A simple harmonic model as a caricature for mismatch and relaxation effects for ion hopping dynamics in solid electrolytes

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Abstract
We formulate a simple harmonic mean-field model with N+1 particles and analyse the relaxation processes following a jump of one of these particles. Either the particle can jump back (single-particle route) or the other N particles adjust themselves (multi-particle route). The dynamics of this model is solved analytically in the linear response regime. Furthermore we relate these results to a phenomenological approach by Funke and coworkers (concept of mismatch and relaxation: CMR) which has been successfully used to model conductivity spectra in the field of ion dynamics in solid electrolytes. Since the mean-field model contains the relevant ingredients of the CMR-approach, a comparison of the resulting rate equations with the CMR-equations becomes possible. Generalizations beyond the mean-field case are discussed.

1 Introduction
The complexity of ion dynamics in disordered systems is reflected by the strong frequency dependence of the conductivity $\sigma(\nu)$, observed at low temperatures [1]. The dispersion can be directly interpreted as the presence of correlated backward-forward dynamics of the mobile ions [2, 3, 4]. From a theoretical point of view, two different mechanisms may contribute to the complex dynamics. First, the ions move in an energy landscape, supplied by the basically immobile network and which for amorphous electrolytes is expected to be disordered. Second, the ions interact via Coulomb interaction which tries to repel the ions from each other. Furthermore,
on longer time scales and at lower temperatures the ionic dynamics can be described as hops between adjacent ionic sites [5, 6, 7]. A theoretical description of ion dynamics on longer time scales can therefore be restricted to hopping dynamics. So far, however, the problem of ion dynamics in solid electrolytes is too complicated to formulate an analytic microscopic theory. Neglecting, however, one of the two ingredients, significant progress can be made. Without the interaction among the ions it is possible to extract information about the ion dynamics via percolation theory or effective medium theory [8, 9]. More specifically, in most cases a random energy landscape or a random barrier landscape has been analysed [10]. Not all predictions are compatible with experimental data. Experimentally, it is observed that the length scale \( L \) on which the ion dynamics can be described as a random walk is of the order of the nearest neighbor distance of two typical ionic sites and is temperature independent [3]. In contrast, for the random barrier model a significant temperature dependence as well as much longer values of \( L \) are observed [11].

Other workers have stressed the relevance of Coulomb interaction among the mobile ions. Analytical calculations [12] and simple model systems have been constructed along this line [13, 14]. In particular Funke and coworkers have devised phenomenological models which are based on the relevance of Coulomb interaction [15, 16, 17, 18, 19, 20]. They consider the interaction among the ions as the relevant ingredient, incorporating also effects of stress and strain. The picture is as follows: after a jump of a well-equilibrated ion at site A to an adjacent empty site B the new ionic environment will often lead to an energetic mismatch, i.e. could be quite unfavorable. Thus it is very likely that the ion jumps back to A (single-particle route). If, by chance, the backjump does not occur immediately, the adjacent ions may have time to adjust to the new situation and the ionic site B becomes more favorable. Thus the backjump probability decreases with time. If finally site B has become more favorable than the initial site A the jump can be viewed as successful (multi-particle route). This interplay between both routes gives rise to the complex ionic dynamics, involving many correlated back- and forth jumps. Funke has formulated two coupled differential equations, involving two different functions [19, 20]. One function basically describes the mean square displacement of the individual ions, the second function the response of the neighbor ions to an ionic jump. In the previous version of the model (concept of mismatch and relaxation: CMR) this coupled set has been solved analytically and agrees well with measured conductivity spectra [19]. In the original CMR-approach no adjustable parameters are present except for the simple scaling of the time and the length scale. Presently, Funke and coworkers work on a more refined model with one adjustable parameter to further improve the agreement with experimental data [20].

So far, the CMR-equations have not been derived from first principles. Unfortunately, it is not possible to verify the approach from comparison with experiments. The good agreement of the mean square displacement with experiment (see below for a closer discussion) is in a strict sense only a necessary condition for the validity of the CMR-approach. Therefore, we feel that a thorough theoretical discussion of the CMR-equations may be valuable. The CMR-approach
casts the interplay of single-particle and multi-particle relaxation into two rate equations, using phenomenological arguments. In particular, the precise nature of the interaction among the ions does not enter these equations. The scope of the present work is to analyse a very simple but non-trivial model which leads to exactly the effects, incorporated into the CMR-approach. It will be shown that indeed two equations can be derived with a formal structure identical to the CMR-equations. A more detailed analysis, however, will reveal differences of the exact solution as compared to the CMR-equations. The effect of additional disorder will be also taken into account. Furthermore it will be argued that the present modifications of the CMR-equations can be justified also from a strictly theoretical point of view.

The organization of this paper is as follows. In Section 2 we introduce the CMR-approach. In Section 3 our model is introduced which is then exactly solved in Section 4 in the limit of vanishing disorder. Section 5 contains the derivation of the two coupled rate equations which are formally identical to the CMR-equations. Numerical simulations of the model, partly also including disorder effects, are presented in Section 6. We end with a discussion and a summary in Section 7.

2 CMR: a short summary

The CMR-approach is based on two central quantities $W(t)$ and $g(t)$. $W(t)$ is formally defined as the normalized derivative of the single-particle mean square displacement ($W(0) = 1$). As already mentioned above the key idea of the CMR-approach is to consider the mismatch generated by a hop of a central ion (at time $t=0$). In the multi-particle route the neighbors rearrange and thus adjust to the new position of the central ion. In the single-particle route the central ion jumps back.

The multi-particle relaxation is characterized by the function $g(t)$. It expresses the normalised distance between the actual position of the ion and the position at which it would be optimally relaxed. During this relaxation process the central ion is supposed to stay at its position so that it can be viewed as fixed [20]. Due to the multi-particle relaxation the actual position of the central ion gets closer to its optimum position as determined by the neighbor positions so that the energetic mismatch is slowly released. The initial situation after the jump is characterized by $g(t = 0) = 1$. Finally $g(t)$ approaches 0 when the initial mismatch has decayed. The value $-\dot{g}(t)$ is thus proportional to the rate of mismatch relaxation along the many-particle route.

Let $S(t)$ denote the fraction of ions which have not performed a correlated backjump after time $t$, i.e. still correspond to the successful jumpers. Then $-\dot{S}(t)/S(t)$ can be interpreted as the rate of mismatch relaxation on the single-particle route. The factor $1/S(t)$ takes into account that a relaxation process at time $t$ of a successful ion requires that the ion has remained at the new position up to time $t$. The central assumption of the CMR is that the single-particle and
the multi-particle rates are proportional to each other at all times, i.e. (CMR-Ia)

\[- \dot{S}(t)/S(t) \propto -\dot{g}(t).\] (1)

Furthermore Funke assumes that the single-particle rate can be also expressed via (CMR-Ib)

\[\dot{S}(t)/S(t) \propto \dot{W}(t)/W(t).\] (2)

This means that the rate of mismatch relaxation on the single-particle route is proportional to \(-\dot{W}(t)/W(t)\). For a random-walk with no correlated backward jumps one obviously has \(S(t) = 1\). Furthermore due to the strictly diffusive behavior one also has \(W(t) = 1\). Here CMR-Ib is trivially fulfilled. Combining CMR-Ia and CMR-Ib one finally gets (CMR-I)

\[- \dot{W}(t)/W(t) \propto -\dot{g}(t).\] (3)

Next a rate equation for \(g(t)\) is formulated. Here it is argued that the decay of \(g(t)\) is proportional to the convolution of the driving force and the velocity autocorrelation function of the neighboring mobile ions. Noting that the derivative of \(W(t)\) is proportional to the velocity autocorrelation function and assuming that \(W(t)\) decays much faster than \(g(t)\) (this can be afterwards checked in a self-consistent manner) one ends up with (CMR-II)

\[- \dot{g}(t) \propto W(t)g(t).\] (4)

In the most recent version of the CMR Funke and coworkers have included another time-dependent function which may represent the time-dependent effective number of mobile neighbors available for the relaxation [20], i.e. (CMR-II\text{new})

\[- \dot{g}(t) \propto W(t)g(t)n(t).\] (5)

From the fitting it turns out that the choice \(n(t) = g(t)\) yields a very good agreement with the experimental data. In the latter part of this manuscript we briefly discuss this modification of CMR-II.

These relations form a closed system. Note that all relations are based on general arguments. If CMR-I and CMR-II were valid they should be applicable to a large class of models for which the relaxation occurs by the interplay of single-particle and multi-particle routes. The function \(W_{\text{CMR}}(t)\), obtained from the solution of CMR-I and CMR-II, can finally be compared with experimental conductivity spectra and thus with the experimental \(W(t)\).

Now we are in a position to discuss why the empirical agreement of \(W_{\text{CMR}}(t)\) with the experimental \(W(t)\) does not imply that the CMR-equations are correct. Validation of the CMR-equations naturally requires knowledge of \(g(t)\). The definition of \(g(t)\), however, is based on the specific situation of a particle fixed after its jump. Whereas \(g(t)\) can be determined from computer simulations or in some cases even analytically (see below), no experimental access is presently available. In principle, it may turn out that both CMR-I and CMR-II are not correct but the final solution of \(W_{\text{CMR}}(t)\) can be used to describe experiments. In any event, the goal of this work is to analyse CMR-Ia, CMR-Ib, CMR-II and later on also CMR-II\text{new} individually.
3 Harmonic model

We want to construct a possibly very simple model which allows for the presence of a single-particle and a multi-particle route. The single-particle route requires an interaction term which is a minimum when adjacent particles have their respective equilibrium distance. This can be most easily achieved by a harmonic potential. The multi-particle route is facilitated by a translationally invariant model. After the jump of a particle and the consecutive jumps of all adjacent particles in the same direction the original configuration is recovered. For reasons of simplicity one may take a mean-field model in which all particles are identical. Both properties are contained in the Hamiltonian

\[ H = \left( \frac{k}{N} \right) \sum_{i=1}^{N} \sum_{j>i}^{N} (y_i - y_j)^2 + \left( \frac{k}{N} \right) \sum_{i=1}^{N} (y_i - x)^2 \equiv H_y + H_{xy}. \]  

(6)

The ground state of this system is \( x = y_1 = \ldots = y_N \). Of course, at finite temperature there will be a spread of the \( y_i \) which can be easily quantified by minimization of the free energy (not shown in this paper). All \((N+1)\) particles are treated identically in this mean-field Hamiltonian. The particle with coordinate \( x \) is formally viewed as the central particle and we define it as the \( x \)-particle. Furthermore we define the center-of-mass \( y \) of the other \( N \) particles as

\[ y = \left( \frac{1}{N} \right) \sum_{i=1}^{N} y_i. \]  

(7)

The set of particles \( y_1, \ldots, y_N \) will be denoted \( y \)-cloud. If after the jump \( x \neq y \), the \( x \)-particle will experience a back-dragging force until \( x = y \). On the one hand, this can be achieved by a jump of the \( x \)-particle to this favorable position (single-particle route). On the other hand, the \( y \)-cloud can adjust to the new position of the \( x \)-particle (multi-particle route).

In order to mimic the hopping dynamics the coordinates \( y_i \) of the individual particles are discretised \((y_i = \ldots, -3/2, -1/2, 1/2, 3/2, \ldots)\). Without interaction among the particles \((k = 0)\) the rates for all jump processes are identical. With finite interaction the rates have to reflect the energy variation due to the transition. In the spirit of the Metropolis criterion the rate for a jump process of one particle is unmodified as compared to the \( k = 0 \) case if the energy decreases due to the jump and is decreased by \( \exp(-\beta \Delta U) \) if the energy increases by \( \Delta U \) \cite{21, 22}.

In this model it is possible to take into account disorder effects, as present in amorphous ion conductors for which the CMR-approach has been applied as well. Here we restrict ourselves to barrier disorder. For the barriers between any two sites \((a, a+1)\) of the \( i \)-th particle we choose a random but fixed value \( E_i(a, a+1) \), equally distributed between 0 and \( V_{\text{max}} \). Then the individual transitions are modified by multiplying every rate with the factor \( \exp(-\beta E_i(a, a+1)) \) if a transition of the \( i \)-th particle from \( y_i = a \) to \( y_i = a + 1 \) (or vice versa) is considered. The discretised positions as well as the barrier disorder are sketched in Fig.1. For \( k > 0 \) the particles are confined to a finite region of \( y_i \) values, as also indicated in Fig.1.
For comparison with the two CMR rate equations we need to express \( W(t) \) and \( g(t) \) in terms of the system coordinates. Formally, we define

\[
W(t) = w(t)/w(0)
\] (8)

where \( w(t) \) is the derivative of the single-particle mean square displacement

\[
w(t) \equiv (d/dt)\langle(x(t) - x(0))^2\rangle.
\] (9)

For \( k = 0 \) and without disorder one would have a simple random walk of the x-particle, i.e. \( \langle(x(t) - x(0))^2\rangle = \Gamma t \) and thus \( w(t) = \Gamma \) where \( \Gamma \) is a rate constant. With additional disorder \( (V_{\text{max}} \neq 0) \) the short-range dynamics is still diffusive albeit with a smaller rate \( \Gamma \), reflecting the slowing-down due to the presence of higher barriers.

It is possible to write \( W(t) \) in a more elegant way which will be of relevance later on. Let \( \langle \cdot \rangle_0 \) denote the ensemble average over all events where at time \( t = 0 \) the x-particle jumps one site to the right. We start from the general relation (valid for \( t > 0 \))

\[
2\langle\hat{x}(0)\hat{x}(t)\rangle = \dot{w}(t) = \Gamma \dot{W}(t)
\] (10)

The term in the brackets of the l.h.s. is non-zero if there is a jump happening at \( t = 0 \). The probability for such a jump during a time interval \( \Delta t \) is \( \Gamma \Delta t \). Using a discrete notation \( \hat{x}(0) = (x(\Delta t/2) - x(-\Delta t/2))/\Delta t \) one can write in case of a jump: \( \hat{x}(0) = 1/\Delta t \). This yields

\[
\langle\hat{x}(0)\hat{x}(t)\rangle = (\Gamma \Delta t)\langle(1/\Delta t)\hat{x}(t)\rangle_0 = \Gamma \langle \hat{x}(t) \rangle_0
\] (11)

and thus

\[
\dot{W}(t) = 2\langle \dot{x}(t) \rangle_0.
\] (12)

In order to obtain \( W(t) \) from this relation one has to recognize that for reasons of time reversal symmetry

\[
\langle x(0+) - y(0) \rangle_{\text{after jump}} = -\langle x(0-) - y(0) \rangle_{\text{before jump}}
\] (13)

where \( x(0_{\pm}) \) denotes the position of the x-particle after and before the jump at \( t = 0 \), respectively. This relation expresses the fact that before a jump to the right the x-particle is typically left to the center of mass of the y-cloud and after a jump by the same amount right to it. Since the jump length is unity one can directly conclude

\[
\langle x(0+) - y(0) \rangle_0 = 1/2.
\] (14)

Integration of Eq.12 under the condition \( W(0) = 1 \) thus yields

\[
W(t) = 2\langle x(t) - y(0) \rangle_0.
\] (15)
On a qualitative level this relation shows that the mean square displacement can be obtained from analysing the response of the system after a jump at $t = 0$.

For later purposes we also consider the multi-particle mean square displacement $\langle (y(t) - y(0))^2 \rangle$ if the x-particle were not present, i.e. exclusively for the Hamiltonian $H_y$. In analogy to $W(t)$ we define $w_y(t)$ as its derivative and $W_y(t)$ as its normalized derivative. Since for short times the N particles behave independently of each other the short-time diffusion constant of the center of mass is scaled by a factor of $1/N$ as compared to the single-particle case. Thus $w_y(0) = w_x(0)/N = \Gamma/N$. $w_y(t)$ can be simply calculated for the case of no disorder. Since all interaction terms cancel out, the center of mass of the y-cloud will just perform a random walk, i.e. $w_y(t) = \Gamma/N$. In contrast, in the presence of disorder the dynamics of the center of mass can be highly non-diffusive. Later on it will be important that exactly for the case of diffusive dynamics the sum over all displacements during one time step is independent of the sum over all displacements at a previous time. In analogy we introduce $w_x(t)$ as the derivative of the mean-square displacement of the x-particle if no interaction with the y-cloud is present.

As a next step, we define $g(t)$ as the relaxation of the y-cloud for a fixed x-particle with the normalization condition $g(0) = 1$. This definition is motivated by the use of $g(t)$ in the CMR-approach. Let $\langle \cdot \rangle_F$ denote the ensemble for which at time $t=0$ the x-particle has jumped to the right and remains there fixed forever. Since on average $\langle x - y(0) \rangle_F = 1/2$ the appropriate definition is

$$1 - g(t) = 2\langle y(t) - y(0) \rangle_F.$$  \hspace{1cm} (16)

$g(t)$ describes how the y-cloud approaches the fixed position of the x-particle, corresponding to a decay of $g(t)$ from 1 to 0. Note that an equivalent expression is given by

$$g(t) = 2\langle x - y(t) \rangle_F.$$  \hspace{1cm} (17)

4 Analytic solution of the model

In this section we calculate the particle dynamics in this model without disorder. We start with the analysis of the dynamics of the y-cloud (first, without the x-particle, i.e. for the Hamiltonian $H_y$) under some perturbation. In case of a time-dependent force $F(t)$, i.e. an interaction Hamiltonian $F(t)y$, one can apply linear response theory for small $F(t)$ to express the dynamics of $y$ under the perturbation in terms of equilibrium correlation functions, yielding \cite{23}

$$\langle \dot{y}(t) \rangle_{\text{pert}} = \beta \int_0^t d\tau F(\tau) \langle \dot{y}(t)\dot{y}(\tau) \rangle \approx (1/2)\beta F(t)w_y(t)$$  \hspace{1cm} (18)

with $\beta = 1/(k_B T)$. The final approximation is valid if the time-dependence of the force is much slower than the decay of the velocity-velocity autocorrelation function.
In the present case we have no fixed force $F$ but the perturbation energy for a fixed $x$-particle is given by $H_{xy}$. It can be rewritten as

$$H_{xy} = k(y - x)^2 + (k/N) \sum_{i=1}^{N} (y - y_i)^2$$  \hspace{1cm} (19)$$

The second term is independent of $x$. Its average value results from a free energy minimization of the positions of the particles which are part of the y-cloud. Thus it is irrelevant for the perturbation. For given $y$ and $x$ the force $F$ thus reads $2k(x - y)$ which shifts the y-cloud towards the x-particle. For not too small $N$ it is evident from Eq.18 that the response of the y-cloud is slow due to the factor $1/N$, which is contained in $w_y(t)$. Thus one can use the approximation in Eq.18 and finally obtains (omitting the index $\text{pert}$)

$$\langle \dot{y}(t) \rangle = k\beta(x - y(t))w_y(t).$$  \hspace{1cm} (20)$$

Furthermore, the linear response relation Eq.20 is also valid if the x-particle is allowed to be mobile, i.e. $x$ is substituted by $x(t)$. Thus one has, using the $\langle \rangle_0$-ensemble,

$$\langle \dot{y}(t) \rangle_0 = \beta kw_y(t)(\langle x(t) \rangle_0 - \langle y(t) \rangle_0).$$  \hspace{1cm} (21)$$

Note that this relation also holds for disorder, since the disorder is taken into account by the term $w_y(t)$. Without disorder one may insert $w_y(t) = \Gamma$/N. In analogy one can also formulate how the x-particle is attracted by the y-cloud. For this purpose we consider an isolated x-particle which is distorted by the energy $F(t)x$ with $F(t) = -2k(x - y)$. We obtain

$$\langle \dot{x}(t) \rangle_0 = \langle \dot{x}(t) \rangle_{0,do} + (\beta k w_x(t))(\langle y(t) \rangle_0 - \langle x(t) \rangle_0).$$  \hspace{1cm} (22)$$

The function $w_x(t)$ characterizes the dynamics of an isolated x-particle. The first term on the right side corresponds to the behavior of the x-particle if no coupling to the y-cloud were present. Without disorder one has $w_x(t) = \Gamma$ (random-walk) and $\langle \dot{x}(t) \rangle_{0,do} = 0$. With disorder $w_x(t)$ may display a complex time-dependence.

This set of rate equations can be solved in a straightforward way. With the initial conditions $\langle x(0) \rangle_0 = 1/2$ and $\langle y(0) \rangle_0 = 0$ one obtains (using the abbreviation $C = \beta k$)

$$W(t)/2 = \langle x(t) \rangle_0 = \frac{1}{2(1 + N)} (1 + N \exp(-CTt))$$  \hspace{1cm} (23)$$

and

$$\langle y(t) \rangle_0 = \frac{1}{2(1 + N)} (1 - \exp(-CTt)).$$  \hspace{1cm} (24)$$
Furthermore one can easily calculate $g(t)$ from Eq.21 by keeping the x-particle fixed. Together with Eq.17 one obtains

$$g(t) = \exp(-C\Gamma t/N).$$

(25)

In agreement with typical experimental situations the decay of $g(t)$ is much slower than the decay of $W(t)$.

Interestingly, on the level of the linear response the fact that the y-cloud is composed of individual particles is lost. Rather one could have started from the very beginning with a two particle problem, i.e. with the Hamiltonian $H = k(x - y)^2$ and postulate that for $k = 0$ the equilibrium dynamics of the x-particle is characterized by $w_x(t)$ and that of the y-particle by $w_y(t)$. This simplified view will be of importance later on.

For checking the validity of the CMR-equations for the present case $V_{\text{max}} = 0$ (no disorder) we will proceed in two steps. First, we will derive rate equations in terms of $g(t)$ and $W(t)$ for this Hamiltonian, thereby generalising the above analysis to the case of additional disorder. Due to the strict derivation all proportionality constants can be expressed in terms of system parameters. Second, comparison with CMR-Ia, CMR-Ib, and CMR-II will reveal under which conditions the phenomenological CMR-equations can be indeed applied. Third, we will check the validity of our rate equations by comparison with numerical simulations.

5 Analytical derivation of CMR-like equations

First we consider CMR-Ia. As mentioned before, without disorder the center of mass of all particles performs diffusive dynamics. This can be expressed more formally. Let $\Delta x(t)$ denote the distance moved by the x-particle at time step $t$ ($\Delta x(t)$ can be either $-1, 0, 1$). In analogy, we define $\Delta y(t)$ as the motion of the center of mass of the y-cloud at this time step. Since the motion to the left and the right side are equally likely one (trivially) has

$$\langle \Delta x(t) \rangle + \sum_{i=1}^{N} \langle \Delta y_i(t) \rangle = \langle \Delta x(t) \rangle + N \langle \Delta y(t) \rangle = 0$$

(26)

where the brackets indicate the ensemble average.

It turns out to be helpful to introduce the notation $\langle . \rangle_S$. It denotes the average over the ensemble where at time 0 the x-particle has jumped to the right and for times less than time $t$ has on average stayed at its new position. Qualitatively, this is the ensemble of events for which the initial jump at $t = 0$ is successful at least until the jump at time $t$. Formally this means that $\langle x(t) \rangle_S = \langle x(0+) \rangle_0$. Because of the independence of the dynamics during successive time steps for the purely diffusive case (no disorder; see above) one also has

$$\langle \Delta x(t) \rangle_S + N \langle \Delta y(t) \rangle_S = 0.$$  

(27)
Obviously, the total system relaxes towards the equilibrium situation in a non-oscillatory manner. Qualitatively, this implies that those particles which are still successful at time \( t \) (after a jump to the right at \( t = 0 \)) will, on average, have a tendency to move to the left afterwards. Thus it is possible to iteratively define the fraction \( S(t) \) of successful particles, and thus the S-ensemble, by two conditions: (i) the average value of \( \Delta x(t) \equiv x(t_+) - x(t_-) \) is zero for those particles which remain in the S-ensemble after the jump at time \( t \). (ii) the average value of \( \Delta x(t) \) is -1 for those particles which were part of the successful ensemble before the jump at \( t \) and fall out of the S-ensemble after the jump. Of course, this does not imply that all particles jumping to the left, leave the S-ensemble but only those which are not balanced by particles jumping to the right. Therefore for a random walk, leading to purely diffusive dynamics, one has \( S(t) = 1 \) because on average the fraction of particles moving to the left and to the right is identical. The construction of the fraction of particles, belonging to the S-subensemble, is sketched in Fig.2.

The definition of the S-subensemble implies

\[
\langle \Delta x(t) \rangle_S = \frac{S(t - \Delta t) - S(t)}{S(t - \Delta t)} \cdot (-1) + \frac{S(t)}{S(t - \Delta t)} \cdot 0 = \frac{S(t) - S(t - \Delta t)}{S(t - \Delta t)}. \tag{28}
\]

In the limit \( \Delta t \to 0 \) one thus obtains

\[
\frac{\dot{S}(t)}{S(t)} + N \langle \dot{y}(t) \rangle_S = 0 \tag{29}
\]

For more general energy landscapes, e.g., with random barriers, the center of mass dynamics is not simply diffusive. Rather a jump will be typically followed by correlated backward dynamics. Thus the presence of a jump of the x-particle at time \( t = 0 \) to the right implies that \( \Delta x(0) + N \Delta y(0) \) on average is positive and correspondingly will be negative at later times. Thus in general one expects

\[
\frac{\dot{S}(t)}{S(t)} + N \langle \dot{y}(t) \rangle_S = f_{do}(t) \leq 0 \tag{30}
\]

where \( f_{do}(t) \) (do: disorder) represents the effect of disorder.

We can proceed further by using Eq\( \text{[20]} \). This relation has important implications for our analysis. Due to the linearity of the r.h.s. in \( x \) the average time-dependence of \( y(t) \) is the same whether one considers an ensemble where all x-particles are fixed at some position \( x_0 \) or whether the x-particles are distributed around this position with exactly the average value \( x_0 \). This implies that the S-ensemble and the F-ensemble yield the same time-dependence for the relaxation of the y-cloud. Thus Eq\( \text{[30]} \) can be rewritten (using the relation \( \dot{g}(t) = -2\langle \dot{y}(t) \rangle_F = -2\langle \dot{y}(t) \rangle_S \) from Eq\( \text{[19]} \) as

\[
- \frac{(d/dt)S(t)}{S(t)} = -\frac{N}{2} \dot{g}(t) - f_{do}(t). \tag{31}
\]
Except for the disorder-term $f_{do}(t)$, which for weak disorder may be small, relation CMR-Ia has been recovered.

Eq. 20 can be also used to derive CMR-II. After expressing both sides in the F-ensemble and using Eq 17 as well as $\dot{g}(t) = -2\langle \dot{g}(t) \rangle_F$ one gets

$$\dot{g}(t) = k\beta g(t)w_y(t).$$

(32)

The only difference to CMR-II is the substitution of the single-particle quantity $w_y(t)$ by the multi-particle quantity $w(t)$ (thus yielding the proportionality to $W(t)$). Since, however, in typical experimental situations $w(t)$ and $w_y(t)$ are quite similar this substitution may be justified for practical purposes.

It remains to check CMR-Ib. For this purpose we consider the situation that at $t = 0$ the $x$-particle jumps to the right side and ends up at a position which, on average, is given by $y(0) + 1/2$ (see above). For reasons of simplicity we choose $y(0) = 0$. After the next jump processes at $t = \Delta t$ there will be a higher probability for the $x$-particle to jump to the left than to the right because of the back-dragging effect of the $y$-cloud. $p_1$ denotes the fraction of $x$-particles which effectively jump to the left side (which means, which are not balanced by particles moving to the right side; see above). Thus the number of successful particles at $t = \Delta t$ is given by $S(\Delta t) = 1 - p_1$. Furthermore this implies

$$\langle x(\Delta t) \rangle_0 = (1/2)(1 - p_1) + (-1/2)p_1.$$  

(33)

Together with Eq 15 one gets

$$W(\Delta t) = 1 - 2p_1.$$ 

(34)

Thus one has

$$\frac{W(0) - W(\Delta t)}{W(0)} = 2\frac{S(0) - S(\Delta t)}{S(0)}.$$ 

(35)

This relation implies that if CMR-Ib were valid one should choose

$$\frac{\dot{W}(t)}{W(t)} = 2\frac{\dot{S}(t)}{S(t)}.$$ 

(36)

Now we analyse the next jump process at $t = 2\Delta t$. The $x$-particles, which are still successful after $t = \Delta t$ and thus are still centered around $x = 1/2$ will again have a tendency for a jump to the left side. In analogy to $p_1$, we define $p_2$ as the fraction of these $x$-particles, which effectively jump to the left side. In contrast, the $x$-particles which were unsuccessful after the first jump and are thus centered around $x = -1/2$ will also be attracted by the $y$-cloud. For these particles this will result in a preference of jumps to the right side. In analogy to $p_2$ we define $q_2$ as the fraction of these $x$-particles which effectively jump back to $x = 1/2$. With these parameters one directly gets

$$S(2\Delta t) = S(\Delta t)(1 - p_2)$$ 

(37)
and

\[(1/2)W(2\Delta t) = \langle x(2\Delta t) \rangle_0 = (1/2) \cdot [(1-p_1)(1-p_2)+p_1 q_2]+(-1/2)[p_1(1-q_2)+(1-p_1)p_2]. \quad (38)\]

Straightforward algebra yields

\[\frac{W(\Delta t) - W(2\Delta t)}{W(\Delta t)} = 2 \cdot \frac{1 - (1 + q_2/p_2)p_1}{1 - 2p_1} \cdot \frac{S(\Delta t) - S(2\Delta t)}{S(\Delta t)}. \quad (39)\]

Thus the proportionality of the normalised W- and S-derivative is equivalent to the relation \(q_2/p_2 = 1\). This relation is, however, strongly violated at longer time-scales. The physical origin of this violation is straightforward. Due to the attraction of the x-particles the y-cloud will slowly shift to the right, i.e. one expects \(\frac{1}{2} > y(\Delta t) > 0\). This implies that x-particles at \(-\frac{1}{2}\) will have a stronger tendency to jump to the right than x-particles at \(\frac{1}{2}\) to jump to the left. Formally this can be expressed as \(q_2 > p_1 > p_2\). Thus on scales for which the y-cloud starts to move to the right the proportionality between \(\dot{W}(t)/W(t)\) and \(\dot{S}(t)/S(t)\) breaks down.

Qualitatively, this means that \(W(t)\) decays more slowly than expected because those particles which have performed a backward jump (after the initial jump) have a very strong tendency to perform afterwards a forward jump. Note that for this general analysis no relation to specific properties of the present model was necessary.

We can explicitly check that CMR-Ib is indeed violated for longer times when taking the analytical solution. If CMR-Ia and CMR-Ib and thus CMR-I were valid the ratio \(\dot{W}(t)/(W(t)\dot{g}(t))\) should be constant for all times. Here we get

\[\frac{(N + 1)\dot{W}(t)}{N^2 W(t)\dot{g}(t)} = \frac{(N + 1) \exp(-C \Gamma t(1 - 1/N))}{1 + N \exp(-C \Gamma t))} = D(t). \quad (40)\]

Whereas \(D(t)\) is 1 for short times it approaches 0 for long times. Thus in agreement with our general arguments \(W(t)\) decays slower than expected by CMR-Ia and CMR-Ib. More insight is gained by rewriting \(D(t)\) after a Taylor-expansion of \(\ln D(t)\) in \(1/N\) as

\[\ln D(t) = \frac{1}{N} (1 + C \Gamma t - \exp(C \Gamma t)) \approx -\frac{C^2 \Gamma^2 t^2}{2N}. \quad (41)\]

This approximation is valid for \(\exp(C \Gamma t)/N \ll 1\). Thus the time-dependence of this term becomes relevant for \(C^2 \Gamma^2 t^2/N = O(1)\). On this time-scale \(\tau\) one has \(W(\tau) = (1+N \exp(-\sqrt{N})/(1+N)\) which for large \(N\) is already close to \(W(t \to \infty)\). In agreement with our general discussion the deviations occur if \(g(t)\) starts to decrease. At the crossover time \(\tau\) one has \(g(\tau) \approx 1-1/\sqrt{N}\).

For a direct visualisation of this effect we calculate \(W_{CMR}(t)\). From CMR-Ia and CMR-Ib together with Eq.25 one obtains after appropriate normalization

\[W_{CMR}(t) = \exp[N(\exp(-C \Gamma t/N) - 1)]\]

\[\text{(42)}\]
$W(t)$ and $W_{CMR}(t)$ are compared in Fig.3. Since for $t < \tau$ the time-dependence of $W_{CMR}(t)$ is close to the true solution (for large $N$) the function $W_{CMR}(t)$ reproduces the time-dependence of $W(t)$ up to the final plateau. This can be explicitly seen in Fig.3. Note that the plateau value of $W_{CMR}(t)$ is $\exp(-N)$ which is much smaller than the limiting value of $W(t \to \infty) = 1/(1+N)$. The weak deviations of $W(t)$ and $W_{CMR}(t)$ at short times result from a term proportional to $1/N^2$ which has been neglected in the Taylor expansion.

6 Comparison with numerical simulations

In this section we perform a detailed comparison of the different rate equations of the CMR-approach, involving the functions $W(t)$ and $g(t)$, with the outcome for our model system. From the previous discussion we already know that CMR-Ia and CMR-II hold without disorder whereas CMR-Ib is violated for long times. From our general discussion we anticipate that in case of additional disorder also CMR-Ia should be violated. Since no exact solution is available with disorder we have performed kinetic Monte-Carlo simulations of the hopping dynamics using the Metropolis criterion. To check our analytical solution we have performed simulations without and with disorder. We have chosen $N = 64$ and $C = 1.23$ for most simulations.

The functions $w(t)$ and $w_y(t)$ can be easily extracted from the simulated dynamics. For the calculation of $g(t)$ we used a slightly modified simulation strategy. If during the simulation the (randomly selected) x-particle has jumped to the right this particle was excluded from further jumps for a fixed time interval. During this time interval the relaxation of the other particles were taken for the determination of $g(t)$. After this time interval this particle is again allowed to perform hopping processes and another particle is selected as the x-particle and so on. Averaging over a sufficient number of iterations one obtains $g(t)$. During these runs we also calculated $\langle \Delta x(t) \rangle_F$ and $\langle \Delta y(t) \rangle_F$. For $\langle \Delta y(t) \rangle_F$ we simply determined the dynamics of the y-cloud at time $t$ after the jump of the selected x-particle. For the determination of $\langle \Delta x(t) \rangle_F$ we calculated the probability that the x-particle would jump at time $t$ either to the right or to the left. This directly yields $\langle \Delta x(t) \rangle_F$, i.e. the average variation of the position of the x-particle at time $t$ under the condition that it was fixed after its initial jump at $t = 0$. It is evident that the determination of $g(t)$ as a multi-particle quantity is more time-consuming than that of $W(t)$ as a single-particle quantity.

For a direct comparison of the CMR-equations with simulated data it turns out to be helpful to integrate the CMR-equations. CMR-I and CMR-II yield

$$-\ln W(t) = \lambda_I(1 - g(t))$$

and

$$-\ln g(t) = \lambda_{II}\langle r_y^2(t) \rangle,$$
respectively, with proportionality constants $\lambda_i$. Comparison of CMR-II with Eq.32 indicates that $\langle r_y^2(t) \rangle$ would be a more appropriate choice for a quantitative comparison. In any event, due to the similarity of $\langle r_y^2(t) \rangle$ and $\langle r^2(t) \rangle$ for typical experiments on ion conductors this modification does not hamper the applicability of the CMR-approach [24, 25].

In Fig.4 we analyse the validity of CMR-I for the harmonic model without disorder. The numerically determined functions $W(t)$ and $g(t)$ agree very well with the respective analytical predictions. As already discussed in Section 4 one expects deviations for long times. For shorter times, however, $\ln W(t)$ and $1 - g(t)$ are proportional to each other. Combination of Eq.30 and Eq.36 shows that $\lambda_1 = N$ in agreement with the simulated data.

The test of CMR-II can be seen in Fig.5. Here a perfect agreement can be found for the full time regime. This was expected from Eq.32. The predicted proportionality constant $\lambda_2 = C$ is also recovered.

Simulations with disorder ($V_{\text{max}} = 2.0$) can be found in Figs.6 and 7. One can see that CMR-I again displays significant deviations (Fig.6). CMR-II is fulfilled very well (Fig.7). Here the proportionality constant $\lambda_{II}$ is close to the value of $C$. The agreement for CMR-II does not come as a surprise since we were able (see above) to derive CMR-II via linear response theory. Further insight about the effect of disorder can be obtained from analysis of Eq.30 using again the original parameters $C = 1.23$ and $V_{\text{max}} = 2.0$. With disorder the center of mass of the x-particle together with the y-cloud displays non-diffusive dynamics, i.e. $f_{do}(t) < 0$. This is explicitly shown in Fig.8 where we display $\langle \Delta x(t) \rangle_F$, $N\langle \Delta y(t) \rangle_F$ and $f_{do}(t)$. As anticipated, the function $f_{do}(t)$ is negative. Already for $t = 10$ the function $N\langle \Delta y(t) \rangle_F$ and thus $-(N/2)\dot{g}(t)$ is much smaller than $-f_{do}(t)$. With Eq.34 this implies that already for $t > 10$ the dispersion of the x-particle as characterized by $\langle \Delta x(t) \rangle_F$ is mainly determined by disorder rather than the mismatch effect due to the y-cloud.

### 7 Discussion and Summary

We have presented a simple harmonic mean-field model which contains single-particle as well as multi-particle relaxation modes. The main goal was to check whether the CMR equations which are based on the interplay between these two relaxation modes can be derived for this model. First, CMR-II could be derived in linear response theory after substituting $w_y(t)$ by $w(t)$. Given the experimental similarity of $w_y(t)$ and $w(t)$ this step may be justified. Second, CMR-Ia is valid without disorder. In contrast, with disorder an additional term enters CMR-Ia which accounts for the dispersive behavior related to disorder. Third, CMR-Ib is only valid for short times. The physical reason for the discrepancy at long times could be identified as the relaxation of the y-cloud after the initial jump of the x-particle. Indeed, this problem is inevitable if one wants to formulate a theory involving a quantity like $g(t)$ where a particle is kept fixed and one deals with the time-dependence of the fraction of successful particles. In
general it is not possible to relate the behavior of the successful particles to the mean square displacement since the latter quantity also involves the behavior of those particles which became unsuccessful at earlier times and may show a complex time-dependence afterwards. Formally, this means that there is no strict way to relate the \( \langle \cdot \rangle_0 \)-ensemble (where \( W(t) \) is defined) to the \( \langle \cdot \rangle_S \)-ensemble (where \( S(t) \) and \( g(t) \) are defined). Due to the generality of our arguments the same problem would hold if one considers dynamics in three rather than one dimension.

Maybe the most dramatic simplification of the model is the fact that one particle interacts with all other particles in an identical way. In reality the interaction strength depends (on average) on the distance between two particles. To get a first impression of this distance dependence one may introduce a step function for the interaction strength in our model such that a particle is only interacting with a fraction of the other particles. In the extreme limit this would coincide with the Rouse model of polymer physics where each monomer only interacts with the two adjacent monomers \[26, 27\]. For such a model one may define the y-cloud such that it is composed of those particles which directly interact with the (again randomly chosen) x-particle (in the case of the polymer the two nearest neighbors) and the z-cloud by the particles which do not interact with the x-particles. Here we use the simplified picture for which we forget that the cloud is composed of individual particles. As shown in Section 4, this simplification was possible for the mean-field case. Since we are only interested in a qualitative discussion of this model extension we apply this simplification also to the present non-mean field case. Then our problem boils down to a 3-particle problem with the Hamiltonian

\[
H = k_{xy}(x - y)^2 + k_{yz}(y - z)^2. \tag{45}
\]

Qualitatively, adding the effect of far away particles as expressed by the presence of the z-cloud, one expects that at short times the decay of \( g(t) \) is unmodified because the only driving force comes from the shifted x-particle. In contrast, at longer times the decay becomes slower because the z-cloud tries to keep back the y-cloud. Somewhat related arguments have been used to rationalize the additional \( h(t) \)-term in CMR-II\textsubscript{new} as compared to CMR-II \[20\]. For the above Hamiltonian we can directly formulate the rate equations in analogy to Section 5.

To be more specific we consider the rate equations for this Hamiltonian (without disorder), evaluated in the \( \langle \cdot \rangle_S \)-ensemble, to determine the effect of a fixed (or, analogously, successful) x-particle

\[
\langle \dot{y}(t) \rangle_S = \beta w_y(t)[k_{xy}(x - \langle y(t) \rangle_S) + k_{yz}(\langle z(t) \rangle_S - \langle y(t) \rangle_S)] \tag{46}
\]

\[
\langle \dot{z}(t) \rangle_S = \beta w_z(t)[k_{yz}(\langle z(t) \rangle_S - \langle y(t) \rangle_S)] \tag{47}
\]

For the simple case \( w_y(t) = w_z(t) = \Gamma/N \) this relation can be directly solved. Here we are particularly interested in the modification of CMR-II. In analogy to CMR-II\textsubscript{new} we use the ansatz \( g(t) = \beta k_{xy}w_y(t)g(t)^{K(t)} \) (CMR-II corresponds to \( K(t) = 1 \)). The function \( K(t) \) can be directly extracted from the numerical solution of Eqs.\[46\] and \[47\]. Here we chose \( k_{xy} = k_{yz} \).
and \( w_y(t) = w_z(t) = \Gamma/N \). Furthermore we determined \( W(t) \) by formulating an analogous equation for the x-particle and solving the resulting three rate equations in the \( \langle \cdot \rangle_0 \)-ensemble (in analogy to the procedure in Section 4). Here we chose \( w_x(t) = \Gamma \). In Fig. 9 we plot the solutions for \( K(t) \) and \( W(t) \) against each other for \( N = 64 \). One can see that \( K(t) \) decays from 2 to 1 where the decay is mainly in the region where \( W(t) \) is close to its final value. Thus for a broad range of times CMR-II\textsubscript{new} with \( K \approx 2 \) is the appropriate rate equation. Interestingly, \( K = 2 \) is a typical value used for the description of experimental conductivity spectra \[20\]. For different ratios \( k_{xy}/k_{yz} \) slightly different \( K(t) \)-dependencies result.

We just mention that a further useful modification is the substitution of the harmonic potential \( k(y_i - y_j)^2 \) by the periodic potential \( 2(1 - \cos(\sqrt{k}(y_i - y_j))) \). In this potential it is possible to include the physical effect that an ion may escape its local ionic cage. Actually, this Hamiltonian has been extensively analysed in a very different context \[28, 29\].

Although we have discussed only a simple Hamiltonian, the arguments, concerning the range of applicability of the CMR-equations, were quite general. Thus one would expect that also for different model systems or even for realistic ion conductors similar arguments might hold.

It may be possible that an appropriate redefinition of the successful ensemble (retaining CMR-II) and thus of the physical interpretation of the function \( g(t) \) may cope with CMR-I. Such a redefinition can be found in very recent work \[30\] although the theoretical implications of such a redefinition concerning, e.g., the validity of CMR-II still have to be worked out. In any event, if such a redefinition is possible one may hope that the very good predictions of the CMR-approach would remain. This speculation is backed by the observation that CMR-I and CMR-II together, expressed via \( W(t) \), agree very well with experimental data and CMR-II has found a strictly theoretical justification in our model. Furthermore it is conceivable that the disorder term \( f_{do}(t) \) may have specific properties which render CMR-I valid for some situations with additional disorder.

Due to the relevance of the CMR-approach in the field of solid ion conductors it is essential to illuminate its applicability from a strictly theoretical point of view. The present work may be regarded as a step in this direction and may hopefully serve as an input for a future development of the CMR-approach, related, e.g., to the interpretation of \( K = 2 \) in the modified CMR-II relation.

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Fig. 1  Sketch of the system of (N+1) ions. The parabola indicates the range of interaction.

Fig. 2  Sketch of the definition of the S-ensemble as the black bars after a jump from -1/2 to 1/2 at t=0. The key idea is that the fraction of particles which effectively jump to the left leave the S-ensemble.

Fig. 3  Numerical representation of $W(t)$ and $W_{CMR}(t)$ together with the numerically determined function $W(t)$.

Fig. 4  $1 - g(t)$ vs. $-\ln W(t)$ for $N = 64$ and $C = 1.23$.

Fig. 5  $-\ln g(t)$ vs. $\langle r_y^2(t) \rangle$ for $N = 64$ and $C = 1.23$.

Fig. 6  $1 - g(t)$ vs. $-\ln W(t)$ for $N = 64$, $C = 1.23$, and $V_{max} = 2.0$. Scaling works best for $a = 2900$.

Fig. 7  $-\ln g(t)$ vs. $\langle r_y^2(t) \rangle$ for $N = 64$, $C = 1.23$, and $V_{max} = 2.0$.

Fig. 8  $\langle \Delta x \rangle_S$, $N\langle \Delta y \rangle_S$, and $f_{do}(t)$ for $N = 64$, $C = 0.07$, and $V_{max} = 2.0$.

Fig. 9  $K(t)$ vs. $W(t)$ for the 3-particle system with $N = 64$ and $k_{xy} = k_{yz}$.
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Fig. 2, J. Chem. Phys., M. Kunow et al.
Fig. 3, J. Chem. Phys., M. Kunow et al.
\[ \text{Fig. 4, J. Chem. Phys., M. Kunow et al.} \]
Fig. 5, J. Chem. Phys., M. Kunow et al.
Fig. 6, J. Chem. Phys., M. Kunow et al.
Fig. 7, J. Chem. Phys., M. Kunow et al.
Fig. 8, J. Chem. Phys., M. Kunow et al.
Fig. 9, J. Chem. Phys., M. Kunow et al.