Dynamic correlations in a charged lattice gas

A. Bunde and W. Dieterich
Fakultät für Physik der Universität Konstanz, D-7750 Konstanz, Germany
(Received 31 August 1984)

The many-particle hopping problem in a one-component lattice gas of charged particles is investigated. A method is pointed out which allows the simultaneous treatment of correlations induced by the lattice and by the Coulomb interaction. Results are obtained for the concentration and temperature dependence of the tracer correlation factor and the quasielastic width of the incoherent scattering function. In addition, we discuss the long-wavelength charge fluctuation spectrum and possible anisotropy effects in layered systems.

I. INTRODUCTION

Atomic diffusion processes in solids have motivated the study of the dynamic properties of stochastic lattice-gas models. In recent years attention has been focused on nondilute lattice gases. In the simplest case where explicit interactions are disregarded, one only requires that occupied sites are inaccessible by other particles. A hard-core repulsion is taken into account in this way. Models of this type have now been studied in great detail. Accurate information on the tracer-diffusion constant and on the finite-wave-vector response of a tracer atom are available both from simulation techniques[1,2] and from analytic approximations.[3–7] Some of the collective properties of such models,[8,9] including nonequilibrium properties,[10] have been worked out exactly.

In actual materials like adsorbed monolayers,[11] intercalation compounds[12,13] or superionic conductors,[14,15] one usually observes pronounced static correlations between the diffusing atoms. This indicates that interatomic interactions should also play a major role in the hopping process. Many attempts have therefore been undertaken to understand transport and dynamic properties of interacting lattice gases.[16–23]

Our present aim is to investigate a lattice gas of charged particles as a model for diffusion in ionic conductors. Concerning the static properties, our system behaves as a one-component plasma on a lattice. The many-particle hopping process is determined from a master equation which describes particle hops from occupied sites to neighboring vacant sites with a rate depending on the local electric field in the instantaneous configuration. Dynamic correlation functions such as the incoherent and coherent scattering function are analyzed by means of the Mori-Zwanzig projector method.[24] To evaluate the corresponding memory functions we use mode-coupling theory. This method has proved very successful in the microscopic theory of neutral and charged liquids[25] and will be adapted here in a simplified version to our diffusive system.

In this paper we extend an earlier treatment,[26,27] limited to moderate interaction strength, by taking into account the short-range correlations between particles. This is achieved by starting from a suitable set of dynamic variables, including occupation numbers of pairs of neighboring atoms. In this way the effect of site blocking is treated explicitly. The long-range correlations, on the other hand, are described within a mode-coupling approximation for the remaining memory function. The problem here has some resemblance to the theory of fluids in the presence of hard-core interactions, where close collisions and long-range effects are treated separately.[28]

After discussing the model and its static properties, the tracer motion will be analyzed in the way described above. Density fluctuations will be considered only briefly. Finally, we comment on effects typical of the long-range Coulomb interaction in a confined geometry, relevant for layered materials.

II. MASTER EQUATION

We consider a regular lattice of equivalent positions l, which are partly occupied by identical particles. The static properties of the system are determined by a lattice-gas Hamiltonian written in terms of the set of occupation numbers $\mathbf{n}=\{n_l\}$,

$$H(\mathbf{n})=\tfrac{1}{2}\sum_{\mathbf{l},\mathbf{l}'} V_{\mathbf{l}-\mathbf{l}'}n_{\mathbf{l}}n_{\mathbf{l}'}-\mu\sum_{\mathbf{l}}n_{\mathbf{l}}\ . \tag{2.1}$$

$V_{\mathbf{l}-\mathbf{l}'}$ denotes the pair interaction, and μ is the chemical potential which determines the average occupation $\langle n_{\mathbf{l}}\rangle=c$.

Now we allow the system to evolve in time through a many-particle jump-diffusion process. Since we are interested in both collective and single-particle motions (tracer diffusion), we introduce pseudospin variables $\sigma_{\mathbf{l}}$ (Ref. 29) which distinguish three states of a site $\mathbf{l}$,

$$\sigma_{\mathbf{l}}=\begin{cases}1 \text{ for a normal particle at } \mathbf{l}\ ,\\ 0 \text{ for a vacancy,}\\ -1 \text{ for a tracer particle}\ .\end{cases} \tag{2.2}$$

$n_{\mathbf{l}}=\sigma_{\mathbf{l}}^2$ is the total occupation and $p_{\mathbf{l}}=(\sigma_{\mathbf{l}}^2-\sigma_{\mathbf{l}})/2$ the tracer occupation, with the properties

$$\begin{aligned}&n_{\mathbf{l}}^2=n_{\mathbf{l}},\quad n_{\mathbf{l}}p_{\mathbf{l}}=p_{\mathbf{l}}\ ,\\ &p_{\mathbf{l}}p_{\mathbf{l}'}=p_{\mathbf{l}}\delta_{\mathbf{l},\mathbf{l}'},\quad \sum_{\mathbf{l}}p_{\mathbf{l}}=1\ .\end{aligned} \tag{2.3}$$

The last relations hold because we consider only a single tracer atom. Let $P(\boldsymbol{\sigma},t)$ denote the time-dependent probability for the configurations $\boldsymbol{\sigma}=\{\sigma_{\mathbf{l}}\}$. Assuming only hops between nearest neighbors, we set up the follow-

ing master equation:

$$\frac{dP(\sigma,t)}{dt}=\frac{1}{2}\sum_{1,\delta}[w_{1+\delta,1}(\tilde{\sigma})P(\tilde{\sigma},t)-w_{1,1+\delta}(\sigma)P(\sigma,t)] . \tag{2.4}$$

The right-hand side involves a summation over all bonds between nearest neighbors 1 and $1+\delta$. $\tilde{\sigma}$ is the configuration which results from σ by interchanging the occupation at 1 and $1+\delta$, i.e., $\tilde{\sigma}_{1+\delta}=\sigma_1$ and $\tilde{\sigma}_1=\sigma_{1+\delta}$. The corresponding transition rate is denoted by $w_{1,1+\delta}=w_{1+\delta,1}$.

Let $f(\sigma,t)$ denote the average of some function $f(\sigma)$ at time t for a given initial configuration σ at time $t=0$,

$$f(\sigma,t)=\sum_{\sigma'}f(\sigma')P(\sigma',t\,|\,\sigma) . \tag{2.5}$$

Here, $P(\sigma',t\,|\,\sigma)$ is the transition probability which satisfies (2.4) with $P(\sigma',0\,|\,\sigma)=\delta_{\sigma,\sigma'}$. Hence, $f(\sigma,0)\equiv f(\sigma)$. From (2.4) we obtain

$$\frac{df(\sigma,t)}{dt}=\frac{1}{2}\sum_{\sigma'}\sum_{1,\delta}w_{1,1+\delta}(\sigma')[f(\tilde{\sigma}')-f(\sigma')]P(\sigma',t\,|\,\sigma) . \tag{2.6}$$

Defining the operator L by

$$Lf(\sigma)=\frac{1}{2}\sum_{1,\delta}w_{1,1+\delta}(\sigma)[f(\tilde{\sigma})-f(\sigma)] , \tag{2.7}$$

we note that repeated differentiation of (2.6) leads to

$$[d^nf(\sigma,t)/dt^n]_{t=0}=L^nf(\sigma) .$$

Therefore the time evolution of $f(\sigma)$ is formally given by

$$f(\sigma,t)=e^{Lt}f(\sigma) . \tag{2.8}$$

As an application of (2.8) let us calculate the time derivative of the tracer occupation. Setting $f\equiv p_l$ we obtain

$$\frac{dp_1}{dt}=Lp_1$$

$$=-\sum_{\delta}w_{1,1+\delta}(\sigma)(p_1-p_{1+\delta}) . \tag{2.9}$$

This expression has the form of a continuity equation on a lattice, where $w_{1,1+\delta}(\sigma)(p_1-p_{1+\delta})$ represents the tracer current along the bond $(1,1+\delta)$. An analogous result holds for the total occupation n_1.

Finally, we must specify the transition rates. Since we assume the jump dynamics to be the same for all particles, the transition rates depend only on the total occupation $\mathbf{n}$, i.e., $w_{1,1+\delta}\equiv w_{1,1+\delta}(\mathbf{n})$. Detailed balance requires that

$$w_{1,1+\delta}(\mathbf{n})e^{-\beta H(\mathbf{n})}=w_{1,1+\delta}(\tilde{\mathbf{n}})e^{-\beta H(\tilde{\mathbf{n}})} . \tag{2.10}$$

For the noninteracting case, where $V_{1-1'}\equiv 0$, we assume that

$$w^0_{1,1+\delta}(\mathbf{n})=\alpha(n_1-n_{1+\delta})^2 , \tag{2.11}$$

which allows a jump only if $n_1\neq n_{1+\delta}$. α is a bare hopping rate. Phenomenologically one may assume a temperature dependence of the Arrhenius form $\alpha\sim\exp(-\beta V_0)$ with some bare potential barrier V_0.

For an interacting lattice gas it is well known that different choices of the transition rates compatible with detailed balance are possible.[19] Our main subject here is a system with long-range interactions. In that case it is natural to assume that the rate for a jump along the bond $(1,1+\delta)$ will be determined by an effective barrier which differs from the bare barrier V_0 through the local force field (see Fig. 1),

$$F_{1,1+\delta}(\mathbf{n})=\sum_{1'}{}'(V_{1-1'}-V_{1+\delta-1'})n_{1'} . \tag{2.12}$$

In the $1'$ summation the sites 1 and $1+\delta$ are excluded. Now we write

$$w_{1,1+\delta}(\mathbf{n})=\alpha n_1(1-n_{1+\delta})\exp[\beta F_{1,1+\delta}(\mathbf{n})/2]$$
$$+\alpha n_{1+\delta}(1-n_1)\exp[-\beta F_{1,1+\delta}(\mathbf{n})/2] , \tag{2.13}$$

which shows explicitly the blocking of an occupied site and the effective barriers for the two possible jump directions. We remark that (2.13) is equivalent to the symmetric expression

$$w_{1,1+\delta}(\mathbf{n})=w^0_{1,1+\delta}(\mathbf{n})\exp\{\beta[H(\mathbf{n})-H(\tilde{\mathbf{n}})]/2\} . \tag{2.14}$$

III. STATIC APPROXIMATION

The aim of this section is to obtain the static properties of a charged lattice gas, where the particles interact via an unscreened Coulomb potential,

$$V_{1-1'}=\frac{e^2}{|1-1'|} . \tag{3.1}$$

In the following we are only interested in the disordered regime, i.e., in temperatures above the critical temperature for possible ordering transitions. In addition, we limit ourselves to a simple-cubic lattice with spacing a and density $\rho=c/a^3$. It is understood that for our Coulomb problem a homogeneous background with charge density $-e\rho$ is added which ensures overall charge neutrality.

First, we investigate the pair-correlation function

$$g(\mathbf{l})=\begin{cases}\langle n_1n_0\rangle/c^2 & \text{for } \mathbf{l}\neq\mathbf{0},\\ 0 & \text{for } \mathbf{l}=\mathbf{0},\end{cases} \tag{3.2}$$

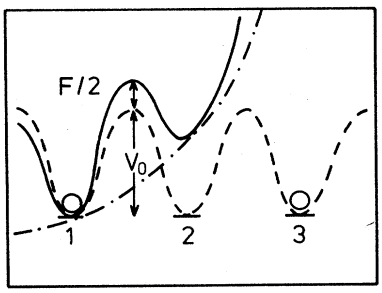

FIG. 1. Illustration of the local barrier $V_0+F/2$ for a hop from an occupied site 1 to a vacant site 2 in the presence of another particle at site 3.

and the static structure factor

$$S(\mathbf{q})=1+c\sum_{\mathbf{l}}[g(\mathbf{l})-1]e^{-i\mathbf{q}\cdot\mathbf{l}} . \tag{3.3}$$

For this purpose it is convenient to start from standard integral equations for the structure of inhomogeneous liquids[30] and adapt them to our discrete system. In this way the Ag^+ pair-correlation function of the superionic conductor α-AgI has been studied recently on the basis of the hypernetted-chain approximation.[31] Here we follow Ref. 26 and employ the simpler mean-spherical approximation (MSA),[32] defined by

$$g(\mathbf{l})=0 \quad \text{for } |\mathbf{l}| \le R , \tag{3.4}$$

$$c(\mathbf{l})=-\beta V_{\mathbf{l}} \quad \text{for } |\mathbf{l}| > R . \tag{3.5}$$

The direct correlation function $c(\mathbf{l})$ and the pair-correlation function $g(\mathbf{l})$ are related by the Ornstein-Zernike relation,

$$g(\mathbf{l})-1=c(\mathbf{l})+c\sum_{\mathbf{l}'}c(\mathbf{l}-\mathbf{l}')[g(\mathbf{l}')-1] . \tag{3.6}$$

In the simplest case the cutoff radius R satisfies $0<R<a$, in agreement with the condition $g(0)=0$. By using (3.3) and (3.5), this leads to

$$S(\mathbf{q})=\{1-c[c(0)-\beta V(\mathbf{q})/a^3]\}^{-1} , \tag{3.7}$$

where

$$V(\mathbf{q})=a^3\sum_{\mathbf{l}\neq 0}(e^2/|\mathbf{l}|)e^{-i\mathbf{q}\cdot\mathbf{l}} . \tag{3.8}$$

In the long-wavelength limit $\mathbf{q}\to\mathbf{0}$, we have $V(\mathbf{q}) \simeq 4\pi e^2/\mathbf{q}^2$. Therefore the perfect screening condition

$$S(\mathbf{q})\simeq q^2/q_D^2 \tag{3.9}$$

holds, where $q_D=(4\pi e^2\beta c/a^3)^{1/2}$ is the inverse Debye length. The quantity $c(0)$ in expression (3.7) is determined from (3.4), which can also be written as

$$\frac{c}{N}\sum_{\mathbf{q}}S(\mathbf{q})=1-c , \tag{3.10}$$

where N is the total number of particles.

Numerical results for the static structure factor in the case of a half-filled lattice ($c=0.5$) are presented in Fig. 2. Note that the system becomes unstable at the critical wave vector $\mathbf{q}_c=(\pi/a)(1,1,1)$. The corresponding ordering temperature is estimated to be $T_c\simeq 11V_{\delta}$.

At lower concentration c, the pair correlation for nearest neighbors $g(\boldsymbol{\delta})$ vanishes as the interaction $\beta V_{\boldsymbol{\delta}}$ exceeds a certain value. This is seen, for example, in Fig. 3, where we have plotted the so-called vacancy availability factor

$$V=1-cg(\boldsymbol{\delta})=\langle n_{\mathbf{l}}(1-n_{\mathbf{l}+\boldsymbol{\delta}})\rangle/c . \tag{3.11}$$

Now a rescaled MSA must be used[33] with a radius of the correlation hole satisfying $R\ge a$. For example, at $R=a$ the static structure factor takes the form

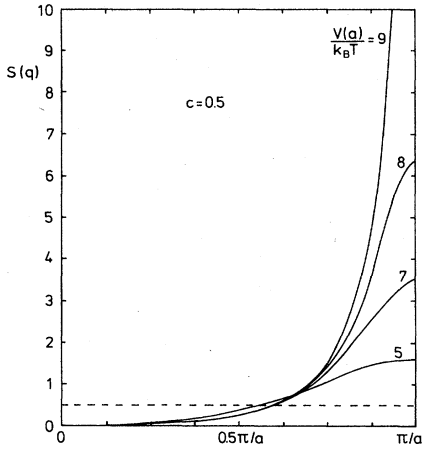

FIG. 2. Static structure factor for a half-filled lattice as a function of wave vector $\mathbf{q}=\zeta(1,1,1)$ for different temperatures. The dashed curve corresponds to the infinite-temperature limit, where $S(\mathbf{q})=1-c$.

$$S(\mathbf{q})=\left[1-c\left[c(0)+[c(\boldsymbol{\delta})+\beta V_{\delta}]\sum_{\boldsymbol{\delta}}e^{i\mathbf{q}\cdot\boldsymbol{\delta}} -\beta V(\mathbf{q})/a^3\right]\right]^{-1} , \tag{3.12}$$

where the two quantities $c(0)$ and $c(\boldsymbol{\delta})$ are determined by (3.10) together with

$$\frac{c}{N}\sum_{\mathbf{q}}S(\mathbf{q})\cos(\mathbf{q}\cdot\boldsymbol{\delta})=-c . \tag{3.13}$$

A more complicated static quantity, which is of central interest in a lattice-gas problem, is the average transition rate $\langle w_{l,l+\delta}\rangle\equiv\langle w\rangle$, which determines the mean residence time τ of a particle according to $\tau^{-1}=6(\langle w\rangle/2c)$. From (2.13) and the detailed balance condition (2.10) we find

$$\langle w\rangle=2\alpha\langle n_{\mathbf{l}}(1-n_{\mathbf{l}+\boldsymbol{\delta}})\exp(\beta F_{\mathbf{l},\mathbf{l}+\boldsymbol{\delta}}/2)\rangle . \tag{3.14}$$

Let us define a conditional average of a function $f(\mathbf{n})$ by[26]

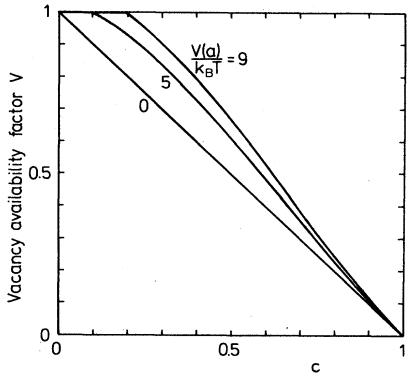

FIG. 3. Vacancy availability factor $V=1-cg(\boldsymbol{\delta})$ as a function of concentration for different temperatures.

$$\langle\langle f\rangle\rangle = \frac{\langle n_l(1-n_{l+\delta})f(\mathbf{n})\rangle}{\langle n_l(1-n_{l+\delta})\rangle} , \tag{3.15}$$

which selects configurations $\mathbf{n}$ with $n_l=1$ and $n_{l+\delta}=0$. Introducing the so-called effective frequency factor[21]

$$W=\langle\langle \exp(\beta F_{l,l+\delta}/2)\rangle\rangle \tag{3.16}$$

we can write (3.14) in the conventional form,

$$\langle w\rangle/2c=\alpha V W , \tag{3.17}$$

where V is given by (3.11).

For a charged lattice gas with interaction (3.1), the average (3.16) involves many-particle correlations of infinite order. One may argue, however, that the contribution to the local field $F_{l,l+\delta}$ from the more distant shells has a Gaussian distribution, which suggests a cumulant expansion of (3.16). For a qualitative discussion, however, we completely neglect the fluctuations of the local field about it mean $\langle\langle F\rangle\rangle \equiv \langle\langle F_{l,l+\delta}\rangle\rangle$, so that

$$W\simeq\exp(\beta\langle\langle F\rangle\rangle/2) . \tag{3.18}$$

Since $\langle n_l n_{l+\delta}F_{l,l+\delta}\rangle=0$ by symmetry considerations, knowledge of the pair correlation $g(\mathbf{l})$ is sufficient to calculate $\langle\langle F\rangle\rangle$. In this way we have obtained numerical results for the average transition rate $\langle w\rangle$, which will be used in later sections. Some preliminary results are shown explicitly in Ref. 26. Later, we will also use more general averages of the form $\langle f(\mathbf{n})\exp(\beta F_{l,l+\delta}/2)\rangle$. By similar arguments, we write

$$\langle f(\mathbf{n})\exp(\beta F_{l,l+\delta}/2\rangle \simeq\langle f(\mathbf{n})\rangle\exp[\beta\langle f(\mathbf{n})F_{l,l+\delta}\rangle/2\langle f(\mathbf{n})\rangle] . \tag{3.19}$$

Higher-order correlations appearing in the exponent on the right-hand side of (3.19) are treated within the Kirkwood superposition approximation, e.g.,

$$\langle n_{l_1}n_{l_2}n_{l_3}\rangle\simeq c^3 g(\mathbf{l}_1-\mathbf{l}_2)g(\mathbf{l}_1-\mathbf{l}_3)g(\mathbf{l}_2-\mathbf{l}_3) . \tag{3.20}$$

IV. INCOHERENT STRUCTURE FACTOR

The motion of a test particle, e.g., a tracer atom, is described by the incoherent structure factor

$$S_{\mathrm{inc}}(\mathbf{q},t)=\langle p(\mathbf{q})\,|\,p(\mathbf{q},t)\rangle \tag{4.1}$$

defined in terms of the tracer density

$$p(\mathbf{q})=\sum_l p_l e^{-i\mathbf{q}\cdot\mathbf{l}} . \tag{4.2}$$

In (4.1) the conventional scalar product notation $\langle f\,|\,g\rangle\equiv\langle f^* g\rangle$ has been used. The detailed-balance condition (2.10) implies that the time-evolution operator L, defined by (2.7), is Hermitian. This allows us to discuss (4.1) in terms of the Mori-Zwanzig projector[24] method in its standard form.

We start from the Laplace transform

$$\hat{S}_{\mathrm{inc}}(\mathbf{q},z)=\int_0^\infty dt\, e^{-zt}S_{\mathrm{inc}}(\mathbf{q},t) =[z+\Omega_{\mathrm{inc}}(\mathbf{q})+\hat{M}_{\mathrm{inc}}(\mathbf{q},z)]^{-1} . \tag{4.3}$$

Here,

$$\Omega_{\mathrm{inc}}(\mathbf{q})=-\langle p(\mathbf{q})\,|\,Lp(\mathbf{q})\rangle , \tag{4.4}$$

and $\hat{M}_{\mathrm{inc}}(\mathbf{q},z)$ is the corresponding memory function.

To calculate $\Omega_{\mathrm{inc}}(\mathbf{q})$ we substitute (2.13) into (2.9), which yields

$$Lp(\mathbf{q})=-\alpha\sum_{l,\delta}(1-e^{-i\mathbf{q}\cdot\boldsymbol{\delta}})p_l(1-n_{l+\delta}) \times\exp(\beta F_{l,l+\delta}/2)e^{-i\mathbf{q}\cdot\mathbf{l}} . \tag{4.5}$$

The average in (4.4) is performed by observing that

$$\langle p_l f(\mathbf{n})\rangle=\langle n_l f(\mathbf{n})\rangle/N$$

for some function $f(\mathbf{n})$. Thus we obtain

$$\Omega_{\mathrm{inc}}(\mathbf{q})=\frac{\langle w\rangle}{2c}\sum_\delta(1-e^{i\mathbf{q}\cdot\boldsymbol{\delta}}) . \tag{4.6}$$

At this stage let us remark that in a mean-field approximation, where the memory function is neglected, the incoherent structure factor has the same form as for independent-particle hopping with an average jump rate $\langle w\rangle/2c$. In general, however, the tracer atom performs a correlated random walk because of the presence of other particles. This fact is accounted for by a wave-vector- and frequency-dependent correlation factor,

$$f(\mathbf{q},z)=1+\hat{M}_{\mathrm{inc}}(\mathbf{q},z)/\Omega_{\mathrm{inc}}(\mathbf{q}) . \tag{4.7}$$

Its long-wavelength and zero-frequency limit represents the conventional tracer correlation factor f_t, which is introduced to write the tracer diffusion constant in the form

$$D_t\equiv\lim_{\omega\to0}\lim_{\mathbf{q}\to0}\Omega_{\mathrm{inc}}(\mathbf{q})f(\mathbf{q},-i\omega)/q^2 =D_0 V W f_t . \tag{4.8}$$

Here, $D_0=\alpha a^2$ is the diffusion constant for infinite dilution, and expression (3.17) has been used for $\langle w\rangle$.

Now the problem remains to calculate $f(\mathbf{q},z)$. One way to proceed is to use the formal expression for $\hat{M}_{\mathrm{inc}}(\mathbf{q},z)$ in terms of higher-order correlation functions.[24] In a simple factorization approximation, one can then reexpress $\hat{M}_{\mathrm{inc}}(\mathbf{q},z)$ by $S_{\mathrm{inc}}(\mathbf{q},t)$, and by the coherent structure factor

$$S_{\mathrm{coh}}(\mathbf{q},t)=\langle n(\mathbf{q})\,|\,n(\mathbf{q},t)\rangle/N \tag{4.9}$$

defined in terms of the density fluctuations

$$n(\mathbf{q})=\sum_l(n_l-c)e^{-i\mathbf{q}\cdot\mathbf{l}} . \tag{4.10}$$

This is a type of mode-coupling theory which was followed in Ref. 27. In the present context it is limited to a moderate interaction strength because it disregards correlations in the occupation of sites which are close to each other. The most important correlations in that respect are those between nearest neighbors. In order to take them into account, it is natural to start from an extended set of variables which consists of p_l and all nearest-neighbor pairs $p_l n_{l+\delta}$ or, equivalently, from

$$A_0(\mathbf{q}) \equiv p(\mathbf{q}) \tag{4.11}$$

and

$$A_\delta(\mathbf{q}) = \sum_1 p_1 (n_{1+\delta} - cg) e^{-i\mathbf{q}\cdot\mathbf{l}} . \tag{4.12}$$

Equation (4.12) contains a term proportional to $A_0(\mathbf{q})$ with $g \equiv g(\delta)$, so that $\langle A_0(\mathbf{q}) \mid A_\delta(\mathbf{q}) \rangle = 0$.

The corresponding memory matrix now involves higher-order correlation functions of quantities, where nearest-neighbor pairs are projected out. A factorization in momentum space then disregards correlations between second or further distant neighbors only and should therefore be more accurate than the simple decoupling mentioned above. The procedure can be tested in the noninteracting case.[7] It reproduces the exact correlation factor f_t at $c=1$ to within about 3%.

The method described so far can be simplified considerably if we select certain symmetry directions for the wave vector $\mathbf{q}$. Let us limit ourselves to the [1,1,1] direction. Then, as shown below, the following linear combinations of pair variables are sufficient:

$$A_1(\mathbf{q}) = (\chi_1)^{-1/2} \sum_\delta [1 - \cos(\mathbf{q}\cdot\delta)] A_\delta(\mathbf{q}) , \tag{4.13}$$

$$A_2(\mathbf{q}) = (\chi_2)^{-1/2} \sum_\delta \sin(\mathbf{q}\cdot\delta) A_\delta(\mathbf{q}) . \tag{4.14}$$

With χ_1 and χ_2 given by (A2) and (A3), the variables $A_i(\mathbf{q})$, $i=0,1,2$, defined by (4.11), (4.13), and (4.14), form an orthonormal set. The Laplace transforms $\underline{\hat{\phi}}(\mathbf{q},z) \equiv \hat{\phi}_{ik}(\mathbf{q},z)$ of the correlation functions $\langle A_i(\mathbf{q}) \mid A_k(\mathbf{q},t) \rangle$ are now written as

$$\underline{\hat{\phi}}(\mathbf{q},z) = [z\underline{\mathbb{1}} + \underline{\Omega}(\mathbf{q}) + \underline{\hat{M}}(\mathbf{q},z)]^{-1} . \tag{4.15}$$

The elements of the Ω matrix,

$$\Omega_{ik} = -\langle A_i(\mathbf{q}) \mid L A_k(\mathbf{q}) \rangle = \Omega_{ki}^* ,$$

are readily calculated by means of (2.7). First, we obtain $\Omega_{00} \equiv \Omega_{\text{inc}}(\mathbf{q})$, which is given by (4.6). The other matrix elements are obtained in a straightforward way from the quantities $\Gamma_{0\delta} = -\langle A_0 \mid L A_\delta \rangle$ and $\Gamma_{\delta,\delta'} = -\langle A_\delta \mid L A_{\delta'} \rangle$, which are given in the Appendix.

Now we turn to the memory matrix in (4.15). Because of our enlarged set of variables, a rather simple approximation for $\underline{\hat{M}}(z)$ seems appropriate. The leading element is

$$\hat{M}_{00}(z) = -\langle QLA_0 \mid (z - QLQ)^{-1} \mid QLA_0 \rangle , \tag{4.16}$$

where

$$Q = 1 - \sum_i \mid A_i \rangle \langle A_i \mid .$$

In the expression (4.5) for $Lp(\mathbf{q}) \equiv LA_0$, the factor $p_1(1-n_{1+\delta})$ suggests a linearization of the local field about its conditional average $\langle\langle F \rangle\rangle$ [see Eq. (3.18)],

$$\exp(\beta F_{1,1+\delta}/2) \simeq [1 + \beta(F_{1,1+\delta} - \langle\langle F \rangle\rangle)/2] \times \exp(\beta \langle\langle F \rangle\rangle /2) . \tag{4.17}$$

Neglecting products of occupational fluctuations on three different sites, we obtain

$$LA_0 \simeq \alpha \exp(\beta \langle\langle F \rangle\rangle /2) \sum_{1,\delta} (1 - e^{-i\mathbf{q}\cdot\mathbf{l}}) [p_1(1-n_{1+\delta})(1 - \beta\langle\langle F \rangle\rangle /2) + p_1(1-c)\beta F_{1,1+\delta}/2] e^{-i\mathbf{q}\cdot\mathbf{l}} . \tag{4.18}$$

The first term is proportional to the expression for the current density in the absence of Coulomb interactions. It may therefore be regarded as a lattice contribution, as opposed to the second term in (4.18), which is a pure Coulomb contribution. Obviously, the lattice contribution can be written as a linear combination of the variables $A_i(\mathbf{q})$. Let us substitute (2.12) into the Coulomb contribution in (4.18) and separate out all terms which contain nearest-neighbor pairs of the form $p_1 n_{n1+\delta'}$. It is easy to see that for wave vectors $\mathbf{q}$ parallel to the [111] direction these terms can again be written as a linear combination of $A_i(\mathbf{q})$. Therefore, for $\mathbf{q} \| [111]$, all the nearest-neighbor terms are projected out when Q operates on LA_0.

Introducing Fourier components according to (4.2) and (4.10), we arrive at

$$QLA_0 = -\bar{\alpha} \frac{1}{\Omega} \sum_{\mathbf{p}} V_{\mathbf{p}}(\mathbf{q}) Qp(\mathbf{q}-\mathbf{p}) n(\mathbf{p}) . \tag{4.19}$$

Here we have used the abbreviation

$$\bar{\alpha} = \alpha(1-c) \exp(\beta \langle\langle F \rangle\rangle /2) , \tag{4.20}$$

and Ω denotes the volume of the system. The coupling constants $V_{\mathbf{p}}(\mathbf{q})$ are given by

$$V_p(q) = (a^3\beta/2) \sum_{1,\delta}{}' (1 - e^{-i\mathbf{q}\cdot\mathbf{l}})(V_1 - V_{1+\delta}) e^{-i\mathbf{p}\cdot\mathbf{l}} , \tag{4.21}$$

where $\mathbf{l}=\mathbf{0}$ and nearest-neighbor sites $\mathbf{l}=\delta'$ are omitted in the $\mathbf{l}$ summation.

Since (4.19) does not involve nearest-neighbor pairs, we use, for the memory function, a factorization in momentum space of the type

$$\langle Qp(\mathbf{q}-\mathbf{p}) n(\mathbf{p}) \mid e^{QLQt} \mid Qp(\mathbf{q}-\mathbf{p}') n(\mathbf{p}') \rangle \simeq N \delta_{\mathbf{p},\mathbf{p}'} S_{\text{inc}}(\mathbf{q}-\mathbf{p},t) S_{\text{coh}}(\mathbf{p},t) . \tag{4.22}$$

Thus we finally obtain

$$\hat{M}_{00}(\mathbf{q},z)=-\bar{\alpha}^2\rho\int_0^\infty dt\, e^{-zt}\int\frac{d\mathbf{p}}{(2\pi)^3}[V_{\mathbf{p}}(q)]^2 S_{\mathrm{inc}}(\mathbf{q}-\mathbf{p},t)S_{\mathrm{coh}}(\mathbf{p},t)\ , \tag{4.23}$$

where $\rho=c/a^3$ is the particle density.[34]

A memory function of the form (4.23) is also obtained in a continuum theory, e.g., in the Smoluchowski treatment of self-diffusion in an overdamped one-component plasma.[35] From there, it is known that the long-range correlations are described in a proper way by (4.23). On the other hand, in our treatment the short-range correlations are taken into account explicitly through the Ω matrix. Therefore we argue that the other elements of the memory matrix besides $\hat{M}_{00}(\mathbf{q},z)$ are of minor importance and can be neglected. Now solving (4.15) for $\hat{\phi}_{00}(\mathbf{q},z)\equiv\hat{S}_{\mathrm{inc}}(\mathbf{q},z)$, we obtain an expression of the form (4.3), where $\hat{M}_{\mathrm{inc}}(\mathbf{q},z)$ is identified as

$$\hat{M}_{\mathrm{inc}}(\mathbf{q},z)=\hat{M}_{00}(\mathbf{q},z)-\frac{|\Omega_{01}|^2(z+\Omega_{22})+|\Omega_{02}|^2(z+\Omega_{11})-2\,\mathrm{Re}(\Omega_{01}\Omega_{12}\Omega_{20})}{(z+\Omega_{11})(z+\Omega_{22})-|\Omega_{12}|^2}\ . \tag{4.24}$$

Let us first consider the limit $\mathbf{q}\to 0$. From (A4)–(A7) it follows that, to order q^2,

$$\hat{M}_{\mathrm{inc}}(\mathbf{q},z)\simeq\hat{M}_{00}(\mathbf{q},z)-\frac{|\Omega_{02}|^2}{z+\Omega_{22}}\ . \tag{4.25}$$

For vanishing Coulomb interaction, the structure factor to order q^2 is then obtained as

$$\hat{S}_{\mathrm{inc}}(\mathbf{q},z)=\left[z+D_0(1-c)\left[1-\frac{2\alpha c}{z+(10-3c)}\right]q^2\right]^{-1}\ . \tag{4.26}$$

This gives

$$f_t(c)=1-2c/(10-3c)\ , \tag{4.27}$$

which agrees with the Monte Carlo data[1] within, typically, 10%.

In the presence of Coulomb interactions we are faced with the problem of determining $\hat{S}_{\mathrm{inc}}(\mathbf{q},z)$ are self-consistently from (4.3) and (4.24). We do this approximately by integrating (4.23) with the input

$$S_{\mathrm{coh}}(\mathbf{q},t)=S(\mathbf{q})\exp[-\Omega_{\mathrm{coh}}(\mathbf{q})t] \tag{4.28}$$

and

$$S_{\mathrm{inc}}(\mathbf{q},t)=\exp[-f_t\Omega_{\mathrm{inc}}(\mathbf{q})t]\ , \tag{4.29}$$

where $\Omega_{\mathrm{con}}(\mathbf{q})=\Omega_{\mathrm{inc}}(\mathbf{q})/S(\mathbf{q})$; see Eq. (5.5). Equations (4.28) and (4.29) are essentially mean-field expressions. Equation (4.29), however, involves the correct tracer-diffusion constant. Self-consistency with respect to f_t is achieved by numerically iterating (4.3), (4.24), and (4.23). The static correlations which enter the Ω matrix are calculated as indicated in Sec. III.

Figure 4 shows the correlation factor f_t obtained in this way as a function of concentration for different coupling strength $V(a)/k_Bt$, where $V(a)\equiv V_\delta=e^2/a$. In the infinite-temperature limit, $f_t(c)$ is given by (4.27). As the ordering transition at $c=0.5$ is approached, the correlation factor shows a pronounced minimum. Consecutive tracer hops therefore show an increased backward correlation. This is to be expected because ions surrounding the tracer ion form a cage which becomes more rigid in the presence of long-range static correlations. The qualitative features of these findings are in agreement with Monte Carlo data by Murch and Thorn,[17] and by Kutner, Binder, and Kehr,[22] for lattice gases with nearest-neighbor repulsion.

A special consequence of the long-range Coulomb interaction is seen for very low concentration c. In that case the memory function (4.24) is dominated by the first term $\hat{M}_{00}(\mathbf{q},z)$. For sufficiently low c, only small momenta $|\mathbf{p}|$ contribute significantly to the integral (4.23). Therefore, as $q\to 0$, the integrand can be replaced by its form in the continuum limit. Then $V_{\mathbf{p}}(\mathbf{q})=\beta(\mathbf{q}\cdot\mathbf{p})4\pi e^2/p^2$ and $S(\mathbf{p})=(1+q_D^2/p^2)^{-1}$. This leads to the analytical result[35,27]

$$\begin{aligned}f_t&=1-(2-\sqrt{2})(\sqrt{4\pi}/6)e^3\rho^{1/2}(k_BT)^{-3/2}\\&=1-0.346c^{1/2}(\beta V_\delta)^{3/2}\ .\end{aligned} \tag{4.30}$$

Thus a $c^{1/2}$ dependence of the diffusion constant is obtained, which is known from Debye-Hückel theory for a charged fluid.[36]

Next, we turn to the incoherent structure factor at finite wave vectors $\mathbf{q}$. The spectral shape $\mathrm{Re}[\hat{S}_{\mathrm{inc}}(q,-i\omega)]$ turns out to be almost Lorentzian as long as the interaction remains small. On the other hand, for strong interactions there is a significant frequency dependence of the

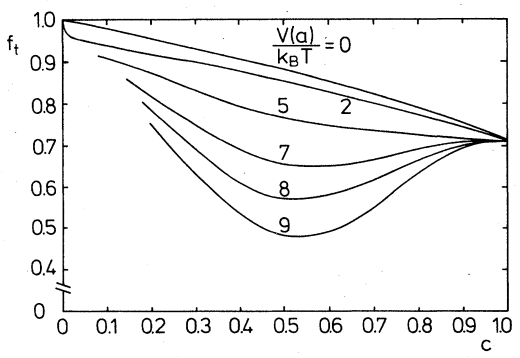

FIG. 4. Tracer correlation factor as a function of concentration for different temperatures.

correlation factor $f(\mathbf{q},-i\omega)$. This causes deviations of the spectral shape from a single Lorentzian, which, however, remain rather small for frequencies of the order of the half-width, i.e., for $\omega\sim\gamma(\mathbf{q})$.

The half-width $\gamma(\mathbf{q})$ of the quasielastic spectrum is shown in Fig. 5. Its $\mathbf{q}$ dependence deviates from the mean-field prediction $\gamma_{\mathrm{MF}}(\mathbf{q})\equiv\Omega_{\mathrm{inc}}(\mathbf{q})$ given by (4.6), especially for strong interactions. This is due to the coupling, expressed by (4.23), of the tracer motion to density fluctuations, which become slow near $\mathbf{p}=\mathbf{q}_c$ as the transition is approached. Within mean-field theory the half-width of the incoherent scattering function is totally determined by the tracer-diffusion constant. If this parameter is taken from experiment, one should obtain a width $f_t\gamma_{\mathrm{MF}}(\mathbf{q})$. The plots in Fig. 5 show that this quantity still does not follow the actual width $\gamma(\mathbf{q})$.

V. COHERENT STRUCTURE FACTOR AND CONDUCTIVITY

Since in our model the background lattice remains rigid, the coherent structure factor defined by (4.9) is identical to the charge-charge dynamic structure factor. In the following we will discuss this quantity only briefly. Its Laplace transform is written in the general form

$$\hat{S}_{\mathrm{coh}}(\mathbf{q},z)=S(\mathbf{q})[z+\Omega_{\mathrm{coh}}(\mathbf{q})+\hat{M}_{\mathrm{coh}}(\mathbf{q},z)]^{-1}\ , \tag{5.1}$$

where

$$\Omega_{\mathrm{coh}}(\mathbf{q})=-\langle n(\mathbf{q})\,|\,Ln(\mathbf{q})\rangle/NS(\mathbf{q})\ . \tag{5.2}$$

The numerator in (5.2) involves averages $\langle n_{1'}\,|\,j_{1,1+\delta}\rangle$, where $j_{1,1+\delta}=w_{1,1+\delta}(n_1-n_{1+\delta})$ is the total current along the bond $(1,1+\delta)$. For $1'$ differing from both 1 and $1+\delta$, we write explicitly, in terms of the equilibrium distribution $P_{\mathrm{eq}}(\mathbf{n})\propto\exp[-\beta H(\mathbf{n})]$,

$$\langle n_{1'}\,|\,j_{1,1+\delta}\rangle=\tfrac{1}{2}\sum_{\mathbf{n}} n_{1'}[P_{\mathrm{eq}}(\mathbf{n})w_{1,1+\delta}(\mathbf{n})(n_1-n_{1+\delta}) +P_{\mathrm{eq}}(\tilde{\mathbf{n}})w_{1,1+\delta}(\tilde{\mathbf{n}})(\tilde{n}_l-\tilde{n}_{l+\delta})]\ . \tag{5.3}$$

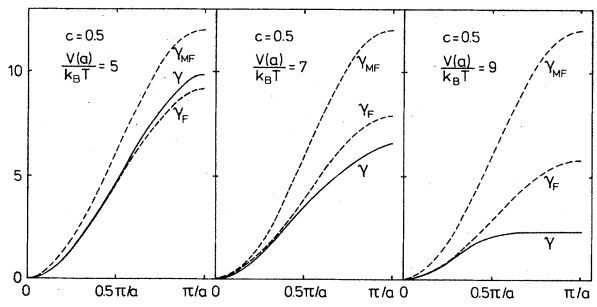

FIG. 5. Quasielastic width $\gamma(\mathbf{q})$ of the incoherent scattering function for wave vectors $\mathbf{q}=\zeta(1,1,1)$, $c=0.5$, and for three different temperatures. The width $\gamma(\mathbf{q})$ is normalized by $\langle w\rangle/2$. For comparison, we also show the width $\gamma_{\mathrm{MF}}(\mathbf{q})$ in mean-field theory and the quantity $\gamma_F(\mathbf{q})=f_t\gamma_{\mathrm{MF}}(\mathbf{q})$, which has the correct curvature at $\mathbf{q}=\mathbf{0}$.

Here the configurations $\tilde{\mathbf{n}}$ with $\tilde{n}_1=n_{1+\delta}$ and $\tilde{n}_{1+\delta}=n_1$ are defined in accord with (2.10), which shows that (5.3) vanishes. Therefore we are left with the terms

$$\langle n_1\,|\,j_{1,1+\delta}\rangle=-\langle n_{1+\delta}\,|\,j_{1,1+\delta}\rangle=\langle w\rangle/2\ . \tag{5.4}$$

This yields

$$\Omega_{\mathrm{coh}}(\mathbf{q})=\langle w\rangle\sum_{\delta}(1-e^{i\mathbf{q}\cdot\delta})/2cS(\mathbf{q})\ . \tag{5.5}$$

In a mean-field treatment, neglecting the memory function $\hat{M}_{\mathrm{coh}}(\mathbf{q},z)$, we have

$$\hat{S}_{\mathrm{coh}}(\mathbf{q},z)\simeq S(\mathbf{q})[z+\Omega_{\mathrm{coh}}(\mathbf{q})]^{-1}\ ,$$

in agreement with (4.28). It shows the usual de Gennes narrowing, as the static structure factor diverges; see Fig. 2.

Corrections to mean-field theory are only discussed in the long-wavelength limit, where the general relation

$$\hat{S}_{\mathrm{coh}}(\mathbf{q},z)\simeq S(\mathbf{q})[z+4\pi\hat{\sigma}(z)]^{-1} \tag{5.6}$$

holds between the charge-charge structure factor and the dynamic conductivity $\hat{\sigma}(z)$.[37] Upon comparing (5.6) with (5.1), we can write

$$4\pi\hat{\sigma}(z)=\lim_{\mathbf{q}\to\mathbf{0}}[\Omega_{\mathrm{coh}}(\mathbf{q})+\hat{M}_{\mathrm{coh}}(\mathbf{q},z)]\ . \tag{5.7}$$

The first term determines the infinite-frequency limit $\hat{\sigma}(\infty)$. Substituting (3.9) into (5.5), we obtain

$$\hat{\sigma}(\infty)=e^2\beta\langle w\rangle/2\ . \tag{5.8}$$

The memory function $\hat{M}_{\mathrm{coh}}$, which determines the frequency-dependent part of $\hat{\sigma}(z)$, is given by

$$\hat{M}_{\mathrm{coh}}(\mathbf{q},z)\equiv-\langle QLn(\mathbf{q})\,|\,(z-QLQ)^{-1}\,|\,QLn(\mathbf{q})\rangle/NS(\mathbf{q})\ , \tag{5.9}$$

where

$$Q=1-[\,|\,n(\mathbf{q})\rangle\langle n(\mathbf{q})\,|\,]/NS(\mathbf{q})\ .$$

Let us examine the expression

$$Ln(\mathbf{q})=-\alpha\sum_{1,\delta}(1-e^{-i\mathbf{q}\cdot\delta})n_1(1-n_{1+\delta}) \times\exp(\beta F_{1,1+\delta}/2)e^{-i\mathbf{q}\cdot\mathbf{l}}\ . \tag{5.10}$$

It is clear that a two-mode contribution to $\hat{M}_{\mathrm{coh}}$ arises from terms $n_1n_{1+\delta}$. It turns out, however, that this contribution vanishes in the limit $\mathbf{q}\to\mathbf{0}$. This shows that an improved theory in the spirit of Sec. IV would be much more complicated because it would have to include variables consisting of products of three occupation numbers. Therefore, after linearizing the exponential in (5.10) with the aid of (4.17), we use a simple factorization method limited to a moderate interaction strength. Following Ref. 26 we obtain the memory function as a sum of two- and three-mode terms, where only the latter survive in the limit $\mathbf{q}\to\mathbf{0}$. The result obtained for $\hat{M}_{\mathrm{coh}}(\mathbf{q}\to\mathbf{0},z)$ differs from Ref. 26 by an additional factor $\exp(\beta\langle\langle F\rangle\rangle)<1$, which brings the charge correlation factor

$f_c=\hat{\sigma}(0)/\hat{\sigma}(\infty)$ closer to unity, e.g., $f_c\sim 0.9$ for $V(a)/k_BT\sim 5$.[38] This indicates that for a Coulomb system the corrections to the mean-field expression (4.28) for $S_{\rm coh}(\mathbf{q},t)$ are substantially smaller than in a model based on nearest-neighbor repulsion only.

The frequency dependence of the real part $\mathrm{Re}[\hat{\sigma}(-i\omega)]$ turns out to be rather weak.[26] It increases monotonously with frequency ω and approaches the constant $\hat{\sigma}(\infty)$. This behavior is typical of pure hopping models. The first relaxation step observed in the dynamic conductivity of the fast ionic conductor $RbAg_4I_5$ may be interpreted in this way.[39] The fact that $\hat{\sigma}(z)$ varies only slightly with z on a scale given by the mean residence time τ^{-1} has implications with respect to the shape of the long-wavelength charge-fluctuation spectrum. From (5.8) we estimate $4\pi\sigma(0)<(2\pi/3)\tau^{-1}c\beta V_\delta$. It follows that, at least for $2c\beta V_\delta\lesssim 1$, one obtains the solution $z\simeq -4\pi\hat{\sigma}(0)$ for the denominator of (5.6) to be zero, because then $\hat{\sigma}(0)\simeq\hat{\sigma}(0)$ for $z\lesssim 4\pi\hat{\sigma}(0)$. This leads to a charge-relaxation spectrum with a quasielastic width $4\pi\hat{\sigma}(0)$, which is also known from the theory of molten salts.[40]

VI. REMARKS ON TWO-DIMENSIONAL AND QUASI-TWO-DIMENSIONAL SYSTEMS

In certain superionic materials, for example, β-alumina, the ionic motion is confined to two-dimensional layers. Let us therefore ask how the effects of Coulomb interactions discussed before are modified in that case.

We examine first the long-wavelength behavior of the coherent structure factor for a single layer perpendicular to the z axis. Within mean-field theory, where memory effects are neglected, we define an effective diffusion constant $D=a^2\langle w\rangle/2c$ in terms of the average rate $\langle w\rangle$ for hops within the layer. Analogous to the preceding section, we obtain

$$\hat{S}_{\rm coh}(\mathbf{q}\to\mathbf{0},z)=S(\tilde{q})[z+D\tilde{q}^2/S(\mathbf{q})]^{-1}\,, \tag{6.1}$$

where $\tilde{q}=(q_x^2+q_y^2)^{1/2}$. For a two-dimensional system the static structure factor $S(\tilde{q})$ is linear in $\tilde{q}$ in the limit $\tilde{q}\to 0$.[41] For qualitative purposes we treat the layer as a continuum and apply Debye-Hückel theory, which leads to

$$S(\tilde{q})=\tilde{q}(\tilde{q}+\tilde{q}_D)^{-1}\,, \tag{6.2}$$

where

$$\tilde{q}_D=2\pi e^2\beta\tilde{\rho}\,. \tag{6.3}$$

$\tilde{\rho}$ is the number of particles per unit area. According to (6.1) and (6.2), the long-wavelength charge-fluctuations are now characterized by a pole with a linear dispersion[42]

$$z=-D\tilde{q}_D\tilde{q} \tag{6.4}$$

in the limits $\tilde{q}\to 0$, in contrast to $z=-4\pi\sigma(0)$ for three dimensions. We remark that the present situation may be regarded as the overdamped analog of the dispersion $\omega_{\rm pl}\sim q^{1/2}$ for classical plasma oscillations in two dimensions.[41]

In a treatment of layered materials the coupling between parallel layers must be taken into account. For a discussion of the resulting anisotropy effects, we take the static structure factor from the linearized Debye-Hückel equations,

$$\Delta\phi(\mathbf{r})=-4\pi e^2\left[\delta(\mathbf{r})+\tilde{\rho}\sum_{n=-\infty}^{\infty}\delta(z-nd)[g_n(x,y)-1]\right] \tag{6.5}$$

and

$$g_n(x,y)\simeq 1-\beta\phi(x,y,nd)\,. \tag{6.6}$$

d is the interlayer distance, ϕ is the screened potential due to a point charge at the origin in the $n=0$ layer, and g_n is the pair correlation in the nth layer. One obtains

$$S(\mathbf{q})\equiv 1+\tilde{\rho}\int d\mathbf{r}\,e^{-i\mathbf{q}\cdot\mathbf{r}}\sum_{n=-\infty}^{+\infty}\delta(z-nd)[g_n(x,y)-1]$$

$$=\tilde{q}[\tilde{q}+\tilde{q}_D s(\mathbf{q})]^{-1}\,, \tag{6.7}$$

where

$$s(\mathbf{q})=\frac{\sinh(d\tilde{q})}{\cosh(d\tilde{q})-\cos(dq_z)}\,. \tag{6.8}$$

The limits $d\tilde{q}\gg 1$ and $d\,|\,\mathbf{q}\,|\ll 1$ in (6.7) correspond to the two- and three-dimensional results (6.2) and (3.9), respectively.

Substituting (6.7) into (6.1), the dispersion of charge fluctuations satisfies

$$z=-D\tilde{q}[\tilde{q}+\tilde{q}_D s(\mathbf{q})]\,. \tag{6.9}$$

We now consider the case $d\tilde{q}\ll 1$, where the charge fluctuations in different layers are strongly coupled. At $q_z=0$ we obtain $z=-2D\tilde{q}_D/d\simeq -4\pi\sigma$, where $\sigma=(\tilde{\rho}/d)e^2\beta D$ is the conductivity parallel to the layers. For nonzero q_z,

$$z=-D\tilde{q}^2\left[1+\frac{d\tilde{q}_D}{1-\cos(dqz)}\right]\,. \tag{6.10}$$

Thus a diffusive behavior is obtained, as regards the $\tilde{q}$ dependence of (6.10). As $\tilde{q}$ is increased such that $d\tilde{q}\gg 1$, the two-dimensional solution (6.4) is recovered from (6.9). Let us remark here that the foregoing discussion resembles the theory of plasma oscillations in semiconductor superlattices.[43]

Finally, we are interested in the correlation factor f_t for tracer diffusion in a plane layer. An effect typical of the Coulomb interaction is expected for low concentrations, where the two-dimensional version of the memory function (4.23) gives the dominant contribution. The corresponding integral over momenta p_x and p_y is split into two parts, $\tilde{p}<p_0$ and $\tilde{p}>p_0$, such that $\tilde{q}_D\ll p_0\ll\pi/a$. In the limit $c\to 0$ the second part, $\tilde{p}>p_0$, becomes independent of c. The first part, $\tilde{p}<p_0$, is evaluated with the aid of the two-dimensional Fourier transform $V(\tilde{p})=2\pi e^2/\tilde{p}$ of the Coulomb potential $e^2/|\,\mathbf{r}\,|$ at $z=0$, and by using (6.1) together with (6.2). In this way it is found that $1-f_t\propto c\ln c$, in contrast to $1-f_t\propto c^{1/2}$ in the three-dimensional case.

VII. SUMMARY AND CONCLUSIONS

The main concern of this paper was to formulate a master-equation description for many-particle hopping in a one-component Coulomb lattice gas and to develop an approximation scheme which takes into account the correlations arising from both the lattice and the Coulomb interactions.

Our method is based on an extended set of dynamic variables which includes nearest-neighbor pairs, and a mode-coupling approximation for the remaining memory function. A systematic extension by including further neighbors is possible in principle, but is too involved from a practical point of view. Some drawback lies in the complicated static correlations which arise in the present formulation. Uncertainties in their computation, however, should not affect our main conclusions.

We have obtained results for the tracer correlation factor f_t and the incoherent structure factor. In the dilute regime $c \to 0$ the long-range part of the Coulomb interaction gives rise to the behavior $1-f_t \propto c^{1/2}$ or $1-f_t \propto c \ln c$ for three- and two-dimensional systems, respectively. As $c \to 1$, on the other hand, correlations in the tracer motion are mainly due to site blocking. In the half-filled case $c=\frac{1}{2}$, the tendency of the system to undergo a transition with a [111] superstructure manifests itself in a pronounced decrease of f_t and a line narrowing in the incoherent scattering spectrum. The last observation arises from the coupling of the tracer motion to density fluctuations.

The dynamic conductivity obtained from the long-wavelength limit of the coherent structure factor depends only weakly on frequency in the regime of moderate coupling strength. Its temperature and concentration dependences are therefore largely determined by the average transition rate $\langle w \rangle$. Finally, within mean-field theory we have discussed anisotropy effects in the long-wavelength charge-fluctuation spectrum which should arise in layered materials.

ACKNOWLEDGMENTS

It is a pleasure to thank D. K. Chaturvedi and K. Funke for helpful discussions. One of us (A.B.) gratefully acknowledges financial support by Deutsche Forschungsgemein schaft.

APPENDIX

First, we give the normalization constants in (4.13) and (4.14). Let us define

$$\chi_{\delta,\delta'}=\langle A_\delta \mid A_{\delta'} \rangle = \begin{cases} \chi_+ & \text{for } \delta=\delta', \\ \chi_- & \text{for } \delta=\delta', \\ \chi_\perp & \text{for } \delta \perp \delta' . \end{cases} \tag{A1}$$

Here, $\chi_+=cg(1-cg)$, $\chi_-=c^2(g_- -g^2)$, and $\chi_\perp=c^2(g_\perp -g^2)$. Furthermore, $g \equiv g(\delta)$, $g_-=\langle n_{-x} n_0 n_x \rangle / c^3$, and $g_\perp=\langle n_y n_0 n_x \rangle / c^3$, where we have used an obvious notation. From (A1) we obtain

$$\begin{aligned} \chi_1(\mathbf{q}) &= \sum_{\delta,\delta'} [1-\cos(\mathbf{q}\cdot\delta)][1-\cos(\mathbf{q}\cdot\delta')]\chi_{\delta,\delta'} \\ &= (\chi_+ + \chi_-) \sum_\delta [1-\cos(\mathbf{q}\cdot\delta)]^2 + \chi_\perp \sum_\delta \sum_{\delta' \perp \delta} [1-\cos(\mathbf{q}\cdot\delta)][1-\cos(\mathbf{q}\cdot\delta)] \end{aligned} \tag{A2}$$

and

$$\chi_2(\mathbf{q}) = \sum_{\delta,\delta'} \sin(\mathbf{q}\cdot\delta)\sin(\mathbf{q}\cdot\delta')\chi_{\delta,\delta'} = (\chi_+ - \chi_-) \sum_\delta [\sin(\mathbf{q}\cdot\delta)]^2 . \tag{A3}$$

For the quantities $\Gamma_{0\delta}=-\langle A_0 \mid LA_\delta \rangle$ and $\Gamma_{\delta,\delta'}=-\langle A_\delta \mid LA_{\delta'} \rangle$, we find

$$\Gamma_{0\delta}=\Gamma^*_{\delta 0}=(1-e^{-i\mathbf{q}\cdot\delta})C_2/c + \sum_{\delta'_\perp,\delta} (1-e^{-i\mathbf{q}\cdot\delta'})C_1/c - \sum_{\delta'} (1-e^{-i\mathbf{q}\cdot\delta'})(\langle w \rangle g/2) , \tag{A4}$$

$$\Gamma_{\delta,\delta}= \left[8C_1+2C_2-D_0 \sum_{\delta'_\perp,\delta} e^{i\mathbf{q}\cdot\delta'} \right] \Big/ c - cg(\Gamma_{\delta 0}+\Gamma_{0\delta}) - (cg)^2\Gamma_{00} , \tag{A5}$$

$$\Gamma_{-\delta,\delta}= \left[4D_2 - D_3 e^{-i\mathbf{q}\cdot\delta} - D_1 \sum_{\delta'_\perp,\delta} e^{i\mathbf{q}\cdot\delta'} \right] \Big/ c - cg(\Gamma_{-\delta 0}+\Gamma_{0\delta}) - (cg)^2\Gamma_{00} , \tag{A6}$$

$$\Gamma_{\delta,\delta'}=[2\mathcal{D}_5+2D_7-(e^{i\mathbf{q}\cdot\delta}+e^{-i\mathbf{q}\cdot\delta'})D_6-2\cos(\mathbf{q}\cdot\delta_\perp)D_4]/c - cg(\Gamma_{\delta 0}+\Gamma_{0\delta'}) - (cg)^2\Gamma_{00} . \tag{A7}$$

The last relation holds for $\delta_\perp\delta'$ and $\delta_\perp$ is perpendicular to both δ and δ'.

In order to define the coefficients C_i and D_i, we introduce

$$t_x(\mathbf{n})=\alpha n_0(1-n_x)\exp[\beta F_{0,x}(\mathbf{n})/2] , \tag{A8}$$

which is the rate for a hop from $\mathbf{l}=\mathbf{0}$ in the positive x direction. From (3.14) we have $\langle w\rangle=2\langle t_x\rangle$. C_i and D_i essentially represent averages of $t_x(\mathbf{n})$ with respect to configurations where the occupation of certain sites near the origin $\mathbf{l}=\mathbf{0}$ is fixed,

$$C_1=\langle n_y t_x(\mathbf{n})\rangle,\quad C_2=\langle n_{-x} t_x(\mathbf{n})\rangle , \tag{A9}$$

$$D_0=\langle n_y n_{x+y} t_x(\mathbf{n})\rangle,\quad D_1=\langle n_y n_{x-y} t_x(\mathbf{n})\rangle , \tag{A10}$$

$$D_2=\langle n_y n_{-y} t_x(\mathbf{n})\rangle,\quad D_3=\langle n_{-x} n_{2x} t_x(\mathbf{n})\rangle , \tag{A11}$$

$$D_4=\langle n_y n_{x+z} t_x(\mathbf{n})\rangle,\quad D_5=\langle n_y n_z t_x(\mathbf{n})\rangle , \tag{A12}$$

$$D_6=\langle n_y n_{2x} t_x(\mathbf{n})\rangle,\quad D_7=\langle n_y n_{-x} t_x(\mathbf{n})\rangle . \tag{A13}$$

The averages (A9)—(A13) have the general form $\langle f(\mathbf{n})\exp[\beta F_{0,x}(\mathbf{n})/2]\rangle$ and are approximated by means of (3.19).

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