\frac{\partial p_{\text{eq}}(\mathbf{r},\mathbf{v})}{\partial \mathbf{v}}\frac{\partial}{\partial \mathbf{r}} \int d^3\mathbf{r}'\, c(\mathbf{r},\mathbf{r}')[p(\mathbf{r}',t) - p_{\text{eq}}(\mathbf{r}')]\end{aligned} \tag{3.4}$$

Here $p_{\text{eq}}(\mathbf{r},\mathbf{v}) = \text{const}\exp(-\beta m \mathbf{v}^2/2)\,\rho(\mathbf{r})$ is the single-particle distribution at equilibrium. The density $\rho(\mathbf{r})$ is written in terms of an effective potential $U(\mathbf{r})$ as

$$\rho(\mathbf{r}) = \text{const}\exp[-\beta U(\mathbf{r})] \tag{3.5}$$

$L[U]$ denotes the single-particle Fokker–Planck operator in the presence of the effective potential. The last term in (3.4) represents the effect of a time-dependent mean field, determined by the spatial distribution $p(\mathbf{r}', t) = \int d^3\mathbf{v}\, p(\mathbf{r}, \mathbf{v}, t)$ and by the direct correlation function $c(\mathbf{r}, \mathbf{r}')$. $U(\mathbf{r})$ and $c(\mathbf{r}, \mathbf{r}')$ can in principle be determined from liquid structure theory⁽⁴²⁾ although this may be a difficult task in practice. Therefore we limit our present discussion to some general consequences of (3.4).

We consider first the stationary case. Here one can show that the velocity distribution and therefore the current is not affected by the mean-field term in (3.4). As a consequence, the dc conductivity is given by

$$\sigma(\omega = 0) = \sigma_0[U] \tag{3.6}$$

where σ_0 denotes the dc conductivity of noninteracting particles in the presence of the effective potential $U(\mathbf{r})$. In principle, the right-hand side of (3.6) can be evaluated by matrix-continued-fraction techniques, as mentioned before. For a one-dimensional system in the large-damping (Smoluchowski) limit the functional dependence $\sigma_0[U]$ is known explicitly,⁽⁴³⁾

$$\sigma_0[U] = \frac{\rho e^2}{m\gamma} \left[\overline{e^{-\beta U(x)}}\ \overline{e^{\beta U(x)}}\right]^{-1} \tag{3.7}$$

where the bar means a spatial average.

Equation (3.6) predicts an enhanced conductivity in cases, where the barrier U_0 of the effective potential is lower than the bare barrier V_0. In fact, detailed model calculations for particles in a periodic potential in the presence of long-range repulsive forces have shown the existence of incommensurate situations with a weak density variation, corresponding to a low effective barrier U_0.⁽⁴⁴,⁴⁵⁾ The low activation energy deduced from dc conductivity data of AgI-type superionic conductors may be interpreted in this way. A more quantitative test of the relationship between conductivity and structural properties, as implied by (3.6), has been made recently for several substances by comparing the magnitude of the activation energy with the effective potential derived from the observed Bragg intensities.⁽⁴⁶⁾

Finally we comment on the qualitative behavior of the ac conductivity. The evaluation of the moments of the velocity-correlation function up to second order allows us to use the representation

$$\sigma(\omega) = \frac{\rho e^2}{m} \left(-i\omega + \gamma - \frac{a_1}{-i\omega + R} \right)^{-1} \tag{3.8}$$

The coefficient a_1 contains the effective potential and the direct correlation function. It turns out, however, that the effects of interaction largely cancel in the expression for a_1. This gives the estimate $a_1 \simeq -\omega_0^2$, where ω_0 is the resonance frequency of the *bare* potential $V^{(1)}$. The coefficient R is determined such that (3.6) agrees with (3.8) at $\omega = 0$. If the damping is not very large, (3.8) yields a resonance at the bare frequency ω_0. This is physically plausible since we are considering a resonance at zero wave vector, where the particles vibrate with the same phase. The expression (3.8) therefore interpolates between the regime of diffusion in a renormalized potential at low frequencies and a collective vibration in the bare potential at $\omega \sim \omega_0$.

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