Collision of polymers in a vacuum

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In a number of experimental situations, single-polymer molecules can be suspended in a vacuum. Here collisions between such molecules are considered. The limit of high collision velocity is investigated numerically for a variety of conditions. The distribution of contact times, scattering angles, and final velocities are analyzed. In this limit, self-avoiding chains are found to become highly stretched as they collide with each other and have a distribution of scattering times that depends on the scattering angle. The velocity of the molecules after the collisions is similar to predictions of a model assuming thermal equilibration of molecules during the collision. The most important difference is a significant subset of molecules that inelastically scatter but do not substantially change direction.

I. INTRODUCTION

Although polymer molecules are most commonly studied in solution or in solid form [1], there has been increasing technological use for them in a vacuum. They are often prepared in this state as part of the technique used to identify protein molecules with mass spectrometry [2].

Recently, the properties of single-chain molecules in a vacuum were studied theoretically and by means of computer simulation [3–7]. It was shown that such molecules have unusual statistical properties and that the dynamics differ substantially from those found for similar molecules in solution. With no excluded volume, the lack of a solvent means that the only damping that can occur is internal to the chain and this leads to slowly damped oscillatory behavior for time-dependent correlation functions of polymer position. With excluded volume, the time constant for relaxation scales with chain length N as $N^{1.15\pm.05}$ substantially faster than for corresponding chains in solution [1]. Oscillatory behavior is quite pronounced for short chains [6] but is suppressed when they are longer [3].

The equilibrium size of such chains is also influenced by the conservation of angular momentum [4], and the exact statistical properties of an ideal chain with this constraint can be calculated. When the total angular momentum is zero, the radius of gyration is smaller relative to a chain without this constraint enforced. In experimental situations, these polymer chains are often charged and are accelerated by an external field. As far as the author is aware, there have been no experiments that have measured their conformations in this state. Such experiments would be very interesting and might allow for the probing of additional features that could be used to characterize the chemical composition of such chains. An important aspect in understanding this situation are the nature of collisions between chains.

In equilibrium, collisions will obey detailed balance and the average properties of two chains before and after a collision will be identical. Under the conditions necessary to perform mass spectrometry, nonequilibrium considerations become necessary. Because the molecules are charged and accelerated by large fields, they acquire a high center-of-mass velocity. It seems likely that under such circumstances, one would have collisions occurring between molecules with high relative

velocities, as their charges and masses are not all identical. Such collisions differ from most collisions in that they are occurring between very large molecules and are expected to have quite a different character than previously studied.

In addition, it should be possible to directly study collisions between molecules with high relative center-of-mass velocities using modifications to the highly sophisticated apparatus that is in current use such as matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS). The acceleration voltage typically of order order 10 kV [8]. So with a single charge on a protein this amounts to a center-of-mass kinetic energy of 10^4 eV. Compared to the center-of-mass thermal energy at 400 K, this is over 10^5 times greater. It should be noted that this large field does not cause further ionization of the molecules because the acceleration occurs over centimeters and so the electric field is still small compared with that needed for ionization. There are many sophisticated variations [9] of MALDI that suggest that modification of the apparatus for the purpose of studying collisions should be feasible.

It should also be emphasized that MALDI is very complex and that the way the physical situation is modeled below is still quite approximate. It is hoped that some of the predictions found by this analysis will motivate further experiments on this very useful technique. Nevertheless, it is of interest to explore situations where the collision velocities of molecules are much larger than the thermal values given by the equipartition theorem [10] and this is done in this paper.

Throughout this work we will consider collisions in the center-of-mass frame. Transforming to other frames is straightforward. For highly inelastic collisions, such as the ones described below, this is the most natural reference frame to use.

II. ANALYTICAL CALCULATION

In general, the dynamics of a collision between two macromolecules is extremely complex and difficult to treat theoretically. However, here we will make two assumptions that will allow us approach this problem analytically and this will be subsequently compared to simulation results.

The first and boldest assumption is that chains interact for long enough to reach thermal equilibrium. It is not obvious that this is the case, and our numerical results will show that it is

a reasonable starting point but clearly not exact. It is expected to work better if the interactions between the molecules are strongly attractive. However, we will not simulate the attractive case in this work, although it is an interesting problem and may also be relevant to some experiments.

The second assumption is that the initial relative velocity is much larger than the internal energy of a chain. Although not as crucial as the first assumption, we will see that it leads to a regime with a dependence on much fewer independent parameters than the general case. This makes it much easier to test numerically.

A. The thermal limit

We first examine what happens if two chains collide that have an arbitrary number of monomers $N_1 \gg 1$ and $N_2 \gg 1$ and corresponding masses $M_1 = mN_1$ and $M_2 = mN_2$. We will consider the collision in the center-of-mass reference frame so, initially, the total momenta of the molecules are $\mathbf{P}_I$ and $-\mathbf{P}_I$, respectively. We will also assume, as we do in subsequent sections, that collisions are nearly head-on so there is little angular momentum about the center of mass.

We assume that each chain is large enough to be well described as being in thermal equilibrium with temperatures T_1 and T_2 and that the internal energy is extensive so the initial energy is the sum of internal energy plus center-of-mass kinetic energy. This gives an initial total energy for the system of

$$E_I = N_1 u(T_1) + N_2 u(T_2) + \frac{P_I^2}{2}\left(\frac{1}{M_1} + \frac{1}{M_2}\right), \qquad (1)$$

where $u(T)$ is the internal energy per monomer.

After the collision has taken place and the molecules have separated, the energy in center-of-mass degrees of freedom is only $3k_B T$ and, by the assumption of large N, is very small compared to the internal energy. Therefore to a good approximation

$$E_F = (N_1 + N_2)u(T_F), \qquad (2)$$

where T_F is the final temperature of both chains. By the assumption that the chains have equilibrated thermally, after the collision, the two chains are at the same temperature. Equating E_I to E_F from the above two equations

$$(N_1 + N_2)u(T_F) = N_1 u(T_1) + N_2 u(T_2) + \frac{P_I^2}{2}\left(\frac{1}{M_1} + \frac{1}{M_2}\right). \qquad (3)$$

Therefore, the final temperature can be computed from the initial temperatures and P_I.

This can be simplified further in the limit where the center-of-mass kinetic energy is small compared to the internal energy, or the heat capacity, $c(T)$, is almost constant, so for both chains $i = 1,2$

$$u(T_i) = u(T_F) + N_i c(T_F)(T_i - T_F), \quad c(T) \equiv \frac{\partial u(T)}{\partial T} \qquad (4)$$

so Eq. (3) yields

$$T_F = \frac{N_1 T_1 + N_2 T_2}{N_1 + N_2} + \frac{P_I^2}{2mc(T_F)}\left(\frac{1}{N_1} + \frac{1}{N_2}\right). \qquad (5)$$

The first term is the weighted average temperature that the two systems would have if brought in contact. The second is the additional increase in temperature due to the energy in the center-of-mass kinetic energies of the molecules.

Now we focus on the limit where the initial internal energy of the chains are negligible compared with the kinetic energy in the center of mass.

B. The high-collision-velocity limit

Aside from the number of monomers, self-avoiding chains are characterized by a mass per monomer m, step length l, and an excluded volume parameter. Excluded volume can be understood as an effective hard core radius that prohibits monomers from getting closer than a certain distance. In the limit where P_I is very large and the internal energy of a chain is kept constant, the internal energy of a chain becomes negligible in comparison with the center-of-mass kinetic energy. During a collision, we will see that, typically, a substantial fraction of this momentum is transferred into internal kinetic energy of the chains. Therefore, in this limit, the internal energy of a chain before a collision can be neglected, and we can set the initial kinetic energy of the chains equal to zero. In this case, with only hard core potentials, the scattering of self-avoiding chains depends only on velocity as a prefactor. The angular dependence of scattering becomes independent of P_I, and the distribution of the final scattered momentum $\mathbf{P}_F$ depends only on $\mathbf{P}_F/P_I$. This is an interesting limit to consider because of the lack of dependence on the chains' temperature, and, therefore, this will be studied in detail below.

Because the velocities of monomers relative to the center of mass for a single chain is very small in comparison with the relative collision velocity, the angular momentum relative to the center of mass of a chain before the collision can be neglected as well. However, the angular momentum of the two chains relative to each other cannot in general be neglected. As mentioned above, because of the large number of parameters that we are considering we will consider only situations where the total angular momentum of the system is zero, that is, head-on collisions of the center of masses.

The distribution of resulting directions emerging from the collision is an interesting quantity to examine. The angle of deflection θ (the inclination angle) after a collision can be anisotropic, but the azimuthal angle ϕ must always be isotropic. We use the convention that $\pi/2 > \theta \geqslant 0$ is the direction of forward scattering. This is shown in Fig. 1.

When two chains collide, they remain in contact for some period of time, t_c, that depends on the precise details of the initial configurations of the chains. Because the chains are flexible, we expect to have highly inelastic collisions. In the limit of a very long t_c, much longer than the relaxation of a chain, the two chains will have fully thermalized. We will now describe what we expect in this limit.

C. Thermal and high velocity limit

When the chains are in contact for long enough that they have fully equilibrated, the energy in the velocity degrees of freedom will then be described by the equipartition theorem [10] with the caveat that they strictly obey conservation of
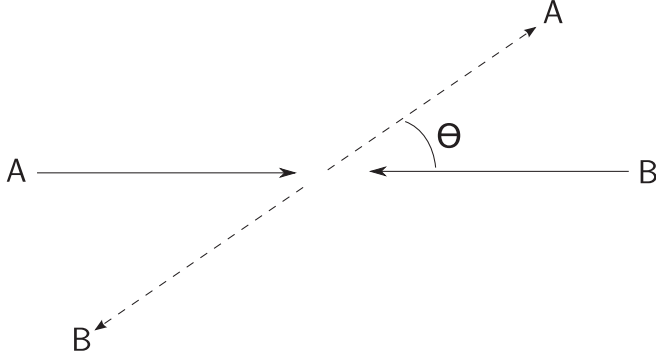
FIG. 1. A collision in the center-of-mass frame. Polymers A and B move toward each other as shown by the solid line. After the collision they come apart as shown by the dashed lines. The angle θ is the angle of deflection.

energy, momentum, and angular momentum. For a large number of monomers, momentum and angular-momentum conservation make a negligible correction to the energy in each degree of freedom. The initial energy is

$$E = \frac{1}{2m} P_I{}^2 \left(\frac{1}{N_1} + \frac{1}{N_2} \right). \tag{6}$$

Assuming thermal equilibrium, when the two chains collide, we can define a temperature T, and statistical mechanics gives the relationship between this and the energy E. The average total kinetic energy is $\langle K \rangle = (N_1 + N_2) d_f k_B T / 2$, where d_f are the number of degrees of freedom per monomer, so in the special case of an athermal system, $E = K$ so

$$k_B T = \frac{P_I{}^2}{d_f m} \frac{\left(\frac{1}{N_1} + \frac{1}{N_2} \right)}{N_1 + N_2} = \frac{P_I{}^2}{d_f m (N_1 N_2)}. \tag{7}$$

Here athermal is taken to mean any system whose partition function is independent of temperature, for example, systems with only constraints in the allowed regions of phase space, such as hard core interactions.

We would like to calculate the average center-of-mass energy of both molecules after the collision. The position and momentum degrees of freedom are independent so we need only consider kinetic energy corresponding to particles with momenta $\mathbf{p}_{j,1}$, and $\mathbf{p}_{j,2}$ where the first subscript, j, indexes the monomer, and the second subscript indexes the polymer

$$K = \frac{1}{2m} \left(\sum_{j=1}^{N_1} p_{j,1}^2 + \sum_{j=1}^{N_2} p_{j,2}^2 \right). \tag{8}$$

The probability of finding the system with a given set of momenta is proportional to $\exp(-\beta K)$, subject to the constraint

$$\sum_{j=1}^{N_1} \mathbf{p}_{j,1} + \sum_{j=1}^{N_2} \mathbf{p}_{j,2} = 0. \tag{9}$$

We would like to find the probability distribution of the total momentum of one chain

$$\mathbf{P}_1 = \sum_{j=1}^{N_1} \mathbf{p}_{j,1}. \tag{10}$$

This problem is mathematically identical to the problem of a Gaussian ring polymer with $N_1 + N_2$ monomers. In particular, one can regard the particle momenta as displacement vectors between nearest neighbors. Then $\mathbf{P}_1$ can be interpreted as the displacement of two monomers separated by N_1 monomers. For the purposes of this calculation, this is the same as two linear chains in parallel of lengths N_1 and N_2. Therefore, probability distribution of $\mathbf{P}_1$ is

$$P(\mathbf{P}_1) \propto e^{-\frac{\beta P_1{}^2}{2} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}. \tag{11}$$

Therefore

$$\langle P_1^2 \rangle = 3 k_B T M_r, \tag{12}$$

where $1/M_r = 1/M_1 + 1/M_2$ is the reduced mass.

Alternatively, this result can be seen by considering a gas in thermal equilibrium and considering the joint momentum distribution of two molecules of mass M_1 and M_2, $P(\mathbf{p}_1, \mathbf{p}_2) \propto \exp(-\beta K)$. We are interested in the distribution of momentum in the center-of-mass reference frame. The kinetic energy K is the sum of the internal plus center-of-mass kinetic energy. Because the internal momenta are equal and opposite, the internal term K_I is

$$K_I = \frac{P_1{}^2}{2} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \tag{13}$$

and is independent of the center-of-mass momentum. This implies the distribution of P_1 is of the form of Eq. (11).

In the athermal limit, we can use the value of T given by Eq. (7) and substitute that into Eq. (12), obtaining

$$\langle P_1^2 \rangle = 3 \frac{P_I{}^2}{d_f (N_1 + N_2)}. \tag{14}$$

Therefore, the variance of the final center-of-mass speed of chain 1, $v_{\text{c.m.},1,F}$, is related to its initial speed $v_{\text{c.m.},1,I}$ as

$$\langle v_{\text{c.m.},1,F}^2 \rangle = 3 \frac{v_{\text{c.m.},1,I}^2}{d_f (N_1 + N_2)}. \tag{15}$$

In a gas of molecules with a large number of internal degrees of freedom, the distribution of total molecular energy is highly peaked. The standard deviation of this energy is smaller than the mean by a factor of $1/\sqrt{N}$. In the limit of large N we can ignore fluctuations in this energy. In thermal equilibrium, we would like to know the distribution of center-of-mass speeds seen that result from a collision.

To derive this distribution, assume we have just two molecules in a container with periodic boundary conditions with total center-of-mass momentum of zero. Assume the size of the container is much larger than the size of a molecule and that the system is in thermal equilibrium. Such a system is expected to be ergodic and hence be able to reach thermal equilibrium. The distribution of the center-of-mass speed measured at one time is Maxwellian. This differs from the distribution of speeds that are measured after a collision. In the latter case, we are not measuring speeds at arbitrary times but, rather, after a collision. This difference in sampling alters the distribution. After a collision the center of mass of molecule 1 will move in a straight line with speed $v_{\text{c.m.},1,F}$ until it suffers another collision. The time spent in this state before undergoing another collision will be $\propto 1/v_{\text{c.m.},1,F}$. So

to compensate for this, the distribution of final speeds must be multiplied by an extra factor of $v_{c.m.,1,F}$ so

$$P(v_{c.m.,1,F})dv_{c.m.,1,F} \propto v_{c.m.,1,F}^3 e^{-\frac{v_{c.m.,1,F}^2}{2\sigma_x^2}} dv_{c.m.,1,F}. \quad (16)$$

Here σ_x^2 is the variance of one of the components of the final velocity, and therefore $\sigma_x^2 = \langle v_{c.m.,1,F}^2 \rangle /3$ or, using Eq. (15),

$$\sigma_x^2 = \frac{v_{c.m.,1,I}^2}{d_f(N_1 + N_2)}. \quad (17)$$

For a gas in thermal equilibrium, the distribution of speeds of molecules striking a wall is well known from the study of effusion [11] and this is the form that is expected in that case as well.

The distribution of directions for the final velocity in this limit should be isotropic. The only subtlety being that the total angular momentum L_t is conserved, so if L_t is zero, it might be thought that this would preclude the two chains rotating relative to each other and that this would cause them separate in a way that preserves their initial relative orientation. However, it is still possible to rotate the two chains by circular motion of only parts of them. For example, if an end monomer rotates by one revolution, this will cause the rest of the system to compensate by rotating in the opposite direction. This will cause a rotation in the relative positions of the two chains, without changing the total angular momentum. Therefore, in the limit of long collision times, the relative orientation of the two chains is not conserved and the final direction should be isotropic.

In terms of the variable

$$z \equiv \cos\theta, \quad (18)$$

the distribution of z should be uniform. For this reason we will use z rather than θ to characterize the results of the simulations discussed below.

Note that the above consideration could apply to any large molecules undergoing collisions, not just polymers. The only thing required is that they remain in contact for sufficiently long that thermal equilibrium is established.

D. Simulation

We model self-avoiding chains as was done previously [3]. The distance between links is maintained at a constant value of $l = 1$. The chain is modeled as freely hinged and there is no chain stiffness. A repulsive potential between all monomers was included. If the distance between two monomers is r, their potential was taken to be $V(r) = 40[1 - (r/l)^2]^5$. For $r > l$, $V(r) = 0$. A diverging hard core was not used for the sake of efficiency. The potential at the center is very high, making chain crossing exceedingly unlikely and no chain crossing was observed.

Rigid links were chosen to avoid equilibration problems that can occur due to the quasi-one-dimensional nature of this system [12,13]. The simulation method solves Newton's laws for this system so all conservation laws are well satisfied. It also implements the rigid link constraints in an efficient way, using $O(N)$ operations for every integration step. The method is described in detail in Ref. [7]. Many collisions were studied with different initial configurations of the chains and their

statistics were analyzed. We took the initial center speed of chains to be 1, and $m = 1$. The time step for the simulations was 0.02.

The chains were initially equilibrated for many relaxation times. For example, for $N = 128$ the equilibration time was 40 000 steps. Then their velocities were made negligibly small by applying a large damping for many damping times so their final velocities were less than 10^{-8}. These chains were given their initial center-of-mass speeds $v_{c.m.,1,I} = 1$ in the direction between the two center of masses. This way there was no initial internal energy of the chains, corresponding to the limit of high relative collision velocity. The chains were initially separated by at least half of their total chain length. This ensures that they are well separated before a collision takes place. To obtain adequate statistics, many collisions, about 10^4, were used with different random initial conditions.

The length of time they remained in contact was determined by monitoring how the center-of-mass velocity $\mathbf{v}_{c.m.}$ changed. Before a collision, as the chains approach each other, $\mathbf{v}_{c.m.}$ remains constant, but then as soon as the chains collide, there will be a change in this velocity. The point where $\mathbf{v}_{c.m.}$ first changes signals the start of a collision. In order for a collision to be considered over, $\mathbf{v}_{c.m.}$ had to remain constant for all subsequent times. Time evolution was not stopped until the chains had completely separated from each. This was implemented by requiring that the evolution continue if there were two monomers from different chains that were closer than half their original separation at the start of the simulation. This eliminated the cases where the two chains appeared to have separated but later collided again. The final speeds were also recorded, as was the angle of deflection θ of the chains after the collision (again, with the convention that $\pi/2 > \theta \geqslant 0$ is forward scattering).

III. RESULTS

Figure 2 shows the distribution of scattering angles as a function of z, as defined in Eq. (18). For $N = 32$, there is more scattering backward, that is, in the direction of negative z.
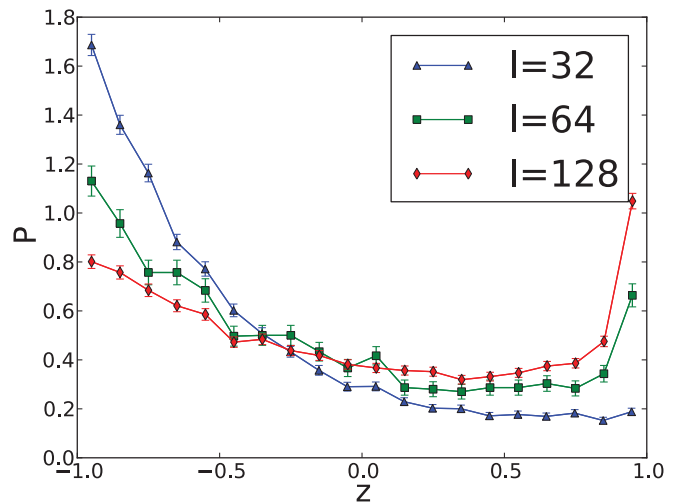

FIG. 2. (Color online) The distribution of scattering angles θ. The horizontal axis is $z = \cos\theta$. The highest curve on the left is for $N = 32$, the middle $N = 64$, and the lowest $N = 128$.
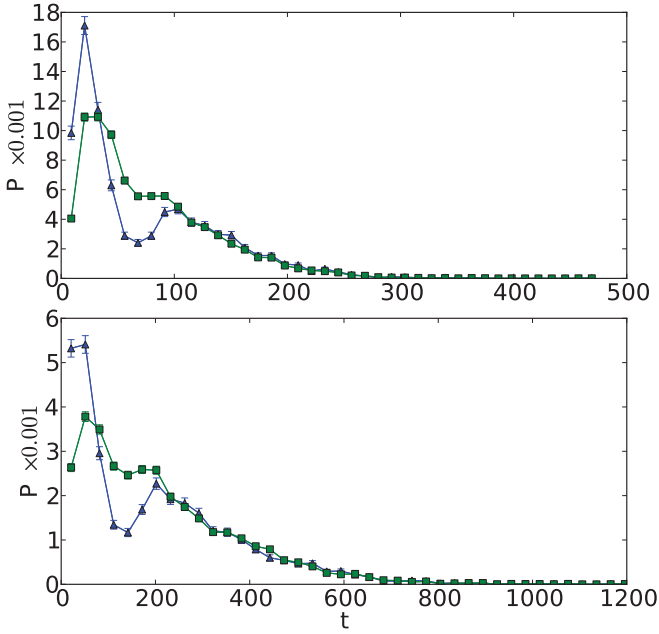
FIG. 3. (Color online) The distribution of collision times t for a chain with $N = 128$ (lower graph) and $N = 64$ (upper graph), and the same distribution excluding those where the scattering angle is greater than $\pi/2$. The latter distribution has a sizable dip at $t \approx 150$ for $N = 128$.

For larger N, this changes and for $N = 128$, the effect of backward scattering is much weaker. Instead, there is a strong peak for $z = 1$. This means that a substantial fraction of collisions deflect the polymers by a very small amount. We will discuss this further below.

Assuming an athermal model, the temperature given by Eq. (7) is $k_B T = 1/2$. The distribution of collision times is shown in Fig. 3 for $N = 128$ (lower graph) and $N = 64$ (upper graph). The average time computed from this distribution, for $N = 128$, is 210. This is comparable but larger than the equilibrium relaxation time $t_{\rm rel}$ seen for similar simulations of equilibrium systems. The latter was determined from measuring the time dependent autocorrelation function as has been described previously; see Ref. [3], Fig. 3. This suggests

that, during the majority of these collisions, the system should be close to thermal equilibrium. There are two sets of data shown on each plot in Fig. 3. One where all scattering angles are included (triangles), the second includes only forward scattering, $z > 0$ (squares). With only forward scattering, there is a prominent dip in the distribution at $t \approx 150$ ($N = 128$). For longer times, the two curves converge quite closely. The reason for this unusual small t behavior will also be discussed.

The distribution of final velocities is shown in Fig. 4(a). The smooth curve without error bars is a fit to the form expected in the thermal limit, Eq. (16). Note that there is a much longer tail in the simulation data. If, instead, one excludes strong forward scattering, $z > 0.9$, as shown in Fig. 4(b), the fit to the thermal distribution is much improved. The fit gives $\sigma_x = 0.064$, for $N = 128$, whereas the predicted value from Eq. (17), the thermal limit, is 0.044. This uses a value of $d_f = 2$, which is the number of kinetic degrees of freedom per monomer for this model because it has links of constant length. This value should be correct in the high-temperature limit. The distribution in Fig. 4(b) is still slightly too wide and this suggests that low final velocities are suppressed compared to the thermal prediction.

The distribution of the maximum end-to-end distances, R, occurring during scattering is shown in Fig. 5 for $N = 64$ and $N = 128$. There is typically substantial stretching that occurs during a collision. For comparison, statistics for the end-to-end distance R_e for $N = 128$ were calculated in thermal equilibrium for a total angular momentum of zero. The same chain has an rms end-to-end separation of $\sqrt{\langle R_e^2 \rangle} = 17.5$, However, the maximum in Fig. 5 is at $R = 38$ and has a significant tail stretching to past $R = 90$. After the chains have separated, the stretching will disappear and tend toward their equilibrium values.

To summarize what we have learned so far, collisions between self-avoiding chains in a vacuum appear be quite close to what one would expect in the thermal limit. For the longest chain studied, $N = 128$, the scattering is close to isotropic with the exception of a spike for strong forward scattering. The time that the chains remain in contact is typically longer than a relaxation time. The distribution of final speeds appears quite comparable to what one would expect from a thermal distribution except for collisions coming from strong forward
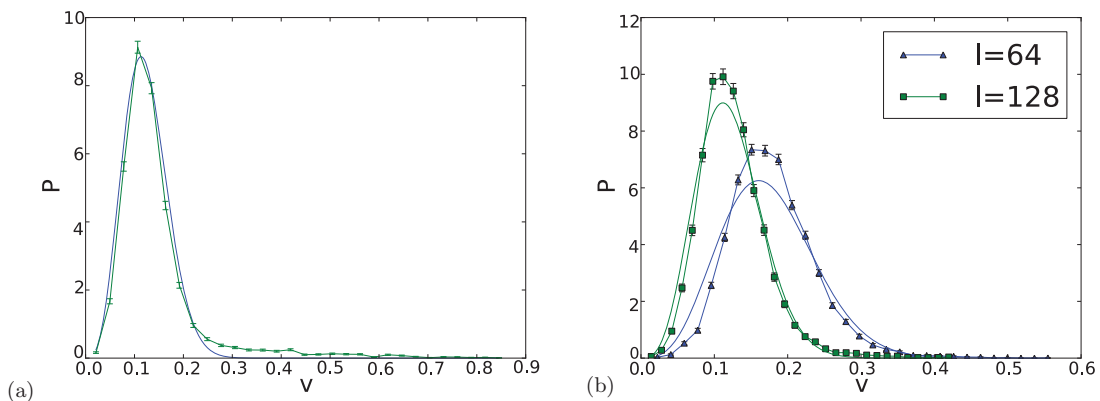

FIG. 4. (Color online) (a) The distribution of final collision speeds v, including all scattering angles and $N = 128$. (b) The same distribution ignoring those where $\cos\theta < 0.9$. For comparison the distribution for $L = 64$ is also shown. The smooth lines are fits to the data as described in the text.
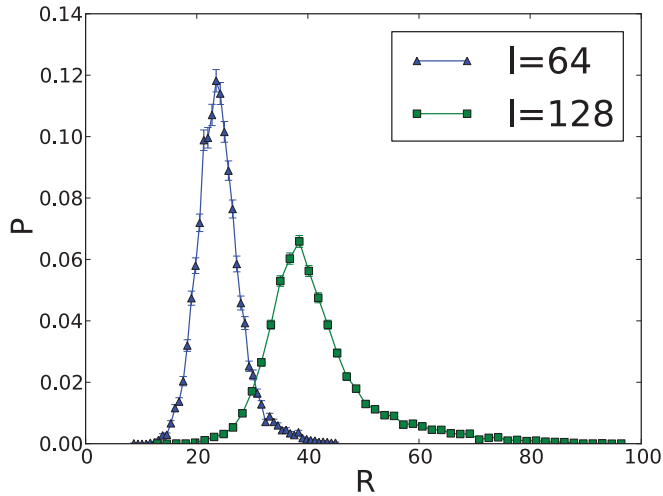
FIG. 5. (Color online) The distribution of the maximum end-to-end distances, R, occurring during scattering for chains with $N = 64$ and 128.

scattering. Finally, at some point while the chains are in a collision, they are typically quite stretched.

From this it appears that these chain collisions are highly inelastic and they have properties close to that of collisions in the thermal limit. However, there are some interesting deviations from this limit as was noted above. There appears to be a fraction of collision where the angle of scattering is very small. If these chains are excluded, then the collisions have statistics much closer to that of the thermal limit. A simple explanation for this would be that this subpopulation of chains are not actually colliding. However, their final velocities differ substantially from their initial ones, so this effect is clearly more subtle. By observing such strong forward-scattering collisions it appears that their behavior can be understood as follows.

The dynamics of chains during collisions can be understood in terms of two factors, entanglement effects and transfer

of momentum. During strong forward-scattering collisions, it appears from visualizations that the chains do strongly collide but only weakly entangle. Different parts of the chains come into contact and when they do, these parts collide very inelastically. That is, they do not bounce off one another but remain in contact for some length of time. Therefore momentum transfer between the chains is still inelastic. If two inelastic masses collide, even with unequal mass, their final velocity will still be along the same line as the initial velocities. Therefore, all such inelastic collisions do not change the final direction. Because the chains have not entangled, they move past each other but have not remained in contact long enough to thermalize. Their final directions are almost unchanged but their speeds have been substantially reduced due to momentum transfer.

The above observations can be seen by examining two dimensional distributions, for $N = 128$ in Fig. 6. In Fig. 6(a), the distribution of collisions is binned in terms of final collision speed, v, and z. One can see that for strong forward scattering, $z \approx 1$, there are a large number of collisions with final speeds much larger than the thermal velocity. In Fig. 6(b), the distribution of collisions is binned as a function of collision time t and z. Again, for strong forward scattering, there is a high peak for atypically short times, indicating that the collisions are weaker than for other scattering angles. Therefore, these strong forward-scattering collisions are short and do not slow down the chains all the way to their thermal values.

The plots in Figs. 3 and 4 are obtainable from these two-dimensional distributions. The enhancement in short time collision frequency seen in Fig. 3 for $z > 0$ is therefore caused by the subset of strong forward-scattering collisions, discussed above, that collide only for short times. All other collisions that more completely thermalize usually remain in contact for longer times. The fact that there is a dip in the distribution of Fig. 3 when considering collisions with $z > 0$ suggests that the quasithermal chains having $z > 0$ have a peak in their collision time distribution at $t \approx 200$.
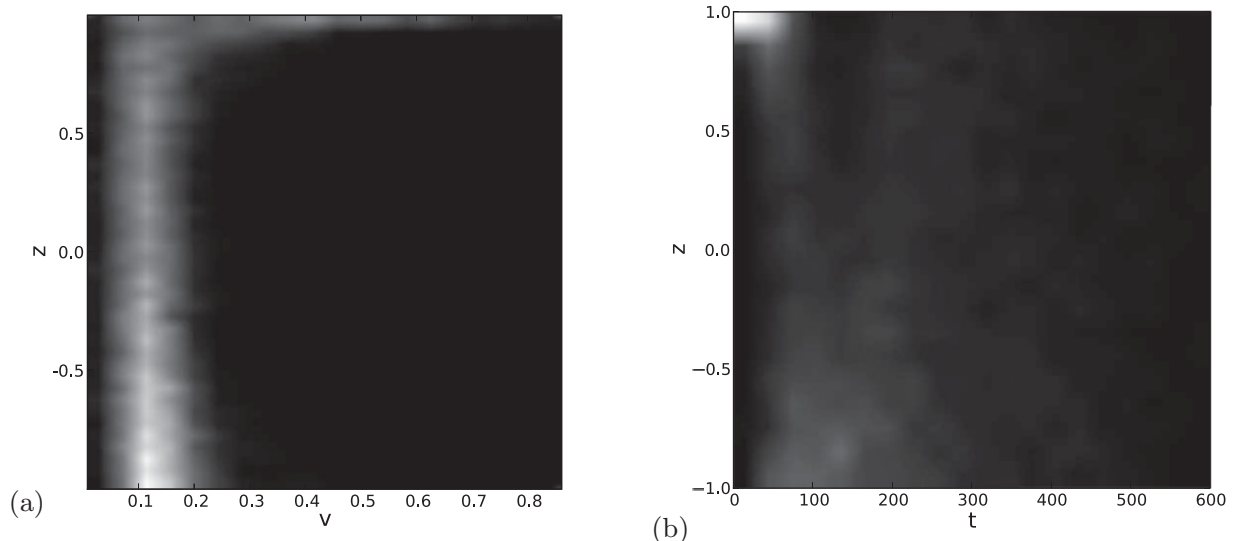

FIG. 6. (a) The probability density as a function of final speed v, and the amount of deflection $z = \cos\theta$. (b) The probability density as a function of collision time t, and the amount of deflection $z = \cos\theta$.
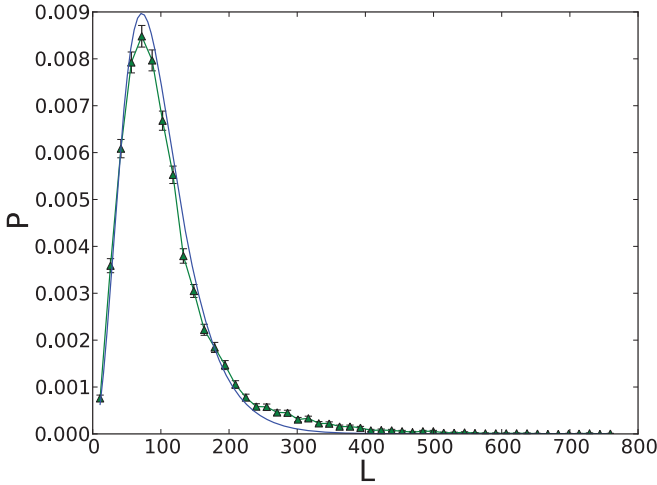
FIG. 7. (Color online) (a) The normalized distribution of angular momentum for chains of length $N = 128$ is shown (triangles) and a fit to the data as described in the text is shown by the smooth curve.

The distribution of angular momentum of the center of mass of a chain after a collision is shown for $N = 128$ in Fig. 7. Note that the distribution goes to zero for small values of L because we are considering the distribution of the *magnitude* of the angular momentum analogous to the Maxwell distribution of speeds. However, the three-dimensional distribution of the angular momentum is not expected to be Gaussian. It has already been calculated exactly for a gas of noninteracting phantom chains in a vacuum [14]. The normalized distribution of angular momentum was shown to be

$$P(L')dL' = \frac{\pi^2 L'}{8} \frac{\tanh\left(L'\frac{\pi}{4}\right)}{\cosh^2\left(L'\frac{\pi}{4}\right)} dL', \qquad (19)$$

where L' is proportional to the magnitude of the normalized angular momentum $L' = \alpha L$, with α given by

$$\alpha = \frac{\sqrt{12}}{Nl\sqrt{mT}}. \qquad (20)$$

The most important qualitative difference between this and a three-dimensional Gaussian distribution is that this distribution decreases exponentially with large L. The exact form of this for a self-avoiding walk is not known but is expected to have a similar dependence on L. Indeed, for the case of a self-avoiding polymer ring it was shown [4] that for large L, $\ln[P(L)] \sim -L^{10/9}$. Therefore Eq. (19) was used to fit the data in Fig. 7 instead of a three-dimensional Gaussian distribution but with α as an adjustable parameter. Denoting the fitted value of α by α_d, we find that $\alpha_d/\alpha = 0.47$. Therefore, the theoretical estimate assuming the thermal limit and phantom chains is about a factor of 2 from the simulation data. Despite this lack of quantitative agreement, the fit by Eq. (19) is closer to that of a three-dimensional Gaussian distribution.

IV. EFFECTS OF FIELD

In the above analysis, we have assumed that there is no external electric field acting on the chains, which meant that we could use conservation of energy and conservation of momentum. Both of these are not conserved when a field is applied. We now examine to what extent an external field changes the energy and momentum of the system.

The external field is typically quite high, of order $E = 2 \times 10^4$ V/m. If the collision times are sufficiently long, energy and momentum gained from the external field will invalidate both conservation laws. To estimate the size of this effect, we note that the collision time is typically of the same order as the relaxation time. We found previously [3] that the relaxation time is of order the time it takes the chain to travel its own radius of gyration, with a velocity being given by the root-mean-square velocity for the chain's center of mass in thermal equilibrium.

The typical amount of ionization is of order one electronic charge e, therefore, the change in energy due to the external field $\Delta U \sim eER_g$. This should be compared with the thermal energy E_T in the chain which is proportional to the number of degrees of freedom of the whole chain and k_BT, that is, $E_T \sim Nd_f k_BT$. Therefore, the ratio is

$$\frac{\Delta U}{E_T} \sim \frac{eER_g}{Nd_f k_BT}. \qquad (21)$$

Because these chains are self-avoiding $R_g \sim lN^{3/5}$, where for proteins and many polymers, $l \sim 10^{-9}$ m. Conservatively taking T to be approximately room temperature, $k_BT \approx 1/40$ eV, and $d_f = 1$, we have that $\Delta U/E_T \approx 10^{-3}/N^{0.4}$. As is evident, the effect of the field is small under these conditions. In addition it becomes even smaller for a molecule having a larger number of degrees of freedom per monomer, d_f, as one would have with a protein molecule. Higher temperature also decreases the size of the effect. However, longer collision times imply that the numerator should be increased. But because collision times are still of the same order as the relaxation time, this does not invalidate this analysis. Therefore the external field in realistic cases only weakly breaks conservation of energy.

Similarly we can estimate to what extent the momentum is altered by the external field. Typical thermal momentum P_T for a chain is

$$P_T^2 \sim 2Mk_BT, \qquad (22)$$

where M is the total mass of the chain. The center-of-mass momentum due to the external field P_E is $P_E^2 = 2\Delta UM$. Therefore, using the above estimates for different experimental parameters,

$$\frac{P_E^2}{P_T^2} \sim \frac{\Delta U}{k_BT} \sim \frac{eER_g}{k_BT} \approx N^{0.6}10^{-3}. \qquad (23)$$

Therefore, for large chains the additional momentum will always dominate the collisional momentum and must therefore be taken into account. However, the crossover to that regime occurs when $N = 10^5$ monomers. For most applications, the number of monomer units $N < 500$ and the effect of the field is not important. As mentioned above, higher temperatures will decrease the importance of momentum nonconservation.

The model used here should best apply to singly ionized chains. Multiple charges on a polymer will lead to strong repulsive forces that will cause stretching and alter equilibrium properties. Although this situation can also be modeled [3], it

leads to additional parameters that makes the analysis much more complex.

V. DISCUSSION

It is of interest to examine the scaling of collisions with N. The radius of gyration of a swollen chain is $R \sim N^\nu$ with $\nu \approx 3/5$ in three dimensions. According to our assumption that the initial kinetic energy of the chains are zero, the probability that a monomer from chain A will collide with chain B is obtained by looking at the projection of the density of chain B into a two-dimensional plane. The average density of this projection is proportional to the probability of a collision. The projected density is proportional to $N/R^2 \sim N^{1-2\nu} \approx N^{-1/5}$. Therefore as $N \to \infty$ the probability that a given monomer in chain A will collide with chain B goes to zero. On the other hand, the total number of contact points in chain A is $N^{4/5}$. Therefore, for large N, the molecules will suffer a collision but the above argument suggests that the number of monomers actually making contact will be a small fraction of the total.

If the amount of time that these points remain in contact is not long enough, the chains will pass each other at some reduced center-of-mass velocities. If the collisions of contact points are highly inelastic, only the speed of the chains, but not their direction, will change. Entanglements will change the above arguments considerably. Only one entanglement between two chains can cause their relative velocity to go to zero. For long-enough chains, one would expect that entanglements would then dominate the collisions. However, their effects usually become dominant only for chains larger than $N \approx 500$, as has been seen with the study of topological effects in flexible polymer rings [15]. To understand the details of the dynamics of these collisions analytically is particularly difficult in light of the topological nature of the interactions and is beyond the scope of the present work. I would hypothesize that the effects of entanglements will strongly suppress these forward-scattering collisions for long-enough chains.

If the chains are of different sizes, then their behavior will depend on their relative sizes. From the above discussion, the probability that a single monomer will collide with a polymer of N_1 links is $\propto N_1^{-1/5}$. Therefore, if a second polymer is of length $N_2 < N_1$, the probability of one collision is approximately $\propto N_2/N_1^{1/5}$. In other words, the second molecule is unlikely to collide if $N_2 \ll N_1^{1/5}$. For chains of comparable sizes, the above results suggest that collisions will still be strongly inelastic and will also show behavior close to the thermal limit. The departure from this due to forward scattering will increase as the mass difference increases.

VI. CONCLUSIONS

In this work, collisions between polymers in a vacuum have been examined. This is quite an unusual situation because collisions typically occur between much smaller molecules, and, consequently, new features of this situation are expected. The focus here is on chains where the initial relative center-of-mass velocity is so large that the initial internal thermal energy of the molecule can be ignored. This is an interesting limit to consider because for athermal chains, the magnitude of the initial velocity factors out.

Typically, in a collision of such long molecules, they remain in contact for long enough to be close to equilibrium so they can be described by thermal averages. The final velocities and scattering angles are close to such averages. However, the main discrepancy with this description is due to a class of collisions that strongly forward scatter and remain in contact for a relatively short amount of time. This is evidence of strongly inelastic collisions of subsections of the chains. It is expected that for long-enough chains, $N > 500$ entanglement effects will diminish the frequency of these kinds of collisions.

The behavior as a function of initial center-of-mass angular momentum has not yet been investigated. When this quantity is large, it is expected to lead to chain configurations that are highly stretched [4] as a result of angular momentum conservation and could also lead to interesting behavior during the collision.

In future work, it would be interesting to consider the case of chains with strong attractive forces as this may also be relevant to experiments and has interesting physical consequences. For example, chains at temperatures that are initially below the coil-globule transition will tend to stick together for low-enough relative velocities. However, beyond a threshold velocity, they would be expected to heat enough on impact to become swollen and then separate from each other.

[1] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1985).

[2] F. Hillenkamp and J. Peter-Katalinic (eds.), *MALDI MS: A Practical Guide to Instrumentation, Methods and Applications* (Wiley, New York, 2007).

[3] J. M. Deutsch, Phys. Rev. Lett. **99**, 238301 (2007).

[4] J. M. Deutsch, Phys. Rev. E **77**, 051804 (2008).

[5] A. Mossa, M. Pettini, and C. Clementi, Phys. Rev. E **74**, 041805 (2006).

[6] M. P. Taylor, K. Isik, and J. Luettmer-Strathmann, Phys. Rev. E **78**, 051805 (2008).

[7] J. M. Deutsch, Phys. Rev. E **81**, 061804 (2010).

[8] C. A. Barnes and N. H. L. Chiu, Int. J. Mass Spectrom. **279**, 170 (2009).

[9] J. H. Moon, S. H. Yoon, and M. S. Kim, Bull. Korean Chem. Soc. **26**, 763 (2005).

[10] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), p. 248.

[11] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), Sec. 12, Chap. 7, p. 273.

[12] E. Fermi, J. Pasta, and S. Ulam, Los Alamos Document LA-1940, 1955.

[13] For a review, see G. P. Berman and F. M. Izrailev, Chaos **15**, 015104 (2005), and references therein.

[14] M. Brunner and J. M. Deutsch, Phys. Rev. E, e-print arXiv:1008.3668v1 [cond-mat.soft] (in press).

[15] J. M. Deutsch, Phys. Rev. E **59**, R2539 (1999).