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Correlation functions of particles hopping on a chain and the dramatic influence of nonergodicity

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One-particle and two-particle correlation functions have been computed of particles hopping on a chain by using simulation techniques. No indications for the long-time behavior $\propto t^{-1/4}$ have been found. Moreover, the two-particle correlation function does not decay to zero, owing to the nonergodicity of the hopping model with excluded volume. In a magnetic-resonance experiment this would appear as a nonzero averaged dipolar interaction, if the most important magnetic interaction would be the dipole-dipole coupling between the hopping particles. The magnetic-resonance spectrum of such a system strongly resembles that of a one-dimensional rigid-lattice spectrum.

I. INTRODUCTION

One-dimensional (1D) dynamics are of much current interest.[1] The occurrence of slow long-time tails seems to be a feature of almost any 1D model. A hydrodynamic argument gives a $t^{-1/2}$ behavior for a local correlation obeying a 1D diffusion equation. Even in 1D disordered or random systems the $t^{-1/2}$ decay manifests itself.[2,3] Richards showed that in the dynamics of particles on a chain correlation functions are involved which, due to excluded-volume effects, decay even slower than $t^{-1/2}$.[4] Computer simulations demonstrated that the mean-square displacement is $\propto t^{1/2}$, rather than $\propto t$, indicating that no self-diffusion coefficient can be defined for this model. This property of the mean-square displacement was proven subsequently by describing the local concentration fluctuation in the neighborhood of a particle in terms of the deviation of the location of this particle from a configuration of regular spaced particles.[5] This proof depends in a crucial way on the fact that the particles cannot pass each other in the 1D hopping problem. In other words it leans on the nonergodicity of the model. The absence of a self-diffusion coefficient is a well-known property of low-dimensional liquids.[6]

Fedders calculated a two-particle correlation of the 1D hopping model.[7] In the frequency domain he found a low-frequency behavior $\propto \omega^{-3/4}$, pointing to a $t^{-1/4}$ tail. The same long-time behavior was suggested by Richards for a one-particle corrrelation function.[4] We have sampled in a computer simulation of this model one- and two-particle correlation functions. No evidence for a $t^{-1/4}$ behavior was found. We will present our results in the next section. We will also discuss the consequences of our results for the magnetic resonance properties of the 1D hopping model.

II. CORRELATION FUNCTIONS

We will start with the two-particle correlation functions, because they show the most spectacular effects. The two-particle correlation function we will discuss is $C(t)$,

$$C(t)=N^{-1}\sum_{i\neq j}\sum_{\alpha,\beta}\langle p_\alpha^i(0)p_{\alpha+1}^j(0)p_\beta^i(t)p_{\beta+1}^j(t)\rangle \quad , \quad (1)$$

in which the stochastic operator p_α^i is defined to vanish unless particle i occupies site α, in which case the operator equals unity. N is the number of particles and M the number of sites. The occupation density or simply the density $\rho=N/M$. $C(t)$ measures the probability that two particles occupy neighboring sites at time t given they were neighbors at time 0. It is straightforward to show that $C(0)=\rho$. To calculate the $t=\infty$ limit of a correlation function one generally assumes that no correlations are left, and that decoupling is appropriate. Adopting this decoupling procedure, and using $\langle p_\alpha^i p_{\alpha+1}^j\rangle = 1/M^2$, one finds that $C(t\rightarrow\infty)=N/M^2$, which can be neglected in the thermodynamic limit. Our computer simulations, however, indicate that $C(t\rightarrow\infty)=\rho^2$, which certainly cannot be neglected. The discrepancy between the two results can be understood readily. The particles cannot pass each other, so the sequence of the particles is a constant of the motion. In decoupling the correlation function and averaging the two parts individually, one averages over all possible orders of the particles, which is incorrect. This difficulty becomes very clear if we label the particles in such a way that particle i is situated in between particle $i-1$ and $i+1$. In this notation $C(t)$ can be written as

$$C(t)=N^{-1}\sum_{i}\sum_{\alpha,\beta}\langle p_\alpha^i(0)p_{\alpha+1}^{i+1}(0)p_\beta^i(t)p_{\beta+1}^{i+1}(t)\rangle \quad . \quad (2)$$

Decoupling at infinite time is permitted now, because in doing so we do not alter the sequence of the particles any longer. The order of the particle remains constant, and is determined by the initial conditions. Using $\langle p_\alpha^i p_{\alpha+1}^{i+1} \rangle = N/M^2$, we find $C(t \to \infty) = \rho^2$, in agreement with the simulations. If we would like to characterize the long-time dependence of $C(t)$, we would have to subtract the infinite time limit ρ^2.

An interesting one-particle correlation is $A(t)$,

$$A(t) = N^{-1} \sum_{i,\alpha} \langle p_\alpha^i(0) p_\alpha^i(t) \rangle \ . \tag{3}$$

According to Richards $A(t \to \infty) \propto t^{-1/4}$. This dependence was inferred from the $t^{1/2}$ behavior of the mean-square displacement and the Gaussian probability distribution function for the probability that a particle has traveled a certain distance.[4]

We have analyzed $A(t)$ and $C(t) - \rho^2$ with the help of simulation experiments. The results for both correlations have been fitted to

$$E(\Gamma t)^{-\gamma} \ , \tag{4}$$

Γ being the hopping rate. We hasten to add that the simulations can never prove expression (4). However, if one assumes expression (4) to be valid, simulations can give reliable estimates for both γ and E. In Table I we have presented the results for three densities: $\rho = \frac{1}{2}, \frac{1}{5}$, and $\frac{1}{8}$. The number of sites used in the calculations was 2500 and the results presented in the table are the average of 1000 different initial conditions. The longest times in the experiment were $70/\Gamma$. We have also monitored different densities than those displayed in Table I, but the results of those simulations did not differ in an essential way from the results of Table I. It is clear that none of the correlations show a $t^{-1/4}$ dependence. One could argue that one should sample correlation functions at still longer times to find their asymptotic time dependence. However, in the first place the normalized density correlation function $d(t)$, defined by

$$d(t) = \left[\sum_{\alpha,\beta} \langle p_\alpha^i(0) p_\beta^i(t) \rangle - \rho^2 \right] (\rho - \rho^2)^{-1} \ ,$$

already displayed its $t^{-1/2}$ dependence very clearly on the time scale of the experiment, and in the second place the asymptotic time dependence would only be of academic interest if one should extend the time scale dramatically. Since in any physical experiment short-time corrections would be very important. In Fig. 1 the single-particle correlation function $A(t)$ and the two-particle correlation function $C(t)$ are shown for a half-occupied chain ($\rho = \frac{1}{2}$). To compare these 1D particle correlation functions with a 1D site correlation function in Fig. 1 the density correlation function $d(t)$ is also displayed. The rather fast decay of $C(t)$ to its infinite-time limit ρ^2 is clear. To illustrate the inherent "slow" character of all 1D correlation functions the density correlation function of a 3D (cubic) hopping model is included in Fig. 1.

TABLE I. Long-time dependence of correlation functions.

Correlation function	ρ	E	γ
$A(t)$	$\frac{1}{8}$	0.30 ± 0.02	0.39 ± 0.01
$A(t)$	$\frac{1}{5}$	0.34 ± 0.02	0.36 ± 0.01
$A(t)$	$\frac{1}{2}$	0.55 ± 0.02	0.33 ± 0.01
$C(t) - \rho^2$	$\frac{1}{8}$	0.04 ± 0.02	0.66 ± 0.09
$C(t) - \rho^2$	$\frac{1}{5}$	0.10 ± 0.03	0.82 ± 0.07
$C(t) - \rho^2$	$\frac{1}{2}$	0.12 ± 0.02	0.87 ± 0.05

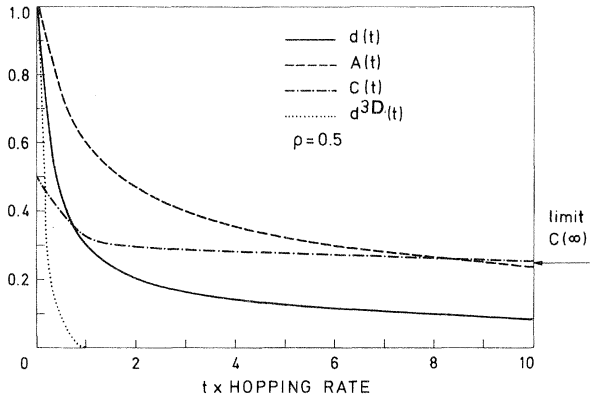

FIG. 1. Particle and site correlation functions for a 1D hopping model. $d^{3D}(t)$ represents the density correlation function for a three-dimensional hopping model. See Eqs. (2) and (3) for the definition of the 1D correlation functions.

III. MAGNETIC RESONANCE

If the hopping particles would possess a magnetic moment, magnetic-resonance experiments could probe the correlation functions we discussed in the previous section. In a resonance experiment the total Hamiltonian can be partitioned according to

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{lattice}} \ , \tag{5}$$

in which $\mathcal{H}_Z$ is the Zeeman Hamiltonian, $\mathcal{H}_{\text{lattice}}$ represents the hopping model, and $\mathcal{H}_{\text{int}}$ stands for the

interaction between lattice and subsystem. The standard procedure to treat Hamiltonian (5) is the weak-coupling approximation (WCA).[8] An interesting aspect of 1D motion, however, is the breakdown of the WCA in describing line shapes and relaxation times. The slow long-time dependence of correlation functions in 1D induces divergencies in the WCA. Line-shape analysis of magnetic resonance experiments in 1D paramagnets has given ample evidence for the failure of the WCA.[9,10] The spin-lattice relaxation time still can be interpreted within the weak-coupling scheme, but should display a characteristic dependence on the Larmor frequency ω_L connected with the long-time behavior of the local correlation function.

If $\mathcal{H}_{\rm int}$ is a site-particle interaction the relevant correlation function for magnetic resonance will be $A(t)$. The long-time tail of $A(t)$ excludes the WCA as a possible description for the magnetic resonance experiments, and more sophisticated approaches, like mode-mode coupling, should be chosen.

If $\mathcal{H}_{\rm int}$ would be a particle-particle interaction, viz., the dipole-dipole interaction, the relevant correlation function for magnetic resonance would be $C(t)$. The nonvanishing of $C(t)$ for long times introduces an interesting complication to the problem. Rather than having to study a slow decay of the local correlation of the resonance problem, $C(t)$, we are faced with a local correlation decaying to a constant value. The philosophy of the WCA, and essentially of any form of time-dependent perturbation theory, is that the interaction term should represent the fluctuating part. A constant term in $\mathcal{H}_{\rm int}$ should be transferred to the subsystem Hamiltonian. An expansion in the new interaction Hamiltonian will be free from divergencies due to persistent correlations. Divergencies due to slow decay should be renormalized, but that is no principal problem. The new subsystem Hamiltonian reads, restricting the dipolar interaction to nearest neighbors only,

$$\mathcal{H}_{\rm sub}=\mathcal{H}_z+\left\langle \rho \sum_i \mathcal{H}_{\rm dip}^{i,i+1} \right\rangle , \tag{6}$$

where $\mathcal{H}_{\rm dip}^{ij}$ represents the dipolar interaction between particles i and j. The new partitioning of $\mathcal{H}$ can be interpreted as having subtracted from the dipolar interaction the part proportional to $\langle r_{ij}^{-3}\rangle$, and having added this invariant part to the Zeeman interaction. The invariant part $\langle r_{ij}^{-3}\rangle$ vanishes in the higher-dimensional lattices. The new partitioning of the Hamiltonian seems to reflect all the standard properties of a standard motional-narrowing Hamiltonian. This is deceptive, because our subsystem Hamiltonian has been modified into an *interacting* many-body system. That is to say without any coupling at all to the lattice the magnetic resonance spectrum would already have finite linewidths of the order of $\rho\omega_D$, ω_D being a typical dipolar frequency. Whatever the influence of the remaining interactions will be, $\rho\omega_D$ sets a lower limit to the linewidth. All the other interactions, the broadening mode ($\mathcal{H}_{\rm int}$), and the narrowing mode ($\mathcal{H}_{\rm lattice}$) can be neglected if they give contributions much smaller than $\rho\omega_{\rm D}$. Estimates of the additional "narrowed contributions" show that they are at least an order of magnitude smaller than the intrinsic dipolar broadening. For instance, assuming a $t^{-\gamma}$ decay for $C(t)-\rho^2$, using a hopping rate of 10^8 Hz and a dipolar broadening of 10^4 Hz, we find the narrowed contributions to be smaller than $\rho\omega_D$ by a factor of 10 when $\rho=0.1$, and by a factor of 20 when $\rho=0.5$. So one will hardly ever encounter a situation where the narrowing motion is the dominating factor determining the linewidth.

The many-body character of the subsystem Hamiltonian will influence the spin-lattice relaxation. The contribution of the interaction term is essential because it is needed for the exchange of energy with the lattice. The condition for the observation of relaxation times $\propto \omega_L^{1-\gamma}$ is $\rho\omega_D \ll \omega_L \ll \Gamma$. The condition $\omega_L \ll \Gamma$ originates from the fact that only the long-time behavior of the correlation functions is $\propto t^{-\gamma}$, and short-time contributions would spoil the scaling behavior with frequency of the relaxation times. The condition $\rho\omega_D \ll \omega_L$ expresses the fact that the magnetization should be damped by the interaction term, and not in the many-body subsystem itself. For realistic values of hopping rates and dipolar interaction these conditions do not leave much space in the frequency domain to observe the characteristic frequency behavior of the relaxation rates.

Our analysis is in disagreement with Fedders' calculation of the relaxation rates. Fedders apparently did not encounter the fact that $C(t\rightarrow\infty)$ is finite.[7] Fedders' calculation is of the mode-coupling form. Reiter has pointed out that mode-coupling theories can be qualitatively incorrect if a correlation does not decay to zero due to coupling to a conserved variable.[11] More specific in this case, Fedders calculated the moments of the correlation function to leading order in ρ. We will give a simple example to show that such an approach will never give the constant value at infinite time if this constant is of lower order in ρ than the value of the correlation function at $t=0$. For instance, summing moments of the function $(1-\rho)e^{-\alpha\rho|t|}+\rho$ to leading order in ρ will result in the function $e^{-\alpha\rho|t|}$. In this way one has lost all information about the infinite-time limit.

IV. SUMMARY

We have shown that the magnetic resonance of particles hopping on a chain with excluded volume hardly exhibits any features of motional narrowing if the relaxation is mediated by the dipolar interaction

between the hopping particles. This is due to the nonergodicity of the model. The average distance between two particles remains finite in this model. This is reflected in the fact that the two-particle correlation function $C(t)$, defined in Eq. (1), does not decay to zero, but tends to ρ^2 for long times. The single-particle correlation $A(t)$, defined in Eq. (3), is shown to decay with an exponent of about -0.36, which is faster than the previous estimate of -0.25.[4] The results of our computer simulations for $C(t)-\rho^2$ point to exponents in the neighborhood of -0.85, which is even faster than the decay of the density correlation function.

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