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Anomalously slow trapping of nonidentical interacting particles by random sinks

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We find an anomalously slow trapping rate $\dot{Q}$ for trapping of nonidentical interacting particles in topologically linear systems with randomly distributed sinks which are selective for particles below a critical radius r_S. The particles have an arbitrary size distribution and interact by a hard-core repulsion. Our quantitative result, $\dot{Q} \sim \exp(-At^{1/5})$, is general, and the amplitude A can be tuned since it depends on the concentration of the nontrappable particles.

How fast can randomly diffusing particles be released by random holes in a topologically linear structure under the conditions that the particles interact, and are characterized by a wide range of sizes—some of which can be released (smaller than the hole's radius r_S) and others of which cannot (larger than r_S). Basically, this problem of particle release belongs to a more general class of "trapping" problems.[1-3] So far, trapping models have been successfully used in studying several physical phenomena such as dielectric relaxation,[4] self-attracting polymer chains,[5] and excitation relaxation in crystals.[6] With the exception of very recent work on Lévy flight walks,[7-9] all efforts[4-6,10-12] have arrived at the same equation for the dependence of the flow rate $\dot{Q}$ on time t and dimension d,[13]

$$\dot{Q}(t) \sim \exp(-At^{d/(d+2)}) \ . \tag{1a}$$

Here we shall argue that generally particle release problems cannot be understood by the theory for identical noninteracting particles, since (i) the particles may occur in many sizes, and (ii) they interact with each other—and clearly excluded volume interactions are relevant.

These two effects are particularly important for topologically linear chains where two molecules cannot even "pass by" each other. Fick's law $l \sim t^{1/2}$ for the rms displacement of a single tagged molecule becomes[14-17]

$$l(c,t) \sim \{[(1-c)/c]^2 t\}^{1/4} \ . \tag{1b}$$

Here l denotes the "chemical" distance along the chain, and c is the total particle concentration.[18] Both T and F particles have excluded volume interactions and cannot cross each other. Only T particles are trapped. Equation (1b) shows that the motion of a tagged hard-core particle is dramatically slowed down compared with the motion of noninteracting particles. Correspondingly, we shall see that the trapping rate for linear chains will also be strongly slowed down due to the hard-core interaction.

In this paper, we consider a topologically linear chain of hard-sphere molecules with a broad distribution of all possible radii r, and a set of sinks all with the same radius r_S (Fig. 1). Since the physics of particle release is the same for all molecules with $r \leq r_S$ ("thin" molecules) and is also the same for all molecules with $r \geq r_S$ ("fat" molecules), we treat only two kinds of diffusing particles: $T \equiv$thin and $F \equiv$fat.[19] The release rate $\dot{Q}$ is defined as the mean number of T molecules that leave the chain per unit of time. In the infinite chain with a single sink the release rate is changed from $\dot{Q} \sim t^{-1/2}$ for noninteracting molecules to $\dot{Q} \sim t^{-3/4}$, where now the proportionality factor depends on the ratio of concentrations $c_F/c_T(0)$ of fat and thin particles.[19] On the chain with a nonzero concentration of sinks c_S, the *asymptotic* rate $\dot{Q}$ will not depend on the initial concentration of T molecules. Thus the physics question we address is how the asymptotic release rate $\dot{Q}$ depends on t, c_S, and c_F.

To answer this question, consider first a finite sink-free segment of length L with traps at both ends. The probability $P_0(L)$ of finding such a sink-free region of length L in an infinite chain with randomly positioned sinks is given by the Poisson distribution

$$P_0(L) \sim \exp(-Lc_S) \ . \tag{2}$$

Consider now the probability $P(L,t)$ that a given T molecule survives time t in a segment of length L. For random-

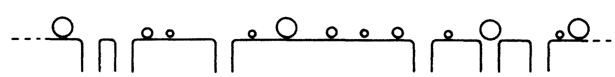

FIG. 1. Schematic drawing of a topologically linear system (e.g., a linear polymer), containing particles of random sizes, and a random distribution of sinks with constant size r_S. Those particles with $r > r_S$ are called F particles (fat) and those with $r < r_S$ are called T particles (thin). Both T and F particles have excluded volume interactions and cannot cross each other. Only T particles are trapped.

ly distributed sinks, the probability to survive $P_T(t)$ is dominated by the large but rare sink-free regimes.[10] Hence, for $t \to \infty$

$$P_T(t) \sim \max_L [P(L,t) P_0(L)] \ . \tag{3}$$

I. CASE (i): NONINTERACTING IDENTICAL MOLECULES

Asymptotically,

$$P(L,t) \sim \exp[-\text{const}\, t/\tau(L)] \ , \tag{4a}$$

where

$$\tau(L) \sim L^2 \tag{4b}$$

is the average time a molecule diffuses before it gets trapped at the ends of the finite chain. Maximizing (2) yields[10]

$$P_T(t) \sim \exp(-At^{1/3}) \ , \tag{5a}$$

where A depends on the concentration of sinks

$$A \sim c_S^{2/3} \ . \tag{5b}$$

This result is confirmed by exact analysis.[3,11-13]

II. CASE (ii): INTERACTING NONIDENTICAL MOLECULES (OUR MODEL)

Note that the trapping rate and the probability of survival for identical hard-core particles are the same as for identical noninteracting particles because they are not labeled.[19,20] For our model, (4b) is replaced by[21]

$$\tau(L) \sim \left[\frac{c_F}{1-c_F} \right]^2 L^4 \ , \tag{6}$$

which follows from (1b). If (4a) still holds, then we can combine (6) and (4) to obtain the new result that (5a) is replaced by

$$P_T(t) \sim \exp(-At^{1/5}) \ . \tag{7a}$$

The amplitude A of (5b) now depends on c_F as well as c_S,

$$A \sim c_S^{4/5}(1-c_F)^{2/5} \ . \tag{7b}$$

The decay in (7a) is much slower than for noninteracting particles. Moreover, the amplitude A can be *selectively tuned* by varying either c_F or c_S.

We have checked our predictions (4a) and (6) by extensive Monte Carlo simulations. In order to achieve reasonable statistics when calculating $P(L,t)$, we consider large chains with equidistant traps at sites $1, L+1, 2L+1, \ldots$. We varied L and the concentrations c_F and $c_T(0)$. To determine the asymptotic behavior of $P(L,t)$, we have calculated the corresponding release rate $Q(L,t) = -\dot{P}(L,t)$, where $\dot{Q}$ is the total outgoing flux of released particles. Our results (Fig. 2) clearly confirm the validity of (4a) for the case of interacting particles. For testing our prediction (6) for $\tau(L)$, we changed c_F and L systematically. In Fig.

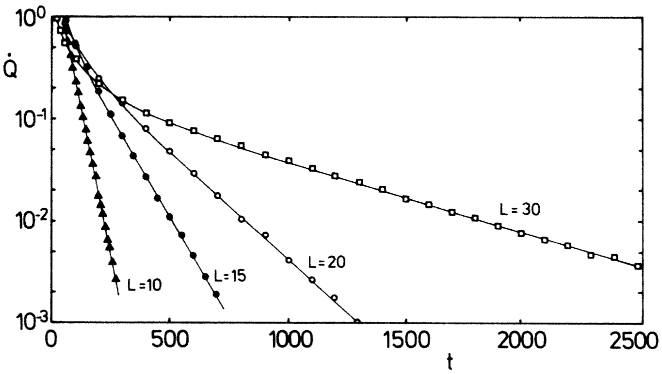

FIG. 2. Test of Eq. (4a), $P(L,t) \sim e^{-t/\tau}$; shown in a semilogarithmic plot of $\dot{Q} \equiv -\dot{P}$ as a function of time for $c_F = 0.1$, $c_T(0) = 0.2$, with $L = 10$ (△), 15 (●), 20 (○), and 30 (□). The results are based on 2000 runs (or more) for each L value.

3(b), c_F is varied with $L = 25$ fixed, while in Fig. 3(a) L is varied and c_F is held fixed. In both figures, we observe a crossover from the noninteracting limit to the interacting case at roughly $c_F = 1/L$. For c_F fixed and L varying we have

$$\tau \sim \begin{cases} L^2 \text{ for } c_F \ll 1/L \\ L^4 \text{ for } c_F \gg 1/L \ , \end{cases} \tag{8a}$$

while for L fixed and c_F varying we find

$$\tau \sim \begin{cases} \text{const for } c_F \ll 1/L \\ c_F^2/(1-c_F)^2 \text{ for } c_F \gg 1/L \ . \end{cases} \tag{8b}$$

Therefore, (6) is valid for $c_F L \gg 1$, as predicted, and accordingly relations (7a) and (7b) are valid for $c_F/c_S \gg 1$.

Finally, we checked our prediction (7) by direct computer simulation. We calculated the number of surviving particles for the case $c_S = 0.20$, $c_T(0) = 0.20$, and (a) $c_F = 0.2$ and (b) $c_F = 0$. In the latter case the T particles are not labeled and we expect the result for noninteracting particles, Eq. (4). In Fig. 4 we have plotted $\log_{10} \times [\log_{10} P_T(t)]$ vs $\log_{10} t$ for both cases. For $c_F = 0$ the curve bends down and nearly reaches the predicted slope of $\frac{1}{3}$ at $t = 1000$. For $c_F = 0.2$ the curve is more flat; the slope reaches a value of 0.25 at about 10000 time steps. We have calculated successive slopes as a function of $1/t$ and it seems likely that asymptotically our predicted value $\frac{1}{5}$ will be reached.

In summary, then, we have discovered that trapping of *nonidentical interacting* particles by randomly distributed sinks is anomalously slow in that the trapping rate $\dot{Q}$ is slower than exponential, and even slower than the "anomalous" slow result of Ref. 13. Moreover, we have obtained a *quantitative* expression for $\dot{Q}$, $\ln \dot{Q} \sim -t^{1/5}$, which shows that the excluded volume changes the universality class of trapping for topologically one-dimensional structures. The physical origin of our new result resides in the fact that hard-core particles diffuse anomalously slowly in one dimension, with an rms displacement varying as t^{1/d_w} with $d_w = 4$, *not* $d_w = 2$. For $d = 2,3$ we know that $d_w = 2$, so we expect that $\ln \dot{Q} \sim -Bt^{d/(d+2)}$ with the amplitude B being dependent upon c_F, the concentration of

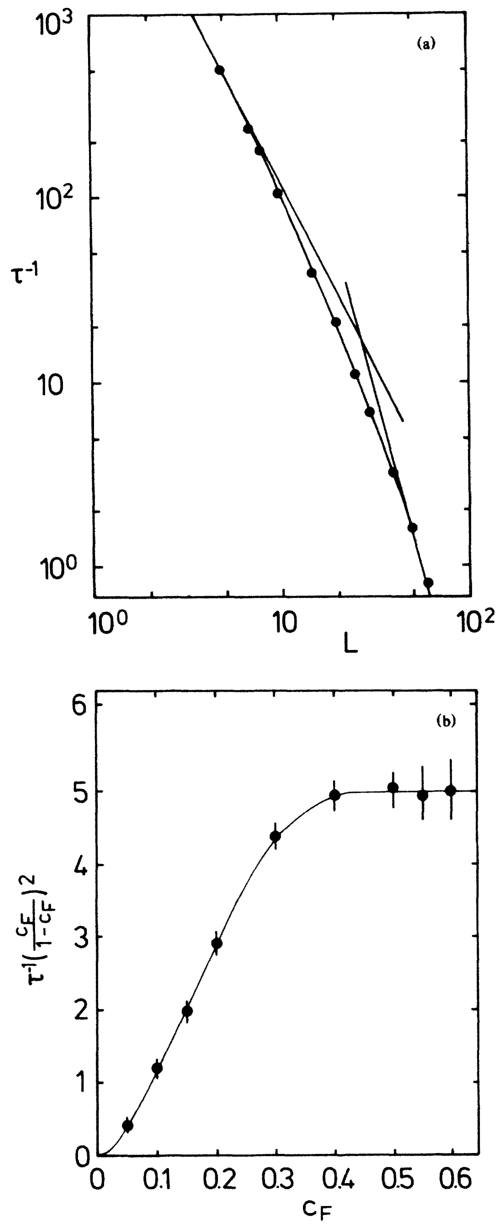

FIG. 3. Test of Eq. (6), $\tau \sim L^4 c_F^2/(1-c_F)^2$, for $c_F > 1/L$. In (a) τ is plotted vs L for fixed $c_F = 0.1$, while in (b) $\tau(1-c_F)^2/c_F^2$ is plotted vs c_F for fixed $L = 25$. The results are based on 2000 runs (or more) for each set of parameters.

fat particles.

Our results are thus applicable to particle release in real systems (e.g., in drug release devices)[22,23] if they can be made effectively topologically one-dimensional over some length range. There are many examples from colloid structures, such as a linear polymer (which *is* topologically one dimensional), or the backbone of a percolation cluster (which is topologically one-dimensional for length scales shorter than the spacing of the blobs). Since the difference between the Ref. 13 result $\ln Q \sim -t^{1/3}$ and our result $\ln Q \sim -t^{1/5}$ is so striking on large time scales, experiments might be able to demonstrate this anomaly.

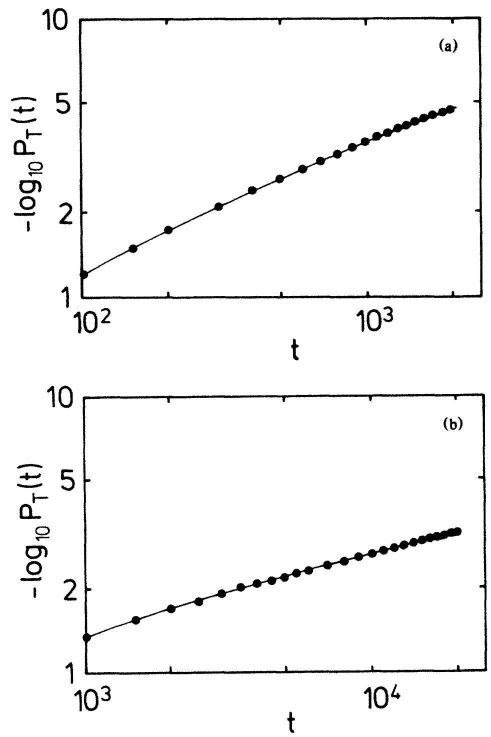

FIG. 4. Dependence on $\log_{10}t$ of $\log_{10}\log_{10}P_T$, where P_T is the probability of survival of T particles. In (a) *identical* hard-core particles $[c_F = 0, c_T(0) = 0.2]$ are considered and the slope approaches the predicted value $\frac{1}{3}$ for large times. In (b) *nonidentical* hard-core particles $[c_F = 0.2, c_T(0) = 0.2]$ are considered. Although the asymptotic regime has not been reached, the extrapolation of the successive slopes appears to be approaching 0.2.

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