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# Molecular Dynamics Simulation of a Polymer Chain in Solution by Collisional Dynamics Method

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## ABSTRACT

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This article describes the collisional dynamics (CD) method adapted for molecules with geometrical constraints within a description using Cartesian coordinates for the atoms. In the CD method, stochastic collisions with virtual particles are included in usual molecular dynamics simulations to couple the considered polymer molecule to a solvent. The actual presence of the solvent is not explicitly included in the simulation. The results of CD simulations of a polymer chain immersed in the time-dependent elongational flow field are presented. The influence of nonbonded interactions on the coil-stretch transition of the chain occurring in the flow is discussed. © 1996 John Wiley & Sons, Inc.

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## Introduction

Computer simulation techniques represent an active area of research for understanding of the behavior of macromolecules in solution. Molecular dynamics (MD) simulations of polymers provide the most detailed information for theoretical investigations of their structural and dynamical properties. In a usual MD approach, the dynamics of the solvent molecules as well as the polymer

molecules are simulated explicitly. However, the available computer time imposes restrictions on its application: only short polymer chains (about 20 atoms) can be considered during short simulation times.<sup>1-3</sup> These restrictions can be eliminated by treating explicitly only one polymer molecule, whereas the solvent molecules are represented implicitly by their stochastic influence on the simulated molecule. The variety of models has been used for both a polymer molecule<sup>4</sup> and the molecule coupling to the solvent, treated as an external heat bath.<sup>5,6</sup> We used the polymer model in which atoms are joined together by a fixed bond length and, perhaps, bond angles. The excluded

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volume effects are included in the model when the polymer atoms are allowed to interact with one another via a prescribed potential. As a rule, the interaction potential is of a Lennard-Jones type. The potential may incorporate the potential of mean force due to interaction with the solvent. To couple the polymer molecule to an external heat bath without explicitly simulating solvent molecules, we used the collisional dynamics (CD) method.<sup>7,8</sup> The CD method is a modification of that suggested by Andersen<sup>9</sup> and Ryckaert and Ciccotti.<sup>10</sup> In both methods, Cartesian atomic velocities are modified instantaneously at random times. The difference between Andersen's method and collisional dynamics is based on the way in which velocity jumps are realized. In the first method, new velocities are chosen at random from the momenta part of the canonical ensemble distribution and are independent of those before a jump. In collisional dynamics, the choice of new velocities depends on the point in phase space, where the jump occurs. They are calculated as a result of collision with a virtual bath particle. Andersen's random assignment of the new velocities ignores velocity autocorrelation and yields artificial dynamics. The CD method seems to be more accurate in mimicking the dynamical coupling to the solvent, and yields more realistic dynamical behavior of the simulated molecule. The relation between the CD method and some other closely related MD methods is discussed elsewhere.<sup>11,12</sup>

The main goal of this article is to describe an algorithm of the CD method for molecules with geometrical constraints using the Cartesian coordinate approach. The implementation of the CD method differs from that of Andersen,<sup>10</sup> especially in the case of constrained molecules. The collisions can be easily combined with a standard MD program performing the numerical integration of the Cartesian equations of motions. The use of the constraints introduces new problems, both in the computational scheme and in the velocity modification, due to the collisions (a collisional problem). Two methods have been proposed for integrating the Cartesian equations of motion for a system subjected to holonomic constraints<sup>13</sup>: the matrix method and the SHAKE method. In this work we used the original version of the matrix method developed by Balabaev et al.<sup>14,15</sup> The method has been efficiently used for several years and has proved to be a numerically stable one. The CD simulations for molecules with constraints require the collisional problem to be solved. To achieve

this, changes in velocities of the atoms due to the impulsive force should be found. Such a change in velocities has been implicitly reported in Stratt et al.<sup>16</sup> That study presents an exact procedure for treating the molecular dynamics of holonomically constrained systems in the presence of impulsive forces. The same result was obtained in a different manner by Lemak.<sup>7</sup> The algorithm for performing CD for molecules with constraints and some details of its implementation are presented in the following sections.

Our current interest concerns the behavior of a polymer molecule in a hydrodynamic flow. The polymer molecule in a solution responds to the applied hydrodynamic forces by its stretching and orienting. The flow-induced stretching and orientation of the polymer in a dilute solution are thought to be responsible for the existence of important macroscopically observable phenomena. For example, even very low concentrations of a polymer can cause a substantial decrease of the drag in turbulent flows and an increase of the drag in flows through porous media.<sup>17</sup> The first results on simulation of a polymer chain in an elongational flow by the CD method are reported in Balabaev and Lemak.<sup>8</sup> In this article, we present further results including the comparison of chain behavior, which depends on whether or not the attractive forces are included in the polymer model.

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## Method

### SYSTEM UNDER SIMULATION

A polymer molecule is considered as an assembly of  $N$  atomic point masses connected by  $M$  internal geometrical constraints. The constraints are assumed to be holonomic and they may be represented in terms of fixed distances between certain atoms. For example, bond lengths and angles in a linear chain polymer may be constrained by fixing the distance between neighboring atoms and those separated by one atom.

Let  $\mathbf{r}_i(t)$  and  $\mathbf{v}_i(t)$  be positions and velocities of atoms at time  $t$ ,  $m_i$  be atomic masses,  $i = 1, \dots, N$ . When atoms  $i_\alpha$  and  $j_\alpha$  are connected by a bond of fixed length,  $l_\alpha$ , the constraint:

$$(\mathbf{r}_{j_\alpha} - \mathbf{r}_{i_\alpha})^2 - l_\alpha^2 = 0 \quad (1)$$

holds at all times. Here,  $\alpha$  varies from 1 to  $M$ ,

specifying a particular constrained bond. The vector of the bond number  $\alpha$  is defined as:

$$\mathbf{c}_\alpha = \mathbf{r}_{j_\alpha} - \mathbf{r}_{i_\alpha} \quad (2)$$

The set of the imposed constraints can be specified by the following matrix:

$$s_i^\alpha = \delta_{i_\alpha}^i - \delta_{j_\alpha}^i$$

$$= \begin{cases} 0, & \text{the atom } i \text{ is not connected} \\ & \text{by the bond } \alpha \\ 1, & \text{the bond } \alpha \text{ goes out from} \\ & \text{the atom } i \text{ (} i = i_\alpha \text{)} \\ -1, & \text{the bond } \alpha \text{ goes into the} \\ & \text{atom } i \text{ (} i = j_\alpha \text{)} \end{cases} \quad (3)$$

Index  $i$  specifies an atom and index  $\alpha$  specifies a bond, whereas  $\delta_j^i$  represents Kronecker's delta:  $\delta_j^i = 1$  if  $i = j$ , and  $\delta_j^i = 0$  otherwise.

All atoms of the polymer molecule interact with the potential energy  $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ . The molecule is also supposed to couple to an external heat bath.

### COLLISIONAL DYNAMICS METHOD

In the collisional dynamics method, the coupling to a bath is simulated by collisions with virtual bath atoms. Each stochastic collision is an instantaneous event. Collisions occur in accordance with a Poisson process and the times at which different atoms suffer collisions are statistically uncorrelated. Between stochastic collisions, the system evolves in accordance with the equations of motion as in the usual molecular dynamics. The Lagrangian equations of motion for the molecule under constraints (1) in Cartesian coordinates are:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = - \frac{\partial U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\partial \mathbf{r}_i} - \sum_{\alpha=1}^M \mu_\alpha s_i^\alpha \mathbf{c}_\alpha \quad (4)$$

with Lagrangian multiples,  $\mu_\alpha$ , to be determined by the constraint relations (1). Because the collisions are instantaneous, they do not allow coordinates to change and thus affect only the velocities. The postcollision velocities are found by solving the collisional problem. In this problem, the velocity,  $\mathbf{v}_o$ , of the bath particle is chosen at random from the Gaussian distribution with the following

moments:

$$\langle \mathbf{v}_o \rangle = \mathbf{w} \quad (5)$$

$$\langle (v_o^i - w^i)(v_o^k - w^k) \rangle = \frac{k_B T_o}{m_o} \delta_k^i, \quad i, k = 1, 2, 3 \quad (6)$$

Here,  $m_o$  is a mass of the bath particle,  $T_o$  is the bath temperature, and parameter  $\mathbf{w}$  is considered as a macroscopic velocity of the bath. The nonzero value of  $\mathbf{w}$  means that the bath is in the state of a hydrodynamical flow with the velocity  $\mathbf{w}$ .

### COLLISIONAL PROBLEM

Suppose the bath atom collides with an atom number  $s$  at the time  $t_u$ . The problem is to find a way to use the coordinates and velocities before the collision to calculate the postcollision velocities. It should be noted that the position of the bath atom coincides with the position of the atom number  $s$ . If there are no constraints, the collision modifies only the velocity of atom  $s$  in a well-known manner<sup>18</sup>:

$$[\mathbf{v}_s] = \frac{2}{1 + m/m_o} ((\mathbf{v}_o - \mathbf{v}_s) \cdot \mathbf{n}) \mathbf{n}$$

Here  $[\mathbf{v}_s]$  denotes a jump of the velocity at the time  $t_u$  and the bath atom is numbered by  $o$ . The vector  $\mathbf{n}$  shows the direction of the momentum transfer during the collision.

In the case considered here, the velocities of all atoms of the molecule are modified because of the constraints. There are seven relationships used to find new velocities: conservation laws of energy, momentum, and angular momentum of the system, which consists of a molecule and a bath atom. Only six of them are independent. Three equations can be used to find new velocities of the bath atom. The velocities of the molecule atoms are determined from three other equations. When a molecule consists of more than one atom, it has more than four independent velocities. Hence, there are more unknown variables than equations for them. A unique solution can be found if all the jumps  $[\mathbf{v}_i]$  of the atomic velocities of the molecule are expressed via only three independent variables.

An instantaneous change in the atomic velocities of the molecule can be considered as a result of some impulse,  $\mathbf{P}_s = f_s \mathbf{n} \delta(t - t_u)$ , with  $|\mathbf{n}| = 1$ , which acts on the atom number  $s$ . The jump in velocities due to the impulse  $\mathbf{P}_s$  may be derived

from the equations of motion (4) with the constraints (1)<sup>7</sup>:

$$[\mathbf{v}_i] = \frac{f_s}{m_\alpha} \mathbf{d}_i(\mathbf{n}, \mathbf{r}_1, \dots, \mathbf{r}_N, m_1, \dots, m_N) \quad (7)$$

with:

$$\mathbf{d}_i = \sum_{\alpha=1}^M s_i^\alpha \hat{\boldsymbol{\mu}}_\alpha \mathbf{c}_\alpha + \mathbf{n} \delta_s^i \quad (8)$$

In order to find the Lagrangian multiples  $\hat{\boldsymbol{\mu}}_\alpha$ , the following system of  $M$  linear equations must be solved:

$$\sum_{\beta=1}^M A^{\alpha\beta} \hat{\boldsymbol{\mu}}_\beta = \hat{h}_\alpha \quad \alpha = 1, \dots, M \quad (9)$$

where:

$$A^{\alpha\beta} = \left( \frac{1}{m_{j_\alpha}} s_{j_\alpha}^\beta - \frac{1}{m_{i_\alpha}} s_{i_\alpha}^\beta \right) (\mathbf{c}_\alpha \cdot \mathbf{c}_\beta),$$

$$\hat{h}_\alpha = (\mathbf{c}_\alpha \cdot \mathbf{n}) s_s^\alpha / m_s \quad (10)$$

Now we assume that the collision of the molecule with a bath atom is equivalent to the action of an impulse unknown beforehand. This actually indicates three independent variables (a power  $\mathbf{P}_s$  of the impulse) via which the jumps of the velocities of all the atoms in the molecule are expressed. If the multiples,  $\hat{\boldsymbol{\mu}}_\alpha$ , are known, the unknown variables  $\mathbf{P}_s$  and  $[\mathbf{v}_0]$  can be calculated from the conservation laws. As a result<sup>7</sup>:

$$f_s = q_s \left( \sum_{i=1}^N (\mathbf{d}_i \cdot \mathbf{v}_i) - (\mathbf{v}_0 \cdot \mathbf{n}) \right) \quad (11)$$

with:

$$q_s = -2 \left( \sum_{i=1}^N d_i^2 / m_i + 1 / m_o \right)^{-1}$$

Note that the power of an impulse depends on molecular conformation and on the atom that is affected by the impulse.

The direction of the impulse  $\mathbf{n}$  remains indefinite in the present statement of the collisional problem. Hence, the jumps in the velocities are found with an accuracy in any direction  $\mathbf{n}$ , as in the classical nonelastic collision problem.<sup>18</sup> To find the vector  $\mathbf{n}$ , the geometry of the collision and the law of interaction between collided atoms should be specified in more detail. Our choice of the

direction  $\mathbf{n}$  is based on the assumption that the velocity of the bath atom has an opposite direction after collision in the frame of reference where the atom  $s$  is at rest before the collision. The velocity jump of the bath atom is calculated as<sup>7</sup>:

$$[\mathbf{v}_o] = -\frac{f_s}{m_o} \mathbf{n}$$

Thus, the above assumption leads to:

$$\mathbf{n} = (\mathbf{v}_o - \mathbf{v}_s) / |\mathbf{v}_o - \mathbf{v}_s| \quad (12)$$

In fact, the choice of vector  $\mathbf{n}$  is a parameter of the CD method. We believe that the proposed choice of  $\mathbf{n}$  is quite reasonable when a generalized mechanism to couple the system to a bath is used. Special investigations are required to analyze what way of choosing  $\mathbf{n}$  is appropriate for solving a particular problem.

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## Implementation Details

We use the "leap frog" form of the Verlet algorithm to solve the equations of motion numerically.<sup>19</sup> Coupling to a bath by the collisions with virtual atoms can be easily incorporated into this algorithm. As a result, the following three operations should be performed at every integration time step  $\Delta t$ .

Given coordinates  $\mathbf{r}_i(t)$  and velocities  $\mathbf{v}_i(t - \frac{1}{2} \Delta t)$  for all atoms in molecule, which satisfy the constraints:

- (i) Compute velocities  $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$  satisfying the constraints.
- (ii) Modify velocities  $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$  due to the collisions that the molecule has suffered during the time interval  $(t, t + \Delta t)$ .
- (iii) Compute new coordinates  $\mathbf{r}_i(t + \Delta t)$  by:
 
$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t + \frac{1}{2} \Delta t) \Delta t \quad (13)$$
- (iv) Go to the next time step.

The first two operations are discussed below in more detail.

### COMPUTATION OF CONSTRAINED VELOCITIES $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$

Computation of the velocities  $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$  in accordance with the Verlet algorithm is complicated by constraints. It is required to solve a non-

linear system of equations that is obtained from eqs. (1) and (4) using:

$$\frac{d^2 \mathbf{r}_i(t)}{dt^2} \approx \frac{1}{\Delta t^2} (\mathbf{r}_i(t + \Delta t) - 2\mathbf{r}_i(t) + \mathbf{r}_i(t - \Delta t))$$

and:

$$\mathbf{v}_i \left( t + \frac{1}{2} \Delta t \right) \approx \frac{1}{\Delta t} (\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t))$$

Now we introduce the following notations:

$$\Phi_i(t) = \mathbf{v}_i \left( t - \frac{1}{2} \Delta t \right) - \frac{\Delta t}{m_i} \frac{\partial U(\mathbf{r}_1(t), \dots, \mathbf{r}_N(t))}{\partial \mathbf{r}_i} \quad (14)$$

$$\mathbf{v}_i = \mathbf{v}_i \left( t + \frac{1}{2} \Delta t \right) \quad (15)$$

Then, the nonlinear system takes the form:

$$\mathbf{v}_i = \Phi_i(t) - \frac{\Delta t}{m_i} \sum_{\alpha=1}^M \mu_\alpha s_i^\alpha \mathbf{c}_\alpha(t) \quad (16)$$

$$i = 1, 2, \dots, N,$$

$$2\mathbf{c}_\alpha(t) \cdot (\mathbf{v}_{j_\alpha} - \mathbf{v}_{i_\alpha}) + \Delta t (\mathbf{v}_{j_\alpha} - \mathbf{v}_{i_\alpha})^2 = 0 \quad (17)$$

$$\alpha = 1, 2, \dots, M$$

Here the unknown variables are the velocities,  $\mathbf{v}_i$ , and a set of Lagrangian multipliers,  $\mu_\alpha$ .

The nonlinear system of equations can be solved if its root is approximated well enough. Then the root can be obtained by some iteration process. In the numerical integration of the equations of motions we are performing step by step in time. If the time step  $\Delta t$  is sufficiently small, a good initial approximation for positions of the atoms is given by positions in the preceding step, that is,  $\mathbf{r}_i^{(0)}(t + \Delta t) = \mathbf{r}_i(t)$ . The corresponding initial approximation for the velocities  $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$  is  $\mathbf{v}_i^{(0)} = O$ .

In the Newtonian iteration process, at each iteration, a linear system of equations should be solved to find a new approximation of the root. In our case, the linear system derived from eqs. (16) and (17) has the following form:

$$\mathbf{v}_i^{(k)} = \Phi_i(t) - \frac{\Delta t}{m_i} \sum_{\alpha=1}^M \mu_\alpha^{(k)} s_i^\alpha \mathbf{c}_\alpha \quad (18)$$

$$(\mathbf{v}_{j_\alpha}^{(k)} - \mathbf{v}_{i_\alpha}^{(k)}) \cdot (\mathbf{c}_\alpha + \Delta t \mathbf{u}_\alpha^{(k-1)}) = \frac{\Delta t}{2} \mathbf{u}_\alpha^{(k-1)} \cdot \mathbf{u}_\alpha^{(k-1)} \quad (19)$$

where:

$$\mathbf{u}_\alpha^{(k-1)} = (\mathbf{v}_{j_\alpha}^{(k-1)} - \mathbf{v}_{i_\alpha}^{(k-1)})$$

Here, unknown  $\mathbf{v}_i^{(k)}$  and  $\mu_\alpha^{(k)}$  values are approximations at the  $k$  iteration step, while  $\mathbf{v}_i^{(k-1)}$  values are supposed to be known.  $\mathbf{v}_i^{(k)}$  can be found from eqs. (18) and (19) in two steps. First, by substituting eq. (18) in eq. (19) the following linear system of equations for  $\mu_\alpha^{(k)}$  is obtained:

$$\sum_{\beta=1}^M B^{\alpha\beta} \mu_\beta^{(k)} = h^\alpha \quad \alpha = 1, \dots, M \quad (20)$$

where:

$$B^{\alpha\beta} = \left( \frac{1}{m_{j_\alpha}} s_{j_\alpha}^\beta - \frac{1}{m_{i_\alpha}} s_{i_\alpha}^\beta \right) (\mathbf{c}_\alpha \cdot \mathbf{c}_\beta + \Delta t \mathbf{c}_\beta \cdot \mathbf{u}_\alpha^{(k-1)})$$

$$h^\alpha = \frac{1}{\Delta t} \mathbf{c}_\alpha \cdot \mathbf{q}_\alpha + \mathbf{u}_\alpha^{(k-1)} \cdot \left( \mathbf{q}_\alpha - \frac{1}{2} \mathbf{u}_\alpha^{(k-1)} \right)$$

$$\mathbf{q}_\alpha = (\Phi_{j_\alpha} - \Phi_{i_\alpha})$$

Second, the calculated solution of eq. (20) being substituted into (18) gives  $\mathbf{v}_i^{(k)}$ .

The Newtonian iteration process is stopped when an appropriate approximation of  $\mathbf{v}_i = \mathbf{v}_i(t + \frac{1}{2} \Delta t)$  is achieved. Experience shows that if the iteration process starts from  $\mathbf{v}_i^{(0)} = O$ , only a few iterations are necessary to achieve a good approximation of  $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$ .

## VELOCITY MODIFICATION DUE TO COLLISIONS

In collisional dynamics it is assumed that, during the time interval  $(t, t + \Delta t)$ , the molecule suffers collisions with virtual bath atoms. It is assumed that during this interval the atom positions do not change. The collisions lead to modification of the velocities  $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$  only. To simulate this process, the following operations should be fulfilled.

1. Find the number of collisions  $n_c(\Delta t)$  occurring during the time step  $\Delta t$ .  $n_c(\Delta t)$  is a random integer variable. The collisions occur in accordance with a Poisson process, which is specified by one parameter,  $\lambda$  (collisions frequency). Therefore, the probability of

$P_k(\Delta t)$ , meaning that just  $k$  collisions occur during time step  $\Delta t$ , is:

$$P_k(\Delta t) = \frac{(\Delta t)^k}{k!} \text{EXP}(-\lambda \Delta t) \quad (21)$$

So, to find  $n_c(\Delta t)$  at each step  $\Delta t$ , a random integer number is sampled from the probability distribution given by eq. (21).

2. For each of the  $n_c(\Delta t)$  successive collisions the atom number  $s$ , which collides with the virtual bath atom, is chosen from the uniform distribution.
3. Jumps in the velocities  $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$  due to the collision are found solving the collisional problem, as described previously. In eqs. (7)–(11)  $\mathbf{v}_i$  is replaced by  $\mathbf{v}_i(t + \frac{1}{2} \Delta t)$ , and  $\mathbf{c}_\alpha$  is evaluated using  $\mathbf{r}_i(t)$ .

It should be noted that, in collisional dynamics simulations, additional operations should be done to couple the molecule to a bath and to satisfy the constraints. The solving of the two linear systems of eqs. (9) and (20) consume the most additional operations. Both of these systems are to be solved more than once during each integration step. Matrices **A** and **B** are of the order of  $M$ ,  $M$  being the number of imposed constraints. Therefore, in a general case, a solution of both systems of eqs. (9) and (20) requires operations proportional to  $M^3$ . This makes the calculation for molecules with a large number of constraints progressively more difficult. The structure of the both matrices **A** and **B** is determined by the structure of matrix **I**:

$$\mathbf{I}^{\alpha\beta} = \frac{1}{m_{i_\alpha}} s_{j_\alpha}^\beta - \frac{1}{m_{i_\alpha}} s_{i_\alpha}^\beta$$

Matrix **I** reflects the topology of the net of the constrained distances between certain atoms in the molecule. In some important cases, matrix **I** has a special structure, which permits a reduction in the number of operations required for solving the linear system. For example, if in a linear polymer all valent bonds are fixed, the nonzero elements of matrix **I** are positioned only on the three central diagonals. For such a triangle matrix, the number of operations required to solve the corresponding linear system is proportional to  $M$ . Thus, in this case, an addition of constraints and coupling to an external bath does not perceptibly increase the required computer time, because only a minor

calculation proportional to the number of atoms in the polymer is added.

## Results and Discussion

To perform the collisional dynamics simulations, the value of parameters  $m_o, T_o, \lambda$  and function  $\mathbf{w}(\mathbf{r})$ , characterizing coupling to a bath, should be specified. Here,  $m_o$  is the mass of bath atoms,  $T_o$  is the prescribed bath temperature,  $\lambda$  is the collision frequency, and  $\mathbf{w}(\mathbf{r})$  is the velocity of the hydrodynamic flow of the bath. All these parameters have clear physical meaning. They influence molecular behavior in different ways. To test the effect of the coupling parameters, we have applied the collisional dynamics to simulations of a linear polymer chain consisting of 101 atoms connected by 100 bonds of a fixed length  $l$ . The atoms interact in pairs according to the repulsive (shifted) Lennard-Jones potential:

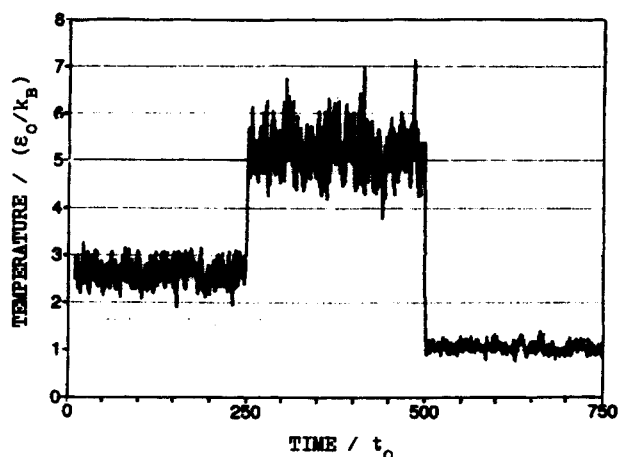
$$U_{LJ}^R(r_{ij}) = \begin{cases} U_{LJ}(r_{ij}) - U_{LJ}(R), & r \leq R \\ 0, & r > R \end{cases} \quad (22)$$

$U_{LJ}^R(r_{ij})$  is the potential energy of interaction of two atoms  $i$  and  $j$  at the distance  $r_{ij}$ ,  $R = 2^{1/6}\sigma$ , while  $U_{LJ}(r) = 4\varepsilon_o((\sigma/r)^{12} - (\sigma/r)^6)$  is a full Lennard-Jones (L-J) potential. At  $r = R$ , the potential  $U_{LJ}$  has its minimum  $U_{LJ} = -\varepsilon_o$ . The shifted L-J potential  $U_{LJ}^R$  takes into account the excluded volume in a convenient manner in that it is repulsive, short ranged, and continuous. All the atoms are assumed to have the same mass  $m$  and the same parameters  $\sigma$  and  $\varepsilon_o$  of the L-J potential. The calculations are performed in usual reduced units. Lengths are measured in units of  $\sigma$ , time in units of  $t_o = \sigma(m/\varepsilon_o)^{1/2}$ , and masses in units of  $m$ . In our calculations we used  $l = \sigma$ , and  $\Delta t = 0.005t_o$ .

We divide all our simulations into two groups corresponding to two distinct physical situations. In one group, determined by the condition  $\mathbf{w} = 0$ , the obtained trajectories are equilibrium ones, while in the other group, determined by  $\mathbf{w} \neq 0$ , the obtained trajectories are nonequilibrium ones.

### POLYMER CHAIN IN HEAT BATH

Let us suppose that  $\mathbf{w} = 0$ . The result of the collisional dynamics procedure will be a trajectory. Under the condition of irreducibility of the motion generated by the collisional dynamics procedure, the time average of any function  $F(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{v}_1, \dots, \mathbf{v}_N)$  calculated from the trajectory is equal



**FIGURE 1.** Behavior of instantaneous temperature of the polymer chain in CD simulation performed at the time-varying bath temperature  $T_o(t)$ :  $k_B T_o / \epsilon_o = 2.5$  for  $0 \leq t \leq 250t_o$ ; 5.0 for  $250 < t \leq 500t_o$ ; and 1.0 for  $500 < t \leq 750t_o$ . The coupling parameters are  $\lambda = 100t_o^{-1}$  and  $m_o = m$ .

to the ensemble average of  $F$  for a canonical ensemble at temperature  $T_o$ . This can be proved in the same manner as done by Andersen.<sup>9</sup> So, in this case the collisional dynamics yields configurations corresponding to the canonical distribution.

Figure 1 shows the evolution of the instantaneous temperature of the chain through the trajectory obtained at the time-varying  $T_o$  value. The first CD run was carried out at  $T_o = 2.5\epsilon_o \backslash k_B$ . Then the temperature of the bath was suddenly increased, initially from  $2.5\epsilon_o \backslash k_B$  to  $5.0\epsilon_o \backslash k_B$ , and then through a  $250t_o$  period to  $1.0\epsilon_o \backslash k_B$ . The chain temperature quickly relaxed to the new prescribed value  $T_o$  (within  $2t_o$  after the jumps) and fluctuated close to this value. The values of the rms fluctuations  $\delta T = (\langle (T - \langle T \rangle)^2 \rangle)^{1/2}$  were in

good agreement with the ones expected in the canonical ensemble (see Table I).

The results of using different  $\lambda$  and  $m_o$  values were compared at  $T_o = 2.5\epsilon_o \backslash k_B$ . Each run started at the same initial conditions and consisted of calculations of 20,000 time steps. The results of the calculated trajectory averages are listed in Table 1. The mean values of the kinetic energy and the energy fluctuations give almost the same results for different  $\lambda$  and  $m_o$  values. To check the dynamic quantity, the energy time autocorrelation function  $C_E(\tau) = \langle (E(t) - \langle E \rangle)(E(t + \tau) - \langle E \rangle) \rangle$  was calculated from various trajectories. Figure 2 shows a plot of the time evolution of the total energy autocorrelations for different  $\lambda$  and  $m_o$  values. It is seen that an alteration of  $\lambda$  and  $m_o$  changes the effective dumping coefficient.

The above CD simulation results demonstrate that the calculated trajectory averages are independent of the choice of  $\lambda$  and  $m_o$ . The time dependence of the fluctuations is very sensitive to  $\lambda$  and  $m_o$ .

The most difficulties arise with the choice of the parameter  $\lambda$  in CD calculations. There are two possible ways to estimate  $\lambda$ . One way involves estimating the collision frequency on the basis of the hard-sphere model of liquids. Another way is based on the relation between  $\lambda$  and the friction constant for an atom or monomer of a polymer.<sup>8,12</sup>

### POLYMER CHAIN IN ELONGATIONAL FLOW

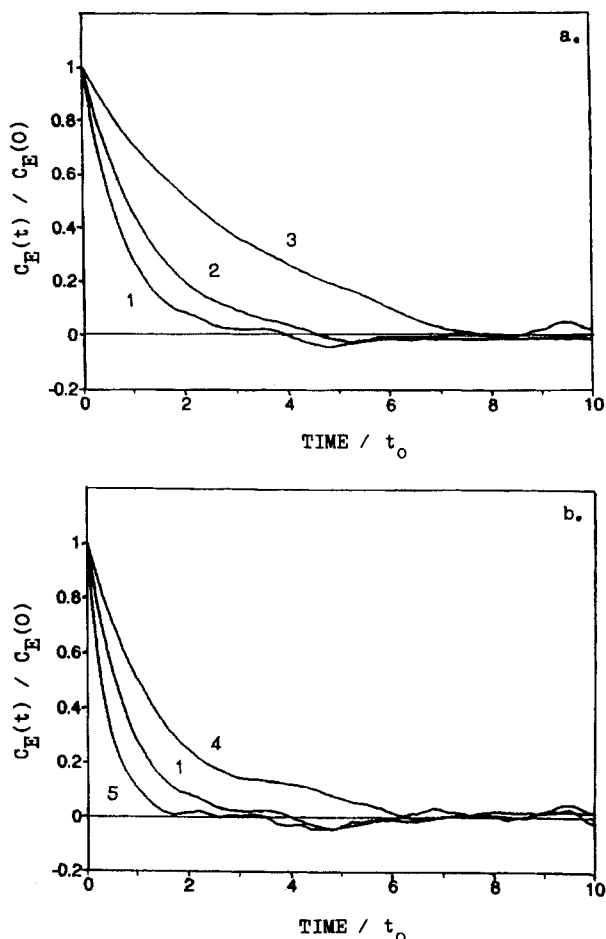
In this section we compare the behavior of two models of a polymer chain immersed in a hydrodynamic flow. The models differ by the type of pair interactions. In one model the repulsive L-J potential  $U_{ij}^R$  is used in the form of eq. (22), while in the other model the full L-J potential  $U_{ij}$  includ-

**TABLE I.** Mean Values and rms Deviations<sup>a</sup> of Total, Kinetic, and Potential Energies in Collisional Dynamics Simulations of Polymer Chain Coupled to an Equilibrium Bath.

Run	$T_o$ ( $\epsilon_o \backslash k_B$ )	$\lambda$ ( $t_o^{-1}$ )	$m_o$ ( $m$ )	$\langle E_{kin} \rangle$	$\delta E_{kin}$ ( $\epsilon_o \backslash k_B$ )	$\delta T_{eq}^b$	$\delta E_{tot}$ ( $\epsilon_o$ )	$\delta E_{pot}$
1	2.5	100	1	2.63	0.256	0.248	26.17	4.53
2	2.5	100	1\3	2.53	0.254	0.248	25.97	4.30
3	2.5	100	1\9	2.52	0.259	0.248	26.69	4.33
4	2.5	200	1	2.62	0.250	0.248	25.56	4.60
5	2.5	50	1	2.59	0.243	0.248	24.74	4.49
6	5.0	100	1	5.21	0.515	0.496	53.09	8.91
7	1.0	100	1	1.05	0.099	0.099	10.13	1.72

<sup>a</sup> All mean values are calculated as time averages using 1000 $t_o$  MD trajectories stored at every 0.1 $t_o$  time step.

<sup>b</sup>  $\delta T_{eq}$  is the expected value of the rms deviation of the kinetic energy in a canonical ensemble with temperature  $T_o$ .



**FIGURE 2.** Comparison of the polymer chain total energy autocorrelation functions  $C_E(t)$  obtained from different  $1000t_0$  trajectories. Simulations were performed using the CD method at  $T_0 = 2.5\epsilon_0/k_B$  and various values of  $\lambda$  and  $m_0$ :  $\lambda = 100t_0^{-1}$ ,  $m_0 = 1.0m$  (line 1);  $\lambda = 100t_0^{-1}$ ,  $m_0 = 1/3m$  (line 2);  $\lambda = 100t_0^{-1}$ ,  $m_0 = 1/9m$  (line 3);  $\lambda = 50t_0^{-1}$ ,  $m_0 = 1.0m$  (line 4); and  $\lambda = 200t_0^{-1}$ ,  $m_0 = 1.0m$  (line 5).

ing the attractive part, is used. The coupling parameters of these simulations are specified by  $m_0 = m$ ,  $T_0 = 2.5\epsilon_0/k_B$ , and  $\lambda = 131.4t_0^{-1}$  as in Balabaev and Lemak.<sup>8</sup> The hydrodynamic flow is incorporated in the collisional dynamics via parameter  $\mathbf{w}(\mathbf{r})$  which is the mean velocity of both atoms in position  $\mathbf{r}$ . We assume that the polymer chain is carried out by the flow and so the center of mass of the polymer chain moves with the flow velocity. The flow over the length of the polymer can be described by a linear field  $\mathbf{w}(\mathbf{r}) = \Lambda(t) \cdot (\mathbf{r} - \mathbf{z})$ , where  $\Lambda(t)$  is the velocity gradient tensor, and  $\mathbf{z}$  is the center of mass vector. In a purely

elongational flow, the velocity gradient has the form:

$$\Lambda(t) = \dot{\epsilon}(t) \begin{pmatrix} 1 & 0 & 0 \\ 0 & -0.5 & 0 \\ 0 & 0 & -0.5 \end{pmatrix}$$

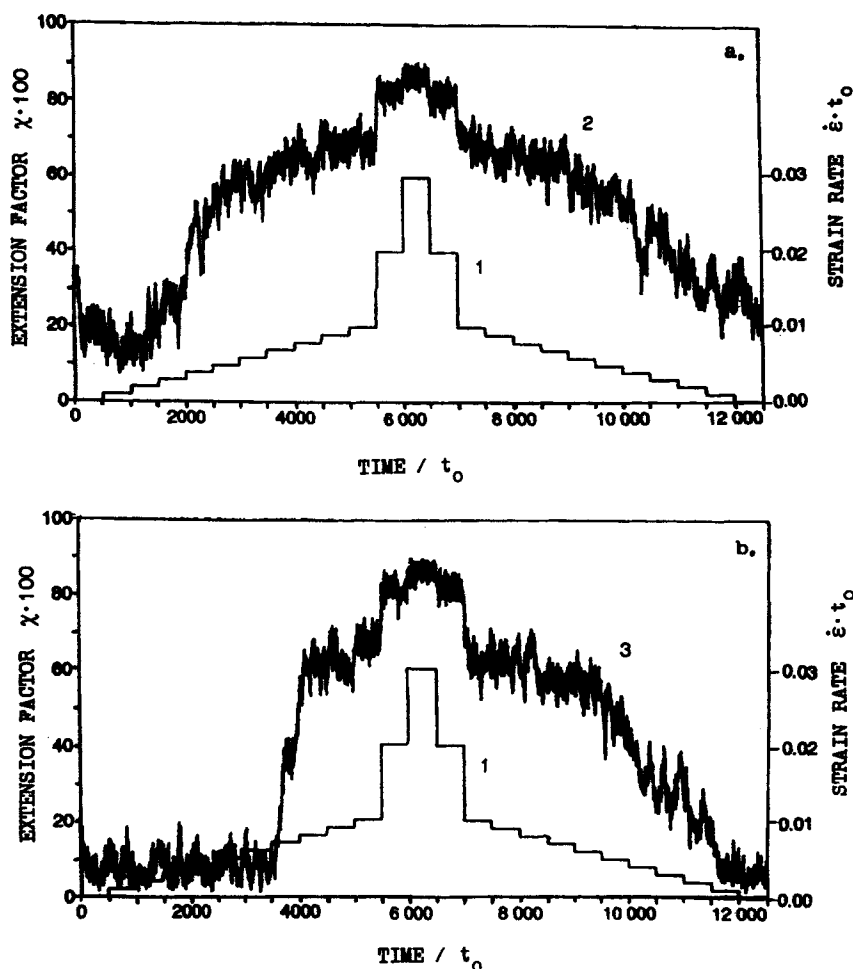
We restrict our consideration to the behavior of the chain extension factor defined as:

$$\chi(t) = h(t)/L$$

where  $h(t) = |\mathbf{r}_N(t) - \mathbf{r}_1(t)|$  is the end-to-end distance and  $L$  is the extended length of the chain. In our case,  $L = 100l$ . A nonlinear dumbbell model of the polymer chain predicts the following behavior of  $\chi$  in a steady elongational flow.<sup>20</sup> When  $\dot{\epsilon}$  increases, the steady-state value for the extension factor  $\langle \chi \rangle$  increases monotonously but steeply. There is one critical value  $\dot{\epsilon}_1^*$ , at which  $\langle \chi \rangle$  rises sharply. This situation is called a transition between the coil (C) and stretch (S) states of the polymer chain. For the reverse situation, the transition from S to C takes place at a particular value  $\dot{\epsilon}_2^*$ , and furthermore,  $\dot{\epsilon}_2^* < \dot{\epsilon}_1^*$ ; i.e., hysteresis is expected.

Here we examine the response of the polymer chain to a time-dependent flow by setting  $\dot{\epsilon}(t)$  as a sequence of constant strain rates  $\dot{\epsilon}_1, \dot{\epsilon}_2, \dots$ , which persist over the time interval  $500t_0$ . In dividing  $\dot{\epsilon}(t)$  into segments, we implicitly assume that the flow intensity changes instantaneously. The chosen values of  $\dot{\epsilon}_1, \dot{\epsilon}_2, \dots$ , first increase from 0 to  $0.03t_0^{-1}$ , and then decrease to 0 in a symmetrical way (see Fig. 3). This time-dependent flow field simulation produces a trajectory that lasts  $12,500t_0$ . We obtained two trajectories of this kind. One was obtained for the chain with a repulsive L-J potential, and the other for the chain with a full L-J potential. The time evolution of the extension factor  $\chi$  along these trajectories is shown in Figure 3. Both trajectories exhibit a critical value for the strain rate, at which the chain switches from coil to stretch. For the chain with the repulsion only this critical value is about  $\dot{\epsilon}_1^* = 0.004t_0^{-1}$ . An addition of the attractive forces in the polymer model results in the coil state being persistent at strain rates up to  $\dot{\epsilon}_1^* = 0.007t_0^{-1}$  and the transition  $C \rightarrow S$  being more conspicuous. To test the hysteresis mentioned above, the strain rate dependence of the quasi-equilibrium values of the extension factor  $\bar{\chi}$  was calculated using the obtained trajectories. The value of  $\bar{\chi}(\dot{\epsilon})$  was calculated as a time average over the portion of the trajectory corresponding to the given



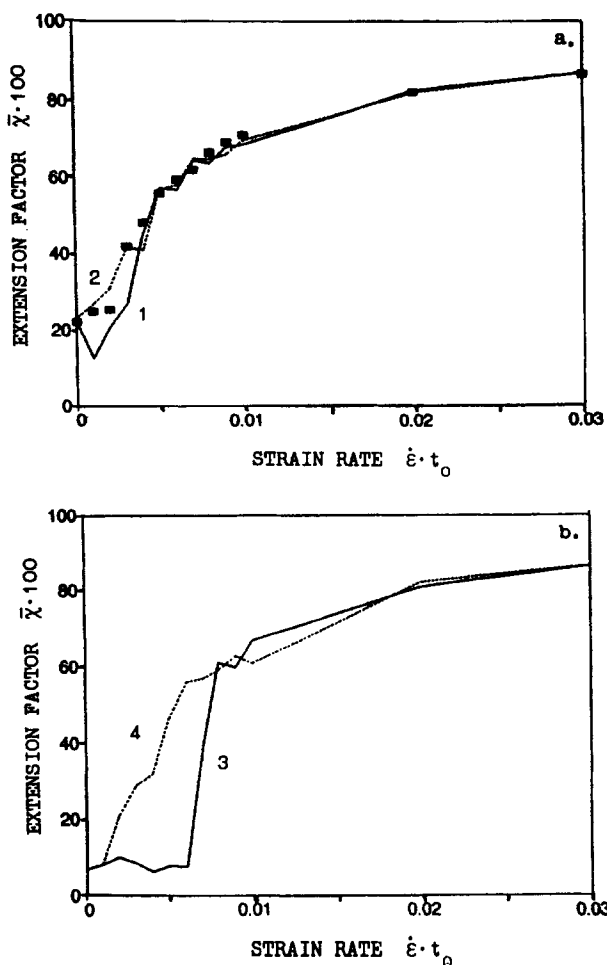


**FIGURE 3.** Evolution of the chain extension factor  $\chi$  in the time-dependent elongational flow field for two models of polymer chain: (a) chain with a repulsive L-J potential; and (b) chain with a full L-J potential. Curves 1, the time dependence of the strain rate  $\dot{\epsilon}$  (scale left). Curves 2 and 3, the time dependence of  $\chi$  (scale right).

value  $\dot{\epsilon}$ . For averaging, we used only the last  $250t_0$  period of this portion. For a given value of  $\dot{\epsilon}$  we can calculate two values of  $\bar{\chi}$ . The first one is calculated over the part of the trajectory where  $\dot{\epsilon}$  increases, and the second one over the part where  $\dot{\epsilon}$  decreases. In Figure 4, the curve for the  $\dot{\epsilon}$  dependence of  $\bar{\chi}$  obtained over the part of the trajectory where  $\dot{\epsilon}$  increases does not coincide with the one obtained over the part where  $\dot{\epsilon}$  decreases. The gap between the curves is more pronounced with the chain model that includes the attraction forces (Fig. 4b).

It should be noted that the calculated averages  $\bar{\chi}$  are not steady-state values. To check this, we performed the following CD simulations for the chain with a repulsive L-J potential. For each value of  $\dot{\epsilon}$  taken in the time-dependent flow field simulations, a separate trajectory was obtained. At given

$\dot{\epsilon}$ , we started from the same initial conditions, corresponding to the coil state, and carried out the CD simulations at a constant strain rate  $\dot{\epsilon}$ . The duration of the simulation was sufficient to achieve a steady state and then to remain in this state for some time. Relaxation times that are necessary to achieve a steady state at various values of  $\dot{\epsilon}$  are given in Figure 5. For some values of  $\dot{\epsilon}$  the relaxation times exceed  $500t_0$ . We also evaluated steady state values of  $\chi$  for each given  $\dot{\epsilon}$  (see Fig. 4a). The calculated  $\bar{\chi}$  at small values of  $\dot{\epsilon}$  does not coincide with the corresponding steady-state values. This is explained by the fact that the chain relaxation time from the coil state toward the steady state is longer than the duration of the simulation at which  $\dot{\epsilon}$  remains constant. Thus, the hysteresis that is seen in Figure 4 can be traced due to a reason different from the one established

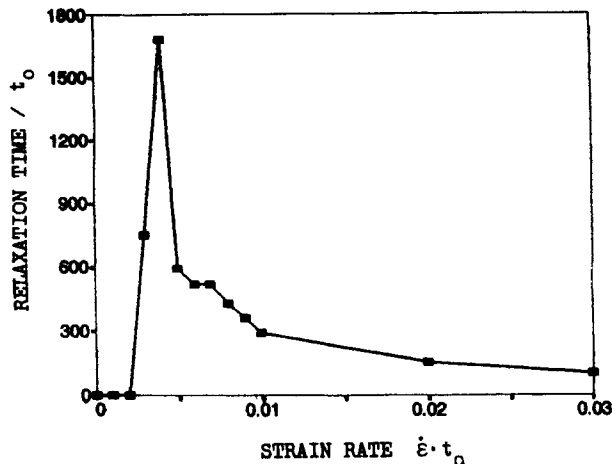


**FIGURE 4.** Quasi-equilibrium values of the chain extension factor  $\bar{\chi}$  in the time-dependent elongational flow field as a function of the strain rate  $\dot{\epsilon}$  for two models of a polymer chain: (a) chain with a repulsive L-J potential; and (b) chain with a full L-J potential. The dependence  $\bar{\chi}(\dot{\epsilon})$  is displayed both for the part of the trajectory where  $\dot{\epsilon}$  increases (curves 1 and 3) and for the part where  $\dot{\epsilon}$  decreases (curves 2 and 4). Steady-state values of the extension factor (■) are shown.

for the nonlinear dumbbell model. The observed hysteresis is of kinetic nature.

**Conclusion**

This article gives a description of the algorithm of the collisional dynamics that merges the trajectory routine of Verlet with both holonomic constraints and stochastic collisions with virtual bath atoms. The collisional dynamics method is believed to be useful to simulate not only static



**FIGURE 5.** Relaxation times (■) for transition of a polymer chain immersed in the elongational flow from an equilibrium coil state to a steady stretched state at different values of the flow strain rate  $\dot{\epsilon}$ . For each value of  $\dot{\epsilon}$  the CD simulation of the chain ( $N = 101$ ) with a repulsive L-J potential immersed in the elongational flow field with constant strain rate  $\dot{\epsilon}$  was performed. Each simulation started at the same initial condition. The relaxation times were evaluated by the times at which the chain extension factor  $\chi$  reached its steady stretched value.

properties, but dynamical behavior as well. The proposed algorithm is numerically stable and can be effectively implemented at least for polymer chains with fixed valence bonds. The number of required additional operations is of the order of the number of atoms in the chain. The proposed algorithm provides for an opportunity to perform CD simulations of polymers subjected to holonomic constraints in stochastic solvents. It includes both equilibrium and nonequilibrium processes. There are, for example, a studies of: coil and globular states of a flexible polymer chain<sup>21, 22</sup>; solvent effects on isomerization dynamics in chain molecules<sup>23</sup>; kinetics of coil-globule transitions; and dynamical behavior of polymers in a hydrodynamical flow with the velocity gradient, etc.

The effect of various CD simulation parameters on the dynamical behavior of a polymer chain with 100 fixed bonds is described. It includes the results of CD simulations of a polymer chain in a time-dependent elongational hydrodynamical flow. The influence of nonbonded interactions on the coil  $\rightarrow$  stretch transition of the chain in such a flow field has been examined. It is found that, due to additional attractive forces, the coil state of the chain persists at larger values of the strain rate,

and the coil  $\rightarrow$  stretch transition is more pronounced than in the case when only repulsive L-J interactions are included. The hysteresis observed in the strain rate dependence of the chain end-to-end distance is discussed. It may be inferred that the hysteresis has a kinetic nature.

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