Nonlinear relaxation and solvation dynamics in a Coulomb lattice gas

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The transient response of ions upon sudden creation or removal of a local, external charge in a one-component Coulomb lattice gas is investigated by Monte Carlo simulations. Our model can be regarded as a simplified description of solvation dynamics processes in electrolyte systems. Effects of the nonlinearity of the relaxation are pointed out and are contrasted with predictions from linear (Debye–Hückel and Debye–Falkenhagen) theories. © *1995 American Institute of Physics.*

I. INTRODUCTION

Classical motion and relaxation of interacting charge carriers in condensed matter can often be described by Coulomb lattice gas models. For example, the linear transport properties of such systems have been studied theoretically in considerable detail in connection with ionic motions in solid electrolytes[1,2] and were used successfully to interpret experimental data.[3] In this paper we apply such models in order to investigate several aspects of solvation dynamics in electrolyte systems.

Solvation dynamics, i.e., the process of solvent relaxation following a sudden change in a solute's charge distribution has been under active study in recent years.[4] Our focus here is on solvation dynamics processes in electrolyte solutions. Several experimental studies by Huppert and co-workers[5] and by Chapman and Maroncelli[6] have indicated that in such systems, in addition to the fast relaxation mode associated with the host dielectric solvent, there exists a slow, nonexponential relaxation component associated with the mobile ions. This latter process occurs on a time scale of up to several nanoseconds, more than an order of magnitude slower than estimates based on the linear Debye–Falkenhagen (DF) theory.[7] For the relaxation of the ionic atmosphere following the sudden creation or removal of an ion of charge Q, this theory, which essentially combines diffusion with the linearized Poisson–Boltzmann equation, predicts

$$E_{DF}(t) = E_{DH} \, \mathrm{erf}(\sqrt{t/\tau_{DF}}), \tag{1}$$

where E_{DF} is the energy of interaction between the central ion and the ionic atmosphere, and τ_{DF} is given by

$$\tau_{DF} = (D\kappa^2)^{-1} \tag{2}$$

with D being the diffusion constant of the ions and κ the inverse Debye length. As $t \to \infty$, Eq. (1) approaches E_{DH}, the equilibrium value obtained from the Debye–Hückel theory.[8] In the weak coupling limit, where the Debye-length κ^{-1} is much larger than the ion radius, E_{DH} is given by

$$E_{DH} = -Q^2 \kappa. \tag{3}$$

A microscopic derivation of the DF dynamics has recently been provided by Chandra and Pater.[10] It should be mentioned that predictions based on Eq. (3) strongly underestimate, by more than an order of magnitude, the ionic contribution to the solvation energy of a charge or a charge distribution in an electrolyte solution, which is obtained experimentally from observed spectral shifts.[6]

The failure of Debye–Falkenhagen-type theories to account for the observed ion dynamics, which accompanies solvation processes in electrolyte solutions, has been attributed to its neglect of correlated ion–solvent motions in the immediate vicinity of the solute.[6,9] However, other factors may contribute as well. The theory, being essentially a mean-field approximation, ignores ion–ion correlations. Furthermore, being a linear theory, it cannot account for nonlinear processes that may affect the observed dynamics. The basic role of these additional factors are the subject of the present work. Rather than aiming at a realistic description of solvation we focus on ionic relaxation in the simplified model of a one-component Coulomb lattice gas. Our primary aim is to analyze the systematic deviations from the DF theory due to both the nonlinearity of the relaxation and the correlated diffusion of ions, while disregarding solvent dynamics. The latter simplification means that we assume that solvent dielectric relaxation is fast enough relative to the ionic motion to permit accounting for it by the trivial static dielectric screening. Studying a lattice system directly pertains to crystalline solid electrolytes, but results for $a\kappa < 1$ should also be applicable to amorphous and liquid electrolytes if the lattice constant a is interpreted as an effective hard core radius. Note, however, that the experimental observation[6] that the ionic contribution to the solvation energy is larger than the DH-prediction is associated with the fact that the solute–ion interaction in the neighborhood of the solute is only partially screened by the solvent molecules. This effect cannot be reproduced by a model which disregards the solvent or represents it by uniformly reducing the strength of the electrostatic interaction.

A Monte Carlo (MC) procedure is used to affect the ion dynamics. Such a dynamic MC-procedure relies on the assumption that the actual time is proportional to the number of Monte Carlo steps per particle. At the same time the use of the MC method together with the exclusion of solvent from the lattice gas model makes it possible to treat systems with much lower concentrations of ions and for much larger times than in full scale MD simulations. We note in passing that the MD simulations of Neria and Nitzan[9] could not be per-

formed under conditions where the DH- and the DF theories could be expected to be valid.

In what follows we first provide more details of our lattice model. We then discuss the deviations of our system from linearity as reflected in its dynamical behavior. One manifestation of nonlinearity is the asymmetry of the relaxation with respect to the sign of the central charge Q. Another is the dependence on Q of the correlation function

$$C(t) = \frac{\langle \delta\phi(t)\,\delta\phi(0)\rangle}{\langle \delta\phi^2\rangle} \qquad (4)$$

of the fluctuations in the potential ϕ induced by the ions at the position of the central charge. For $Q \to 0$ (i.e., when the response to Q is linear) this correlation function is equal to the solvation function

$$S^{\pm}(t) = \frac{E^{\pm}(t) - E^{\pm}(\infty)}{E^{\pm}(0) - E^{\pm}(\infty)}, \qquad (5)$$

where $E^{\pm}(t)$ is the average energy of interaction between the central charge and the mobile ions. $E^{\pm}(0)$ corresponds to the initial situation in which the mobile ions have not yet responded to the onset of the central charge, and $E^{\pm}(\infty)$ is the equilibrium interaction energy after the ionic atmosphere about the central charge has fully formed. In Eq. (5) we have anticipated our later discussion and distinguished between the response to a central charge of sign equal to that of the mobile ions, S^{+}, and the response to a central charge of opposite sign, S^{-}. Linear response theory predicts that $S^{+}(t) = S^{-}(t) = C(t)$. In writing Eq. (5) for the experimentally measured solvation function, we have made the common assumption that solvation (free) energies are approximated by $E^{\pm}/2$, which strictly holds under linear response conditions.

We also investigate the detailed behavior of the relaxation as expressed by $S^{\pm}(t)$, and study the conditions under which it can be accounted for by the DF theory. As expected we find that the observed relaxation deviates from the DF prediction as soon as nonlinearity sets in. In this case the linear theory generally underestimates the relaxation time, in agreement with experimental observations.[5,6] Finally, we present the time-dependent radial distribution function which reflects the dynamics of the screening of the central charge.

II. MODEL AND METHOD

We consider a simple-cubic substrate lattice of spacing a and size L, with periodic boundary conditions. A fraction c of lattice sites is occupied by ions of charge q, which interact via long-range Coulomb-forces, whereas the remaining sites are vacant. Multiple occupation of sites is excluded. Charge neutrality is maintained through a homogeneous background charge density $-qc/a^3$. In our Monte Carlo simulations ions are allowed to hop to vacant nearest-neighbor sites. The corresponding hopping probabilities are determined by the energy difference ΔH between configurations before and after an attempted hop, and are chosen according to the standard Metropolis algorithm.[11] In calculating ΔH we employ Ewald summations.

Equilibrium and linear transport properties of a stochastic Coulomb lattice gas defined in this way have been studied previously in some detail.[2] Here we are interested in both the linear and nonlinear transient response to the addition or removal of a central charge $Q = Zq$; $Z = \pm 1$; at time $t = 0$. The position of this charge is fixed to the center of a unit cube of the underlying simple-cubic lattice, and the neutralizing background is adjusted to keep the overall system neutral. Primarily we are interested in the time-dependent interaction energy $E^{\pm}(t)$ between ions and the central charge, in the comparison of the corresponding solvation function Eq. (5) with the correlation function Eq. (4), and also in the time-dependent radial distribution function $g^{\pm}(r,t)$.

Simulations were carried out for systems up to a size $L = 23$ and the results are averaged over 200 up to 10^4 (for different cases) equilibrated initial configurations. For the ionic concentration we choose $c = 10^{-2}$. Temperature enters via the dimensionless parameter V/k_BT, where $V = q^2/a$ is a typical Coulomb-energy in our lattice system. (The dielectric constant ϵ of the solvent system could be incorporated by the redefinition $V = q^2/\epsilon a$.) In terms of these parameters the Debye-length κ^{-1} is determined by the dimensionless quantity $a\kappa = (4\pi c V/k_BT)^{1/2}$.

III. RESULTS AND DISCUSSION

In this section we present the results of our simulations. The variables of interest are the correlation function $C(t)$, Eq. (4), the solvation functions $S^{\pm}(t)$, Eq. (5), the equilibrium interaction energy $E^{\pm}(\infty)$, and the characteristic relaxation times defined by

$$\tau^{\pm} = 2 \int_0^{\infty} S^{\pm}(t)\,dt. \qquad (6)$$

Under the DF theory, $S^{+} = S^{-}$ and $\tau^{\pm} = \tau_{DF}$.

Before we proceed, some remarks concerning the effects of the finite system size L and the periodic boundary conditions in our simulations are appropriate. The time-dependent energy of interaction between the central charge in the simulation cell with its total environment is then the sum of a contribution $E_L^{\pm}(t)$ due to all mobile ions in the periodic system and the interaction $\Sigma_L = -Q^2\alpha/L$ of the central charge with its periodic images (including a uniform excess background of charge density $-Q/L^3$). The corresponding Madelung constant is $\alpha \approx 2.837$. Consider an equilibrated system ($t \to \infty$) in the physically most interesting case, where the Debye-length κ^{-1} is much smaller than L. Then the periodic images of the central charge together with their ionic atmospheres represent localized, neutral charge distributions whose interaction with the central charge in the simulation cell converges faster as $L \to \infty$ than the individual terms $E_L^{\pm}(\infty)$ or Σ_L. From simulations with varying L we have verified, that results for the quantity $E_L^{\pm}(\infty) + \Sigma_L$ for our largest system ($L = 23$) and for $a\kappa > 1$ are in fact representative of an infinite system and are therefore used for approximating the solvation energy. Clearly, the self-energy Σ_L does not contribute to the solvation function, Eq. (5).

On the other hand, for the purpose of a quantitative test of our simulations against analytic calculations we are inter-
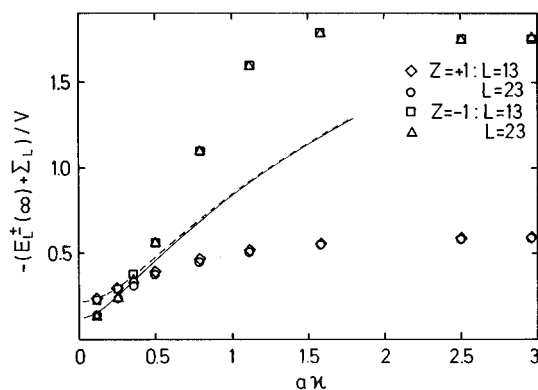
FIG. 1. Calculated interaction energy, including an L-dependent self-energy of the central charge, vs $a\kappa$ for $Z=\pm 1$ and for different system size L. Dashed curve and full curve are derived from Eq. (7) for $L=13$ and $L=23$, respectively. Statistical errors are of the order of the size of symbols.

ested also in the weak-coupling regime $a\kappa \ll 1$, where linear theories are applicable. Covering this regime will also complete our picture on the systematic trends in the results under varying degrees of the nonlinearity. However, because of our limitations with respect to the system size L, the Debye-length will necessarily become of order L as $a\kappa \ll 1$, and results will depend on L in an essential way. Hence the linear DH or DF theory has to be adapted to our situation of periodic boundary conditions. This leads to the following form for the L-dependent potential of the equilibrated ionic atmosphere at the site of the central charge

$$\phi_L = -(4\pi Q/L^3) \sum_{\mathbf{k} \neq 0} \frac{\kappa^2}{k^2(k^2+\kappa^2)}. \tag{7}$$

Here the summation is over components of the wave vector $\mathbf{k}$ which are integer multiples of $2\pi/L$, restricted to the first Brillouin-zone. Similarly, we obtain for the L-dependent solvation function

$$S_L(t) = (1/AL^3) \sum_{\mathbf{k} \neq 0} \frac{\exp-[D(k^2+\kappa^2)t]}{k^2(k^2+\kappa^2)}, \tag{8}$$

where D is the diffusion constant of ions in the dilute limit and A is a normalization factor. By τ_L we denote the relaxation time derived from Eq. (8) in analogy to Eq. (6). As $L \rightarrow \infty$, the familiar expressions $\phi_{DH}=Q\kappa$ and $S_{DF}(t) = \mathrm{erfc}(\sqrt{t/\tau_{DF}})$ are recovered from Eqs. (7) and (8). However, evaluation of Eqs. (7) and (8) for finite L leads to substantially different results which are depicted in Figs. 1–3. Note that $\phi_L \sim \kappa^2$, $\tau_L \sim$ const. for L fixed and $a\kappa \rightarrow 0$.

Now let us turn to our numerical simulations. Figure 1 displays data for the interaction energy in the two cases $Z=\pm 1$ and for systems of size $L=13$ and $L=23$. As seen from the figure, the influence of L on the quantity $E_L^\pm(\infty)+\Sigma_L$ is practically negligible for $a\kappa \gtrsim 1$. In that range of $a\kappa$, the reaction of the system is nonlinear and the solvation energy for $Z=+1$ is found to be substantially smaller than for $Z=-1$. This is to be expected since in the case $Z=-1$ a strong contribution to $E_L^-(\infty)$ of the order of V will arise from ions on nearest-neighbor sites with respect to the
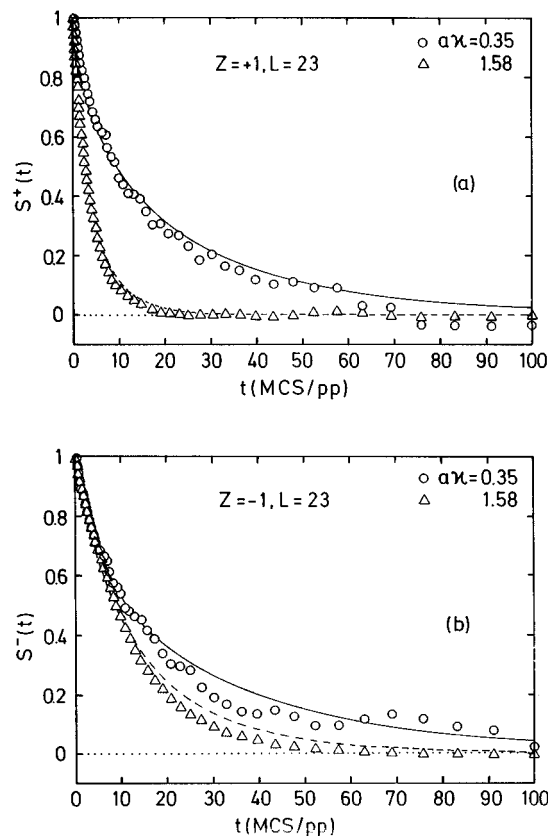

FIG. 2. Solvation functions $S^+(t)$ (a) and $S^-(t)$ (b) for two different values of the parameter $a\kappa$ and $L=23$. Full and dashed curves represent fits to Eq. (8) (see text).

central charge. By contrast, in the case $Z=+1$ a correlation hole will form with strong depletion of ions in the neighborhood of the central charge, in complete analogy with the behavior of the radial distribution function in the unperturbed system.[1,12] Hence, $E_L^+(\infty)$ is roughly estimated as Q^2/r_0, where $r_0 > a$ measures the radius of the correlation hole.

For small $a\kappa$, the two sets of data referring to $Z=\pm 1$ tend to agree. This is an indication of the validity of linear response theory, where $E_L^\pm(\infty)=Q\phi_L \propto Z^2$ is independent of sgn Z. At the same time, an L-dependence of our data appears. By lowering $a\kappa$, the simulations for different L seem to extrapolate to the dashed and the full curve, which were derived from Eq. (7) setting $L=13$ and $L=23$, respectively.

Figure 2 shows plots of the solvation function for two different values of the parameter $a\kappa$, whereas the systematic deviations of the relaxation times, Eq. (6), from the corresponding DF values are shown in Fig. 3. As before, the response in the case $a\kappa \simeq 0.35(V/k_BT=1)$ can be regarded as essentially linear. Indeed, in this case the two functions $S^\pm(t)$ become practically identical and are represented well by the prediction based on Eq. (8), which is given by the full lines in Figs. 2(a) and 2(b). To obtain these lines, the diffusion constants $D^\pm$ in the two cases $Z=\pm 1$ were regarded as fit parameters, with the result that D^+ and D^- are almost identical but both are smaller than the diffusion constant of a noninteracting reference system by about 20%. We note in
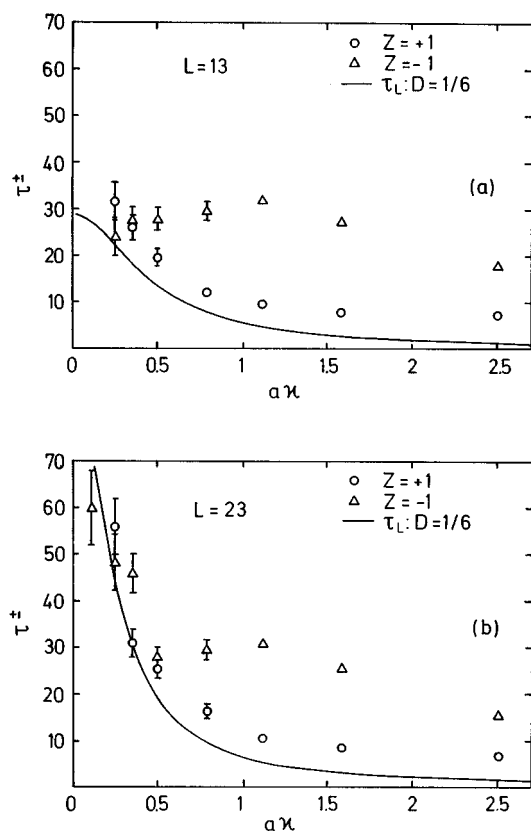
FIG. 3. Relaxation times $\tau^{\pm}$ according to Eq. (6), vs $a\kappa$ for $Z=\pm 1$ and for a system size $L=13$ (a) and $L=23$ (b). Full curves are derived from Eq. (8), using $D=1/6$.

passing that a slowing down in diffusion and conductivity coefficients upon the onset of interparticle interactions is well-known.[1,2] In the nonlinear regime, e.g., for $a\kappa \simeq 1.58(V/k_B T=20)$, fits of $S^{\pm}(t)$ to Eq. (8) become less accurate [see the dashed lines in Figs. 2(a) and 2(b)] and yield vastly different values of D^+ and D^-.

Focusing now our attention on the average relaxation times $\tau^{\pm}$ displayed in Fig. 3, the following trends are observed:

(a) The relaxation of the ionic atmosphere about a central charge of the same sign is in general faster than that about a central charge of the opposite sign, i.e., $\tau^->\tau^+$. This can be qualitatively understood from the inequality $E^-<E^+$ that suggests that relaxation towards a solute particle of opposite charge involves more individual ionic hopping events. The fact that $\tau^->\tau^+$ is seen even more clearly from the (non-normalized) solvation energies $E^{\pm}(t)$ depicted in Fig. 4. It is interesting to note that the same trend has been observed in a recent MD-study including solvent degrees of freedom by Neria and Nitzan,[9] whose results are shown in the inset of Fig. 4.

(b) As $a\kappa \rightarrow 0$, the difference between τ^- and τ^+ seems to disappear within the statistical errors, but both quantities show a pronounced L-dependence, which is accounted for by the results for τ_L obtained from Eq. (8).
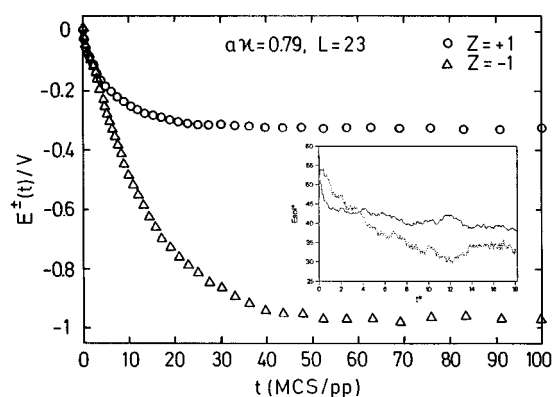

FIG. 4. Time-dependent functions $E^{\pm}(t)$ for $a\kappa \simeq 0.79$ ($V/k_B T=5$) and $L=23$. Molecular dynamics data (Ref. 9) are shown in the inset for a qualitative comparison. Full and dotted line in the inset refers to the contribution of positive and negative ions, respectively, the latter showing slower relaxation. For details see Ref. 9.

(c) As the coupling increases, $a\kappa \gtrsim 1$, the relaxation time becomes less sensitive to the system size L. Consider again the case $a\kappa \simeq 1.58$. The function $S^+(t)$ relaxes considerably faster than $S^-(t)$ (Fig. 2). Both quantities $\tau^{\pm}$ are substantially larger than the corresponding DF time τ_L. For example, $\tau^-/\tau_L \simeq 10$. (Note that in this case τ_L is virtually identical to the corresponding infinite system value τ_{DF}.) This observation reveals another mechanism for the experimental observation that relaxation times measured in electrolyte systems can exceed the DF prediction by more than an order of magnitude,[5,6] in addition to the mechanism of correlated ion–solvent motion mentioned in the Introduction.

We have also determined from our simulations the correlation function defined by Eq. (4). Actually, we determined three different functions, $C^0(t)$ and $C^{\pm}(t)$, referring to fluctuations in systems without a central charge and with a central charge $Q=\pm q$, respectively. We note that calculating the correlation function to within a certain statistical accuracy requires averaging over a much smaller ensemble (typically 200 configurations) than in calculating the solvation function. Figure 5 shows a comparison of the functions $C^{\pm}(t)$ and $S^{\pm}(t)$ for cases of weak coupling ($a\kappa \simeq 0.35$, $V/k_B T=1$) and strong coupling ($a\kappa \simeq 1.58, V/k_B T=20$). In the weak coupling case we find that the functions $C^{\pm}(t)$ are essentially identical and also agree with the corresponding solvation functions $S^{\pm}(t)$, in accordance with linear response theory. In the other strong coupling case, the correlation functions $C^+(t)$ and $C^-(t)$ differ from each other. Interestingly, $C^+(t)$ closely agrees with $S^+(t)$ even in this case [Fig. 5(a)], while $C^-(t)$ decays considerably faster than $S^-(t)$. Preliminary calculations at even higher values of $V/k_B T$ show a slowly decaying tail in $C^-(t)$ which is absent in $S^-(t)$. Such a tail is not observed in $C^+(t)$. To conclude, up to fairly strong interactions ($V/k_B T \lesssim 20$) the correlation functions $C^{\pm}(t)$ and the corresponding solvation functions $S^{\pm}(t)$ show qualitatively similar trends; in the case $Z=+1$ there is even good quantitative agreement.
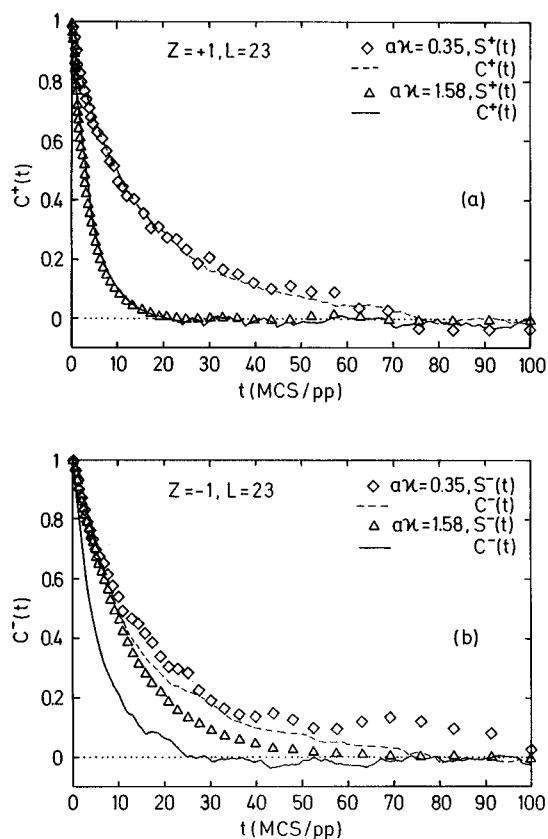
FIG. 5. Time-dependent correlation functions $C^{\pm}(t)$ for $L=23$. Dashed curve, $a\kappa \simeq 0.35$ ($V/k_B T=1$); full curve, $a\kappa \simeq 1.58$ ($V/k_B T=20$). Also shown are data for the solvation functions $S^{\pm}(t)$ from Fig. 2.

FIG. 6. Time-dependent radial distribution functions $g^{\pm}(r,t)$ for the first (r_1) and second (r_2) shell after adding (a) or removing (b) the central charge.

Details of the relaxation process can be deduced from the time-dependent radial distribution function plotted in Fig. 6(a) for the case $Z=-1$. As expected, after putting on the central charge, the occupation of the first shell at distance $r_1 = a\sqrt{3}/2$ strongly grows with time. The occupation of the second shell ($r_2 = a\sqrt{11}/2$) in the case $a\kappa \simeq 1.12$ initially grows, too, but subsequently reaches a maximum and then decays to a value less than its initial value. This behavior clearly reflects the screening of the central charge by ions in the first shell, which ultimately leads to an "antiscreening" effect in the second shell. Conversely, as the central charge is removed suddenly, the decay of $g^-(r_1,t)$ initially leads to an increase of $g^-(r_2,t)$ before the equilibrium state is reached.

IV. CONCLUSIONS

In this paper we have presented the results of a numerical investigation of a lattice gas model for solvation dynamics in a one-component charged system. Though highly simplified, this model makes it possible to study relatively long times and low ion concentrations, thereby allowing us to study the full range of coupling strengths, from the weak coupling limit where the predictions of the Debye–Hückel and Debye–Falkenhagen theories are confirmed, up to the strong coupling regime. In the latter case strong deviations from the predictions of the DH and DF theories are found. These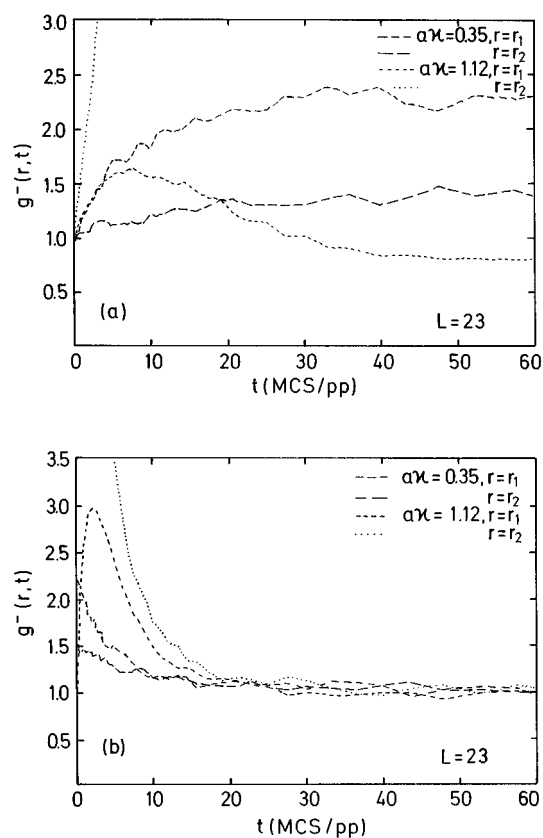 are due to both the nonlinearity of the response and to the importance of correlated ion motions in the immediate vicinity of the "solute." These deviations from the DH and DF theories appear most significantly in (i) the dependence of the response on the nature of the solute's charge distribution (e.g., the sign of the solute charge), and (ii) the significantly slower relaxation relative to the DF prediction.

Obviously, the model presented here disregards some potentially important contributions of the observed dynamics, in particular solvent motion, correlated ion–solvent molecules motion near the solute,[9] and the formation and motion of ionic aggregates in systems containing two species of oppositely charged mobile ions.[13] Therefore the results presented here do not constitute the full picture of solvation in electrolyte solutions. There exist however systems for which the present simulations may be highly relevant. These are framework solid ionic conductors and ionically conducting glasses in which the host relaxation is dominated by local vibrations of high frequencies and small amplitudes. In these systems time scale separability between matrix and ion motions may be assumed and the ion dynamics is dominated by ion–ion interactions. Ion dynamics in such systems have been under active study for many years and solvation dynamics experiments of the kind described here, which so far were limited to liquid electrolyte solutions,[14] may provide a new tool for studies of nonlinear relaxation in solid electrolyte systems.

ACKNOWLEDGMENTS

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