Two-point correlation functions for a distinguishable particle hopping on a uniform one-dimensional chain*

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We derive the two-point corrrelation function for a distinguishable-particle hopping on a one-dimensional linear chain with all sites equivalent. The solution is obtained from a multiple-scattering equation derived from first principles. The results are similar to results obtained from computer experiments and phenomenological arguments.

I. INTRODUCTION

There has been considerable interest lately in the dynamical properties of particles hopping from site to nearest-neighbor site on a linear chain where no two particles can occupy the same site.[1-3] Recently, Richards[2] has shown by computer experiments and phenomenological arguments that the one dimensional two-point correlation function for a distinguishable particle is drastically different than the occupancy (or site) correlation function and than the same correlation function in higher-dimensional systems. In this paper we consider only the simplest version of this one-dimensional problem, the case where all sites on the chain are equivalent. However, we obtain an analytic solution to the problem from equations that are derived from first principles. Crudely speaking, our approximation corresponds to a calculation of the scattering of the distinguishable particle off of a single other particle (or vacancy) via the entire Born series. The other particles or vacancies are taken into account by using the self-consistently obtained distinguishable particle propagator in the Born series. Thus we include the scattering of the distinguishable particle off of many different particles or vacancies, but do not account for the correlations between the other particles or vacancies among themselves.

We recently developed a formalism for calculating all moments of hopping correlation functions and methods for summing infinite classes of these moments to obtain the correlation functions themselves.[4,5] (References 4 and 5 will hereafter be referred to as I.) The methods and notation used in this paper will follow these previous papers quite closely and in the rest of this section we review some of those results that are relevant to the present problem as well as some of the special difficulties encountered in one-dimensional problems. Section II contains the derivation of a scattering equation which uses the mean field distinguishable-particle correlation function internally. This type of equation would be exact in three-dimensional problems when the number of particles in the lattice approaches the number of sites on the lattice. In Sec. III we show how to treat the internal distinguishable propagator self-consistently in order to obtain good results. These results are then discussed and compared with Richard's work.

Following I, we let n_α denote the occupancy of the site α and thus $n_\alpha = 1$ if the site α is occupied and $n_\alpha = 0$ if the site α is vacant. Further, we let p_α denote the occupancy of the site α by a specific (distinguishable) particle and thus $p_\alpha = 1$ if the specific particle is at the site α and $p_\alpha = 0$ otherwise. Further, instead of n_α and p_α, it is more convenient to use variables whose average values are zero and that are orthonormal. These variables are

$$\xi_\alpha = (n_\alpha - c)/a, \quad a = [c(1-c)]^{1/2}, \qquad \rho_\alpha = (N/c)^{1/2} p_\alpha , \tag{1}$$

where N is the number of sites on the chain and c is the concentration of particles on the chain. The two-point correlation functions associated with these variables are

$$D(\alpha, \beta; t) = \langle \xi_\alpha(t)\, \xi_\beta(0) \rangle \theta(t) , \qquad \overline{D}(\alpha, \beta; t) = \langle \rho_\alpha(t) \rho_\beta(0) \rangle \theta(t) , \tag{2}$$

where θ is the step function and $\langle x \rangle$ denotes the ensemble average of $\langle x \rangle$. It is also convenient to introduce a self-energy or memory function $\overline{K}$ defined by the equation

$$i \frac{d}{dt} \overline{D}(\alpha, \beta; t) + i \int_0^\infty d\bar{t} \sum_\gamma \overline{K}(\alpha, \gamma; \bar{t}) \times \overline{D}(\gamma, \beta; t - \bar{t}) = i \delta_{\alpha,\beta} \delta(t) . \tag{3}$$

Finally, $\overline{D}$ and $\overline{K}$ can formally be expanded in terms of their moments as

$$\bar{K}(\alpha,\beta;t)=\bar{L}_1(\alpha,\beta)\delta(t) - \sum_{n=0}^{\infty}\bar{L}_{n+2}(\alpha,\beta)\frac{(-t)^n}{n!}\theta(t)\,, \tag{4a}$$

$$\bar{D}(\alpha,\beta;t)=\sum_{n=0}^{\infty}\bar{M}_n(\alpha,\beta)\frac{(-t)^n}{n!}\theta(t)\,. \tag{4b}$$

All moment expansions for correlation functions will be defined like Eq. (4b) and all moment expansions for self-energies will be defined like Eq. (4a). In the frequency domain these equations read

$$\bar{K}(\alpha,\beta;\omega)=\sum_{n=0}^{\infty}\left(\frac{-i}{\omega}\right)^n\bar{L}_{n+1}(\alpha,\beta)\,, \tag{4a'}$$

$$\bar{D}(\alpha,\beta;\omega)=-\sum_{n=0}^{\infty}\left(\frac{-i}{\omega}\right)^{n+1}\bar{M}_n(\alpha,\beta)\,. \tag{4b'}$$

The fundamental assumption made in I is that at thermal equilibrium, the occupancy of one site does not effect the average occupancy of other sites. That is, $\langle n_\alpha n_\beta\rangle=\langle n_\alpha\rangle\langle n_\beta\rangle$ or $\langle p_\alpha n_\beta\rangle=\langle p_\alpha\rangle\langle n_\beta\rangle$ if $\alpha\neq\beta$, and thus the static correlations (but not the dynamical correlations) are trivial. In a sense that is a high-temperature approximation in that we assume that the interaction energies in the problem are small compared to kT. In this respect our hopping problem resembles the dynamical high-temperature spin problem[6] where an exchange energy J (analogous to our Ω's and V's) is responsible for the dynamical spin behavior but if $(J/kT)\ll 1$, the exchange does not effect the thermodynamics. To complete the analogy one should include a magnetic field H_α that depends on the spin site. Further, it is not necessary that μH_α be small compared to kT where μ is the magnetic moment of the spin. Our problem is also analogous to doing kinetic theory for a perfect gas. In this case the collisions determine the transport properties but do not contribute to the thermodynamics.

In I we showed how to generate diagrammatic expansions for all of the moments of the self-energy. We repeat the rules and diagrams here for the case when $\Gamma_{\alpha\beta}$ (the hopping rate from site α to site β) equals $\Gamma_{\beta\alpha}$ (the hopping rate from site β to site α). Further, we use the definitions

$$\begin{aligned}
&\omega_{\alpha\beta}=(\delta_{\alpha\beta}\Sigma_\gamma\Gamma_{\alpha\gamma})-\Gamma_{\alpha\beta},\\
&\bar{\omega}_{\alpha\beta}=(1-c)\omega_{\alpha\beta}\,,\\
&\bar{\Omega}_{\alpha\beta\gamma}=a\Gamma_{\beta\gamma}(\delta_{\alpha\gamma}-\delta_{\alpha\beta})\,,\\
&\bar{V}_{\alpha\beta\bar{\alpha}\bar{\beta}}=-\Gamma_{\alpha\beta}[2(1-c)\delta_{\alpha\bar{\alpha}}\delta_{\beta\bar{\beta}}+c\delta_{\alpha\bar{\beta}}\delta_{\beta\bar{\alpha}}]\,,\\
&V_{\alpha\beta\bar{\alpha}\bar{\beta}}=2\omega_{\alpha\beta}\delta_{\alpha\bar{\alpha}}\delta_{\beta\bar{\beta}}\,.
\end{aligned} \tag{5}$$

As shown in Fig. 1, we associate solid lines with the occupancy or site variables ξ_α and dashed lines with the distinguishable-particle variables

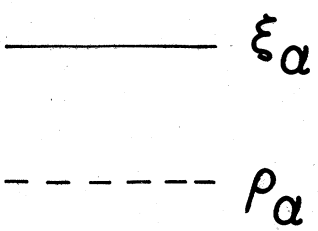

FIG. 1. Diagrammatic representations of the variables ρ_α and ξ_α.

ρ_α. Now consider the basic event diagrams displayed in Fig. 2 and the analytical expressions associated with them, where a single dot $(\cdot)$ is defined as one event. The rules for calculating $\bar{L}_n(\alpha,\beta)$ are as follows: (i) Form all distinct connected irreducible diagrams with n events that start on the left with a single dashed line labeled α and end on the right with a single dashed line labeled β. (ii) Label all internal lines with dummy site indices and associate the proper analytical expression with each diagram that is the product of the analytical expressions associated with each event. (iii) Sum over all internal dummy site indices with the restriction that no two sites at the same "time" (or horizontal position) can be equal.

If the restriction that no two sites at the same "time" can be equal is ignored, one can derive a hierarchy of self-consistent integral equations for the particle and occupancy correlation functions. Although formally the lifting of this restriction introduces relative errors of order one divided by the number of nearest neighbors, in practice the errors are much smaller that that. In fact using these techniques we have calculated particle-diffusion coefficients and correlation functions to better than 1% accuracy for the three-dimensional Bravais lattices.[5,7] Unfortunately, this procedure fails for one-dimensional hopping. The reason is that the lifting of the restriction is tantamount to allowing the particles on the chain to pass each other. Since the fact that the particles cannot pass each other is at the heart of the present

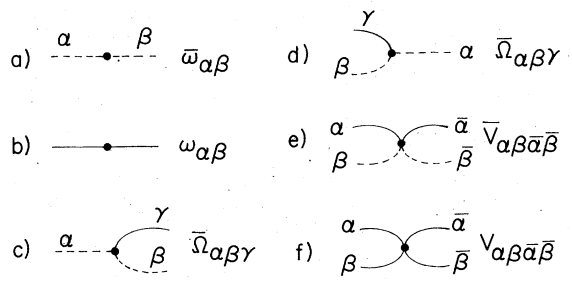

FIG. 2. Basic event diagrams and their corresponding analytical expressions.

problem, these procedures that are successful in three-dimensional problems cannot be used without alterations.

II. DERIVATION

Our procedure in this section will be to examine certain classes of moment diagrams for the $\bar{L}_n(\alpha,\beta)$ and then to devise integral equations that reproduce these classes of moment diagrams. There is only one moment diagram with one event, Fig. 2(a), so

$$\bar{L}_1(\alpha,\beta)=\bar{\omega}_{\alpha\beta}\ . \tag{6}$$

All higher-order ($n>1$) moment diagrams must start with the event in Fig. 2(c) and end with the event in Fig. 2(d). Thus, by the rules in Sec. I, we have

$$\bar{L}_n(\alpha,\bar{\alpha})=\Sigma_{\beta,\bar{\beta},\gamma,\bar{\gamma}}\,\bar{\Omega}_{\alpha\beta\gamma}G_{n-2}(\gamma,\beta;\bar{\gamma},\bar{\beta})\bar{\Omega}_{\bar{\alpha}\bar{\beta}\bar{\gamma}} \tag{7}$$

for $n\geq 2$. The rules for calculating $G_n(\alpha,\beta;\bar{\alpha},\bar{\beta})$ are the same as the rules listed in Sec. I for $\bar{L}_n$, except that the diagrams must start with a solid line labeled α and a dashed line labeled β and end with a solid line labeled $\bar{\alpha}$ and a dashed line labeled $\bar{\beta}$. In addition,

$$G_0(\alpha,\beta;\bar{\alpha},\bar{\beta})=\delta_{\alpha\bar{\alpha}}\delta_{\beta\bar{\beta}}(1-\delta_{\alpha\beta})\ . \tag{8}$$

In order to sum up the moments, it is convenient to Fourier transform in time. All time-dependent quantities $A(t)$ are transformed as

$$A(\omega)=\int_{-\infty}^{\infty}A(t)e^{i\omega t}\,dt\ . \tag{9}$$

Now $\bar{K}(\alpha,\bar{\alpha};\omega)$ can be written

$$\bar{K}(\alpha,\bar{\alpha};\omega)=\omega_{\alpha\bar{\alpha}}-\Sigma_{\beta,\gamma,\bar{\beta},\bar{\gamma}}\,\bar{\Omega}_{\alpha\beta\gamma}\times G(\gamma,\beta;\bar{\gamma},\bar{\beta};\omega)\bar{\Omega}_{\bar{\alpha}\bar{\beta}\bar{\gamma}}\ , \tag{10}$$

where $G(\gamma,\beta;\bar{\gamma},\bar{\beta};\omega)$ is the function whose nth moment is $G_n(\gamma,\beta;\bar{\gamma},\bar{\beta})$. Further, it is convenient to spatially Fourier transform all quantities depending on the difference between two sites $A(\alpha-\beta)$ as

$$A(q)=\Sigma_\alpha A(\alpha-\beta)e^{-iq(\alpha-\beta)}\ . \tag{11}$$

Functions like $G(\alpha,\beta;\bar{\alpha},\bar{\beta})$ that depend on only three independent varibles and can be Fourier transformed as

$$G(q',q'',q)=\Sigma_{\alpha,\beta,\bar{\alpha}}G(\alpha,\beta;\bar{\alpha},\bar{\beta})\times\exp\{-i[(\tfrac{1}{2}q+q')\alpha+(\tfrac{1}{2}q-q')\beta-(\tfrac{1}{2}q+q'')\bar{\alpha}-(\tfrac{1}{2}q-q'')\bar{\beta}]\}\ . \tag{12}$$

With these definitions, Eq. (10) can be written

$$\bar{K}(q,\omega)=2\bar{c}\Gamma_0(1-\cos q)\,[1-4c\Gamma_0G_{ss}(q,\omega)]\ , \tag{13}$$

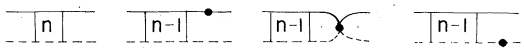

FIG. 3. Diagrammatic representation of Eq. (17) and (18).

where

$$\bar{c}=(1-c) \tag{14}$$

and

$$G_{ij}(q,\omega)=N^{-2}\Sigma_{q'q''}G(q',q'',q;\omega)\times\mathrm{trig}_i\,q'\,\mathrm{trig}_j\,q''\ . \tag{15}$$

In Eq. (15), i and j can be s and c where $\mathrm{trig}_s=\sin$ and $\mathrm{trig}_c=\cos$. In obtaining these equations we have assumed a linear chain with N atoms spaced one unit apart and periodic boundary conditions. Since we assume only nearest-neighbor hopping, we also have

$$\Gamma_{\alpha\beta}=\Gamma_0 f(\alpha),\quad f(\alpha)=\delta_{\alpha,1}+\delta_{\alpha,-1}, \tag{16}$$
$$\Gamma(q)=\Gamma_0 f(q)=2\Gamma_0(1-\cos q)\ .$$

Although it is not our final approximation, it is instructive to calculate $\bar{D}$ in the approximation where the contributions to $G_n(\alpha,\beta;\bar{\alpha},\bar{\beta})$ are restricted to diagrams that have no more than one solid line at the same "time" (horizontal position). It is easily seen that in this approximation

$$G_n(\alpha,\beta;\bar{\alpha},\bar{\beta})=\Sigma_{\beta'\gamma'}F(\alpha,\beta;\alpha',\beta')\times G_{n-1}(\alpha',\beta';\bar{\alpha},\bar{\beta}) \tag{17}$$

for $n\geq 1$ where G_0 is given by Eq. (8) and

$$F(\alpha,\beta;\bar{\alpha},\bar{\beta})=(\omega_{\alpha\bar{\alpha}}\delta_{\beta\bar{\beta}}+\bar{\omega}_{\beta\bar{\beta}}\delta_{\alpha\bar{\alpha}}+\bar{V}_{\alpha\beta\bar{\alpha}\bar{\beta}})\times(1-\delta_{\alpha\beta})(1-\delta_{\bar{\alpha}\bar{\beta}})\ . \tag{18}$$

These two equations are expressed diagrammatically in Fig. 3 where G_n is represented by the part of the figure to the far left. Further, $G(\alpha,\beta;\bar{\alpha},\bar{\beta};\omega)$ satisfies the equation

$$-i\omega G(\alpha,\beta;\bar{\alpha},\bar{\beta};\omega)=\delta_{\alpha\bar{\alpha}}\delta_{\beta\bar{\beta}}(1-\delta_{\alpha\beta})-\Sigma_{\beta',\gamma'}F(\alpha,\beta;\alpha',\beta')\times G(\alpha',\beta';\bar{\alpha},\bar{\beta};\omega)\ . \tag{19}$$

By using equations similar to Eqs. (4a′) and (4b′), it can easily be verified that the moments of $G(\alpha,\beta;\bar{\alpha},\bar{\beta};\omega)$ generated by Eq. (19) are identical to the moments generated by Eqs. (17) and (18).

Although Eq. (19) can be solved directly, the physics of this approximation is much clearer if we rewrite it. By comparing moments it is easily verified that the following equations are identical to Eq. (19):

$$G(\alpha,\beta;\bar{\alpha},\bar{\beta};\omega)=P(\alpha,\beta;\bar{\alpha},\bar{\beta};\omega)-\Sigma_{\alpha',\beta',\alpha'',\beta''}P(\alpha,\beta;\alpha',\beta';\omega)F_2(\alpha',\beta';\alpha'',\beta'')G(\alpha'',\beta'';\bar{\alpha},\bar{\beta};\omega)\,, \tag{20}$$

$$-i\omega P(\alpha,\beta;\bar{\alpha},\bar{\beta};\omega)=\delta_{\alpha\bar{\alpha}}\delta_{\beta\bar{\beta}}(1-\delta_{\alpha\beta})-\Sigma_{\alpha'\beta'}F_1(\alpha,\beta,\alpha';\beta')P(\alpha',\beta';\bar{\alpha},\bar{\beta};\omega)\,, \tag{21}$$

where

$$F(\alpha,\beta;\bar{\alpha},\bar{\beta})=F_1(\alpha,\beta;\bar{\alpha},\bar{\beta})+F_2(\alpha,\beta;\bar{\alpha},\bar{\beta})\,. \tag{22}$$

This holds no matter how one decomposes F into F_1 and F_2. In particular, we chose the decomposition

$$F_1(\alpha,\beta;\bar{\alpha},\bar{\beta};\omega)=(1-\delta_{\alpha\beta})(1-\delta_{\bar{\alpha}\bar{\beta}})\times[\omega_{\alpha\bar{\alpha}}(\beta)\delta_{\beta\bar{\beta}}+\omega_{\beta\bar{\beta}}(\alpha)\delta_{\alpha\bar{\alpha}}], \tag{23}$$

$$F_2(\alpha,\beta;\bar{\alpha},\bar{\beta})=c\Gamma_{\alpha\beta}(\delta_{\alpha\bar{\alpha}}\delta_{\beta\bar{\beta}}-\delta_{\alpha\bar{\beta}}\delta_{\bar{\alpha}\beta}) \tag{24}$$

where

$$\omega_{\alpha\bar{\alpha}}(\beta)=\delta_{\alpha\bar{\alpha}}(\Sigma_{\gamma\neq\beta}\Sigma_{\alpha\gamma})-\Gamma_{\alpha\bar{\alpha}} \tag{25}$$

and $\bar{\omega}_{\alpha\bar{\alpha}}(\beta)=\bar{c}\omega_{\alpha\bar{\alpha}}(\beta)$. The quantity $\omega_{\alpha\bar{\alpha}}(\beta)$ is exactly the self-energy $K(\alpha,\bar{\alpha})$ for the occupancy or site correlation function when the site β ($\beta\neq\alpha,\bar{\alpha}$) is blocked. Further, $\bar{\omega}_{\beta\bar{\beta}}(\alpha)$ is exactly the mean-field self-energy $\bar{K}(\beta,\bar{\beta})$ for the distinguishable-particle correlation function when the site α ($\alpha\neq\beta,\bar{\beta}$) is blocked.

First consider Eqs. (20)–(25) in the limit where $\bar{c}\to 0 (c\to 1)$. Since $\bar{K}(q,\omega)$ is explicitly proportional to $\bar{c}$ because of Eq. (13) we need only evaluate $G_{ss}(q,\omega)$ at $c=1$. In fact Eqs. (20)–(25) should be exact in this limit because the moment diagrams for G omitted in this approximation are proportional to $\bar{\Omega}^2$ and $\bar{\Omega}^2$ is proportional to $\bar{c}$. The equations also have a very simple interpretation in this limit. Since $\bar{c}=0$, the term $\bar{\omega}_{\beta\bar{\beta}}(\alpha)$ in Eq. (23) vanishes and all quantities in Eq. (21) are proportional to $\delta_{\beta\bar{\beta}}$. The quantity $P(\alpha,\beta;\bar{\alpha},\beta,\omega)$ is now just the propagator for a single particle or vacancy hopping on a chain with the site β blocked out.[8] That is, it describes the motion of a single vacancy that cannot move the distinguishable particle at the site β. Equation (20), on the other hand, is in the form of a scattering equation for a propagator G where P is the noninteracting propagator and F_2 is an interaction potential. This equation takes care of the processes whereby the vacancy moves the distinguishable particle.

If Eqs. (20 and (24) are Fourier transformed according to Eq. (12) the resulting equation is an integral equation with a separable kernel. This is trivially solved to yield

$$G_{ss}(q,\omega)=\frac{P_{ss}(q,\omega)}{1+4\Gamma_0 cP_{ss}(q,\omega)}\,, \tag{26}$$

where

$$P_{ij}(q,\omega)=N^{-2}\Sigma_{q',q''}P(q',q'',q;\omega)\times\mathrm{trig}_i\,q'\,\mathrm{trig}_j\,q'' \tag{27}$$

as in Eq. (15). By combining Eqs. (13) and (26), we obtain

$$\bar{K}(q,\omega)=\frac{2\Gamma_0\bar{c}(1-\cos\bar{q})}{1+4c\Gamma_0P_{ss}(q,\omega)} \tag{28}$$

for all values of c.

If Eq. (21) is Fourier transformed according to Eq. (12) the resulting equation is an integral equation whose kernel is a sum of separable kernels. Thus the solution to this equation for $\bar{c}=0$ is also straightforward. The solution requires the evaluation of a number of integrals of the form

$$F(f,\omega)=N^{-1}\Sigma_q f(q)[-i\omega+2\Gamma_0(1-\cos q)]^{-1}\,, \tag{29}$$

where $f(q)$ is some trigonometric function. These integrals can be performed easily by using the following representation:

$$F(f,\omega)=N^{-1}\Sigma\int_0^\infty dt\, f(q)\times\exp\{-t[-i\omega+2\Gamma_0(1-\cos q)]\}\,.$$

If the q summation is turned into an integral and performed first, the remaining integral is the Laplace transform of a modified Bessel function. This can be easily evaluated using standard tables.[9] With a bit of algebra, one can show that $P_{ss}(q,\omega)$ is independent of q and

$$P_{ss}(q,\omega)=(4\Gamma_0)^{-1}\{-1+[\omega(\omega+4i\Gamma_0)]^{1/2}/\omega\}. \tag{31}$$

This function has a branch cut connecting $\omega=0$ with $\omega=-4i\Gamma_0$ and the phase of the square root is the same as the phase of ω when $|\omega|\to\infty$. Thus, in the limit $\bar{c}\to 0$, we obtain

$$\bar{D}(q,\omega)|_{\bar{c}\to 0}=\left(-i\omega+\frac{2\Gamma_0\bar{c}(1-\cos q)\omega}{[\omega(\omega+4i\Gamma_0)]^{1/2}}\right)^{-1}. \tag{32}$$

In any lattice with symmetric hopping rates the analogous equations can be solved to obtain a self-energy $\bar{K}$ that is proportional to $1-c$. For a three-dimensional lattice this yields a two-point correlation function that is exact as c approaches one and corrections for finite values of $1-c$ are of order $1-c$ compared to one. The physics of the situation in this limit is that one need consider the interactions of the distinguishable particle with only one vacancy at a time. The correlation function for this process is often described by an effective diffusion coefficient or correlation fact-

in the long-wavelength limit.[10,11]

The situation for a one-dimensional chain is actually more complicated than in three dimensions. The effective strength of the interaction between the vacancy and the distinguishable particle is much stronger in one dimension because the number of paths away from the particle is severely restricted. In fact the corrections to obtain the correlation factor are of order $2/n$ where n is the number of nearest neighbors.[11] Since $n=2$ for the nearest-neighbor linear chain, the fact that the correlation factor diverges (or does not exist) should not be too surprising. This nonexistence of a correlation factor is reflected in the fact that the mean square displacement[2] of the distinguishable particle is not proportional to t for long times t. Further, as we shall see, Eq. (32) is incorrect unless $\omega \gg (\bar{c}q^2)^2$ no matter how small $\bar{c}$ becomes. The reason is simply that a vacancy interacts with the distinguishable particle for such a long time that one cannot consider the effects of only one vacancy at a time.

Equation (21) can also be solved straightforwardly for finite $\bar{c}$. In this case $P(\alpha, \beta; \bar{\alpha}, \bar{\beta}; \omega)$ is the propagator for the distinguishable particle and another particle (or vacancy) with the restriction that they do not pass each other. However, the distinguishable particle propagates in the mean-field approximation. Since this is a bad approximation, we do not expect the results to be valid. In the next section we will show how to improve upon this approximation by treating this internal distinguishable particle propagates self-consistentently.

III. RESULTS

In this section we shall keep Eq. (20) [and thus Eq. (28)] while improving upon Eq. (21). As discussed earlier, Eq. (20) describes the multiple scattering of the distinguishable particle and another particle (or vacancy). The quantity $P(\alpha, \beta; \bar{\alpha}, \bar{\beta}; \omega)$ describes the propagation of these two entities when they are not interacting. The trouble with Eq. (21) for P is that it describes the propagation for the distinguishable particle in the mean-field approximation. What we wish to do now is renormalize this propagator (represented by the dashed line) so that it is replaced by the self-consistently obtained propagator. This will yield the approximation discussed in the first paragraph of the paper. We shall only attempt to carry out this calculation in the hydrodynamic limit where $\omega \ll \Gamma_0$ and $q \ll 1$. Because of the divergent nature of the integrals involved, $\bar{D}(q, \omega)$ or $\bar{K}(q, \omega)$ can be evaluated self consistently in this limit without knowing their values for larger q and ω.

We now wish to note [see Eq. (27)] that

$$P_{ss}(q, \omega) = P_{cc}(q, \omega),$$

$$P_{cs}(q, \omega) = P_{sc}(q, \omega) = 0, \tag{33}$$

no matter what approximation is made for $(P(\alpha, \beta; \bar{\alpha}, \bar{\beta}; \omega)$ if that approximation preserves the restriction that the distinguishable particle and the other particle (or vacancy) cannot pass as discussed in the last paragraph of Sec. II. For example, using Eq. (27) one can easily derive the equation

$$P_{\substack{cc \\ ss}}(q, \omega) = \tfrac{1}{4}\Sigma_{\alpha-\bar{\alpha}} e^{iq(\alpha-\bar{\alpha})}[P(\alpha, \alpha+1; \bar{\alpha}, \bar{\alpha}+1; \omega) + P(\alpha, \alpha-1; \bar{\alpha}, \bar{\alpha}-1; \omega) \pm e^{iq} P(\alpha, \alpha+1; \bar{\alpha}, \bar{\alpha}-1, \omega) \pm e^{-iq} P(\alpha, \alpha-1; \bar{\alpha}, \bar{\alpha}+1; \omega)]. \tag{34}$$

However, since the two particles cannot pass, $P(\alpha, \alpha \pm 1, \bar{\alpha}, \bar{\alpha} \mp 1; \omega)$ must be zero. Equations (33) can also be verified explicitly for the approximations used in Sec. II. Thus $P_{ss}(q, \omega)$ in Eq. (20) can be replaced by $p_{cc}(q, \omega)$.

If we ignored these restrictions about no passing, $P(\alpha, \beta; \bar{\alpha}, \bar{\beta}; \omega)$ would be the simple convolution $P_{nr}(\alpha, \beta; \bar{\alpha}, \bar{\beta}; \omega)$ where

$$P_{nr}(\alpha, \beta; \bar{\alpha}, \bar{\beta}; \omega) = \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi} D(\alpha, \bar{\alpha}; \bar{\omega}) \times \bar{D}(\beta, \bar{\beta}; \omega - \bar{\omega}) \tag{35}$$

or

$$P_{nr}(q', q'', q; \omega) = N\delta(q' - q'') \times \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi} D(q' + \tfrac{1}{2}q, \bar{\omega}) \times \bar{D}(q' - \tfrac{1}{2}q, \omega - \bar{\omega}). \tag{36}$$

In these equations $\bar{D}$ is the self-consistently determined distinguishable particle propagator and D is the exact occupancy or site propagator

$$D(q, \omega) = [-i\omega + 2\Gamma_0(1 - \cos q)]^{-1}. \tag{37}$$

We now argue that Eq. (36) is a good approximation for computing $P_{cc}(q, \omega)$ in the hydrodynamic limit ($\omega \ll \Gamma_0$, $q \ll 1$). The argument is that all four P's in the square brackets in Eq. (34) are equal in the hydrodynamic limit (α and $\bar{\alpha}$ are well separated) if we ignore the restrictions. Further, $P_{nr}(\alpha, \alpha \pm 1; \bar{\alpha}, \bar{\alpha} \pm 1; \omega)$ is very close to one-half of the value of $P(\alpha, \alpha \pm 1, \bar{\alpha}, \bar{\alpha} \pm 1; \omega)$. This factor of 2 obtains because if the distinguishable particle starts out to the right (or left) of another particle it must always remain to the right (or left). On the other hand, if the restrictions are ignored, the probability of them being to the right or left of each

other at long times later are equal. As a further check of this approximation we have computed $P_{cc}(q,\omega)$ both ways explicitly in the approximation used in Sec. II (for finite $\bar{c}$). In that case we find the two ways of computing $P_{cc}(q,\omega)$ yield identical results in the hydrodynamic limit.

Using the approximation we obtain

$$P_{cc}(q,\omega)=\int_{-\infty}^{\infty}\frac{d\bar{\omega}}{2\pi}\int_{-\pi}^{\pi}\frac{d\bar{q}}{2\pi}D(\bar{q}+\tfrac{1}{2}q,\bar{\omega})\times\bar{D}(\bar{q}-\tfrac{1}{2}q,\omega-\bar{\omega})\cos^2\bar{q}\ . \quad (38)$$

The frequency integration can be done easily using Eq. (37) since $D(q,\bar{\omega})$ has a pole in the lower-half $\bar{\omega}$ plane, and $\bar{D}(q,\omega-\bar{\omega})$ has no singularities in the lower-half $\bar{\omega}$ plane. Further, we assume that only values of $|\bar{q}|\ll 1$ contribute significantly to the integral in the hydrodynamic limit. This assumption is easily verified by the form of $\bar{D}(q,\omega)$ ultimately obtained. Thus, Eq. (38) can be rewritten

$$P_{ss}(q,\omega)=\int\frac{d\bar{q}}{2\pi}\bar{D}(q-\bar{q},\omega+i\Gamma_0\bar{q}^2)\ , \quad (39)$$

where the $\bar{q}$ integration can be extended to form $-\infty$ to $+\infty$. Equations (28) and (39) along with the equation

$$\bar{D}(q,\omega)=[-i\omega+\bar{K}(q,\omega)]^{-1} \quad (40)$$

can be solved self-consistently for $\bar{D}$.

It is now convenient to define a reduced imaginary frequency

$$z=-i\omega/\Gamma_0 \quad (41)$$

and a reduced self-energy

$$k(q,z)=K(q,\omega)/\Gamma_0\ . \quad (42)$$

We shall also assume that $|\Gamma_0 P_{ss}(q,\omega)|\gg 1$, which can easily be verified. By combining the above equations one obtains the equation

$$k(q,z)=\frac{\bar{c}q^2}{c}\left(\frac{2}{\pi}\int_{-\infty}^{\infty}d\bar{q}\,[z+\bar{q}^2+k(q-\bar{q},z+\bar{q}^2)]^{-1}\right)^{-1} \quad (43)$$

This equation can be further simplified by anticipating the final result that

$$k(q,z)=(\bar{c}\,q^2/c)^2 f(x)\ ,$$
$$x=z(\bar{c}\,q^2/c)^{-2}\ . \quad (44)$$

From the form of the final answer it can also be verified that $q-\bar{q}$ can be replaced q in $k(q-\bar{q}, z+\bar{q}^2)$. This obtains because either $\bar{q}\ll q$ or $\bar{q}^2\gg k$ in the important region of integration. Finally the following equation for $f(x)$ is obtained:

$$f(x)=\left(\int_0^{\infty}\frac{4}{\pi}\,dy\,[x+y^2+f(x+y^2)]^{-1}\right)^{-1}\ . \quad (45)$$

We cannot express $f(x)$ in terms of tabulated functions. However Eq. (45) can easily be solved numerically with a computer. In particular, we find that

$$f(x)\to\tfrac{1}{2}x^{1/2},\quad x\gg 1\ , \quad (46a)$$
$$f(0)\approx 0.6\ . \quad (46b)$$

Thus $\bar{K}(q,\omega)$ is a function with a branch cut running from $\omega=0$ to $\omega=-i\infty$, is analytic in the upper-half ω plane, and is real and positive when ω is positive imaginary. Further,

$$\bar{K}(q,\omega)=\Gamma_0(\bar{c}\,q^2/c)^2 f((-i\omega/\Gamma_0)(\bar{c}q^2/c)^{-2})\ , \quad (47)$$

where $f(x)$ is the solution to Eq. (45).

The mean-square displacement of a distinguishable particle $x^2(t)$ is given by

$$x^2(t)=\int_{-\infty}^{\infty}x^2\bar{D}(x,t)\,dx\ . \quad (48)$$

By expressing $\bar{D}(x,t)$ in terms of $\bar{D}(q,t)$ and integrating by parts twice this can be rewritten

$$x^2(t)=\frac{-d^2\bar{D}(q,t)}{dq^2}\bigg|_{q=0}\ . \quad (49)$$

The frequency integral needed to obtain $\bar{D}(q,t)$ can be performed by deforming the contour around the branch cut which transforms the integral into a standard Laplace transform. Since q is eventually taken to zero in Eq. (49), Eqs. (46a) and (47) can be used to evaluate the derivative before the frequency integral is performed. The result obtained is

$$x^2(t)=(2\bar{c}/c)(\Gamma_0 t/\pi)^{1/2}\ , \quad (50)$$

which is valid for long times, $\Gamma_0 t\gg 1$. Thus we recover the $t^{1/2}$ dependence noted by Richards.[2] The numerical factor in front of $t^{1/2}$ is about 30% lower than the value obtained by Richards.

The form of the two-point correlation function suggested by Richards, translated to our notation, is

$$\bar{D}_R(x,t)=(2\pi)^{-1/2}(bt)^{-1/4}\exp[-x^2/2(bt)^{1/2}]\ ,$$
$$b=2.5\Gamma_0(\bar{c}/c)^2\ . \quad (51)$$

This can be Fourier transform easily using standard tables[9] yielding

$$\bar{D}_R(q,\omega)=(i/\omega)[1-(\pi y)^{1/2}e^y\ \mathrm{erfc}\,y^{1/2}]\ , \quad (52)$$

where

$$y=q^2(ib/16\omega)^{1/2}\ , \quad (53)$$

and erfc is the complementary error function and a branch cut extends down the negative imaginary ω axis. In spite of the fact that Eqs. (47) and (52)

look very different, expansions for large and small frequencies are quite similar. A dimensionless measure of the frequency is

$$r = -i\omega c^2/\Gamma_0 \bar{c}^{\,2} q^4 . \tag{54}$$

The expansion of our function for large values of r is

$$\bar{D}(q, \omega) = (i/\omega)(1 - \tfrac{1}{2} r^{-1/2} + \cdots) , \tag{55}$$

while the corresponding expansion of Richards functions is

$$\bar{D}_R(q, \omega) = (i/\omega)[1 - (2.5\pi/16)^{1/2} r^{-1/2} + \cdots] . \tag{55'}$$

In the other limit, for $r = 0$,

$$\bar{D}(q, 0) \sim 1.2(c/\bar{c} q^2)^2 , \tag{56}$$

while Richards obtains

$$\bar{D}_R(q, 0) = (8/2.5\pi)(c/\bar{c} q^2)^2 . \tag{56'}$$

The expansions for high and low frequencies of our correlation function differ from the expansions obtained from Richard's correlation function by about 30% and 20%, respectively. Further, computer evaluations of the real and imaginary parts of $\bar{D}(q, \omega)$ are within 30% of real and imaginary parts of $\bar{D}_R(q, \omega)$ for all values of q and ω in the hydrodynamic regime. Thus we maintain that our analytically derived $\bar{D}(q, \omega)$ represents a good fit to Richard's computer experiments for symmetric hopping rates.

Except for inelastic neutron scattering, one cannot experimentally measure $\bar{D}(q, \omega)$ directly. In general NMR experiments do not measure $\bar{D}(q, \omega)$ directly. In fact, they usually measure various convolutions of $\bar{D}$ or integrals of $\bar{D}(q, \omega)$ over q. The one exception that comes to mind is pulsed-gradient diffusion measurements.[12] Because of the form of $\bar{D}(q, \omega)$ for small q and ω, we would not expect the decay due to diffusion to be the same as that usually obtained.

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