Comments and Addenda

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Diffusion of labeled particles on one-dimensional chains

S. Alexander* and P. Pincus
Department of Physics, University of California, Los Angeles, California 90024
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The diffusion of a labeled particle on a one-dimensional chain is discussed. It is shown that the long-time behavior is dominated by density fluctuations leading to a $t^{1/2}$ dependence of the mean-square deviation in agreement with Monte Carlo results of Richards.

In the context of superionic conductivity, a number of recent investigators[1-3] have considered the classical diffusion of labeled particles. In particular, Richards[1] has obtained the surprising result that, for a one-dimensional chain with exclusions, the *mean-square* excursion of a labeled particle after a time t asymptotically varies as $t^{1/2}$. In Ref. 1, this result was obtained by a Monte Carlo calculation and then some intuitive arguments were presented to provide some physical insight. Fedders and Sankey[2] have developed a multiple scattering formalism for the more general problem. Subsequently[3] this method was applied to the one-dimensional case where results similar to those of Ref. 1 were obtained. The purpose of this note is to point out that the Richards result follows directly from the coupling of the single-particle motion to the density in a one-dimensional geometry.

Consider a simple one-dimensional lattice with lattice constant a. A fraction c of the sites are occupied by classical diffusing particles. At most, one particle may be situated on a given site. This "excluded volume" interaction in a one-dimensional geometry constrains the order of the diffusing particles to be fixed. The particles may then be numbered sequentially with the order remaining invariant. On the average, the spacing between particles is a/c. Let $u_l(t)$ be the displacement of the lth particle from a configuration where the particles are uniformly spaced. Then, for relative displacements which vary slowly, the local particle concentration fluctuation in the neighborhood of the lth particle $n(l)$ is given by

$$n(l) \cong -\left(\frac{c^2}{a}\right)\frac{du_l}{dl}, \tag{1}$$

or upon Fourier transforming,

$$n_k \cong ikcu_k . \tag{2}$$

A precise derivation of these relationships and of their range of validity is given in the Appendix. The concentration fluctuations obey a diffusion equation leading to

$$\langle n_k(t)n_{-k}(0)\rangle = c(1-c)\,e^{-Dk^2t} \quad k \neq 0 , \tag{3}$$

where D is a diffusion constant relevant to the long-wavelength behavior of the chain; it may be expressed in terms of the microscopic transfer rates. The concentration-dependent prefactor explicitly exhibits the role of the exclusion in limiting the amplitude of the diffusive modes. Combining (2) and (3), we find for the mean-square displacement of any particular (labeled) particle in a time t,

$$\tfrac{1}{2}\langle [u_l(t)-u_l(0)]^2\rangle = \langle u_l^2(0)\rangle - \langle u_l(t)u_l(0)\rangle$$
$$= \left(\frac{1-c}{c}\right)\int dk\, k^{-2}(1-e^{-Dk^2t}) , \tag{4}$$

which upon integration yields

$$\langle [u_l(t)-u_l(0)]^2\rangle \cong \text{const} + [(1-c)/c](4\pi Dt)^{1/2} . \tag{5}$$

The constant depends on the short time behavior and is not derivable from Eq. (4). Both the asymptotic time dependence and the concentration dependence exhibited in Eq. (5) are in close agreement with the Richards[1] Monte Carlo results. This unusual behavior is thus purely a one-dimensional effect closely related to the divergence of the mean-square amplitude for the elastic chain. The effect does not carry over to two and three dimensions, where we expected a labeled particle to obey a standard diffusion equation with a renormalized diffusion constant to take into account exclusion effects.

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APPENDIX

The relationship between the density and displacement in Eqs. (1) and (2) can be given a precise meaning using standard lattice dynamics techniques. This also gives some insight into the approximations involved.

One has

$$n_q = \frac{1}{N}\sum_l e^{iq(R_l + u_l)}, \tag{A1}$$

where N is the number of available sites, R_l is the position of the lth particle in a uniformly spaced configuration, and

$$u_l = \sum_q u_q e^{-iqR_l}. \tag{A2}$$

Expansion of Eq. (A1) gives

$$n_q(t)n_{-q}(0) = c^2q^2u_q(t)u_{-q}(0)[1 + O(q^2)], \tag{A3}$$

which leads directly to our (and the Richards[1]) result. One notes however that Eq. (A3) is actually inconsistent. Ressumation on the right-hand side would lead to

$$n_q(t)n_{-q}(0) = F_q c^2q^2 u_q(t)u_{-q}(0)[1 + O(q^2)], \tag{A4}$$

where

$$F_q \approx e^{-q^2\langle u^2\rangle/2} \tag{A5}$$

is a Debye-Waller factor. One notes that the (instantaneous) mean-square fluctuation

$$\langle u^2\rangle = \frac{1}{N}\sum_{q\neq 0}\langle u_q u_{-q}\rangle, \tag{A6}$$

diverges for a truly one-dimensional system. On the other hand our result in the text requires

$$Dt/\langle u^2\rangle \gg 1 \quad (q^2\langle u^2\rangle \ll 1). \tag{A7}$$

This is assymptotically consistent for sufficiently small q (long times) since

$$\langle u^2\rangle \sim N, \quad q \gtrsim 1/N,$$

so that a regime of the type required in (A7) exists for any finite system when $t \gtrsim N$.

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*Permanent address: The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel.

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