

## Computer Simulation of Chains in Solution and Bulk State

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### ABSTRACT

We briefly describe the results of preliminary tests of Monte Carlo and molecular dynamics simulations of static and dynamic properties of a simplified continuum model of polymer chain systems in solution and in bulk melts in the context of other studies in this field. In particular, reptation Monte Carlo studies of these continuum multichain systems at reduced chain densities

of 0.3 and 0.5 for chains of up to 70 segments give the same exponent for the segment dependence as found by De Vos and Bellemans for chains on lattices.

It is a pleasure to participate by means of this progress note in the symposium on Statistical Approaches to Macromolecular Systems in honor of Robert Simha, who has contributed so widely to this field. Computer simulation of polymer chains in solution and in bulk is a fashionable field [1-9] as is clearly seen among other things from the interesting contributions by Drs. Curro, Lacombe, and Stockmayer to this topic at this symposium. We have recently constructed a computer program\* which has the ability to: (1) generate configurations of polymer chains in solution and in the bulk state by Monte Carlo (MC) simulation, (2) to study the temporal evolution of polymer chains by the molecular dynamics (MD) technique of direct numerical solution of Newton's equations of our system, and (3) a combination of MC generation of representative configurations of dense polymer chain systems whose subsequent dynamical behavior can be studied via the MD technique. We report here on some preliminary results obtained by testing parts 1 and 2 of our program. The results on part 2 have already been published [9] and will only be briefly referred to while the more extensive list of results on part 1 and the procedures used to obtain them will be reported in detail elsewhere [10].

To some extent our program reflects the history of computer simulation of polymer chains. MC methods have been extensively employed in the past particularly to study static chain properties on a lattice [11]. Verdier and Stockmayer [12] were the first workers to introduce dynamics in such MC investigations by moving single chains on a lattice in accordance with a set of kinetic rules. Ceperley, Kalos, and Lebowitz [8] developed a MC simulation of a "freely draining" single polymer chain subject to internal polymer forces and random solvent forces. The alternative MD technique has been used to study liquid n-butane by Ryckaert and Bellemans [13] and Weber [14]. A simplified pearl necklace model of 5 and 10 units immersed in a solvent subject to the potential shown as follows, was studied by us [9], while Rapaport [15] has recently studied a freely linked chain of hard spheres in a solvent.

MD studies of static and dynamic properties were carried out [9] on (a) a single pentamer in solution with 120 solvent atoms and (b) a single decamer in solution with 990 solvent atoms. The

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interatomic potential consists of a shifted Lennard Jones potential  $U_{LJ}(R)$  between all  $N_p$  particles in the system and a modified harmonic (FENE) potential  $U_H(R)$  which links the first  $N$  ( $N = 5, 10$ ) atoms into a polymer chain:

$$U_{LJ}(R) = \begin{cases} 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6 + (1/4)] & R \leq 2^{1/6}\sigma \\ 0 & R \geq 2^{1/6}\sigma \end{cases}$$

$$U_H(R) = \begin{cases} -0.5\kappa R_0^2 \ln[1 - (R/R_0)^2] & 0 \leq R \leq R_0 \\ 0 & R > R_0 \end{cases} \quad (1)$$

The MD integrations were carried out in a cubical box of side  $L$ , with periodic boundary conditions, where  $N_p/L^3 = \rho = 0.3$ ,  $R_0 = 1.95\sigma$ ,  $\kappa = 20\epsilon/\sigma^2$ , and an initial Maxwellian velocity distribution corresponding to a reduced temperature  $k_B T/\epsilon = 10.0$ . These parameters correspond to the high temperature and low-density n-butane states examined by Weber [14]. We obtained [9] equilibrium properties such as the virial, solvent, intra-, and extra-chain pair correlation functions, nearest-neighbor distributions, the mean-square end-to-end distance  $\langle R^2 \rangle$ , radius of gyration  $\langle S^2 \rangle$ , and polymer asphericity. Where comparisons with alternative models were possible, the agreement was good [8]. Chain dynamics was monitored by examining the relaxation of the auto-correlation functions of velocity, end-to-end distance, and radius of gyration [8].

Table 1 summarizes our principal results [8] with  $D$  the self-diffusion coefficients obtained by integration of the velocity correlation function,  $\tau(\langle R^2 \rangle)$  and  $\tau(\langle S^2 \rangle)$  the end-to-end distance and radius of gyration relaxation time, respectively. From these results it is quickly apparent that our polymers at  $\rho = 0.3$  are not sufficiently long to probe the asymptotically large polymer region but rather behave still as oligomers. Thus, e.g., the static ratio  $\langle R^2 \rangle / \langle S^2 \rangle = 5.47, 6.04$ , for the pentamer and decamer, respectively, rather than 6.4 expected of a sufficiently long chain; and  $\tau(\langle S^2 \rangle)$  and  $\tau(\langle R^2 \rangle)$  vary as the 0.80 and 1.01 power of  $N$ , respectively, rather than the joint power 2.2 expected from scaling theory and the results of Ceperley et al. [7] or the third power in agreement with Verdier

TABLE 1  
Summary of MD Chain Simulation

System	$\langle R^2 \rangle$	$\langle S^2 \rangle$	D	$\tau(\langle R^2 \rangle)$	$\tau(\langle S^2 \rangle)$
125	$7.16 \pm 0.15$	$1.31 \pm 0.01$	0.55	46	33
1000	$18.79 \pm 0.47$	$3.11 \pm 0.05$	0.57	104	63

<sup>a</sup>  $\rho = 0.3$ , lengths are measured in units  $\sigma$ , velocity in units of  $(\epsilon/M)^{1/2}$ , and time in units of  $\sigma(M/\epsilon)^{1/2}$ , where  $\theta$  is the particle diameter,  $m$  the particle mass, the well-depth of the potential.

et al. [1]. Rapaport's MD studies [15] with freely linked chains at comparable densities yield relaxation times  $\tau(\langle R^2 \rangle)$ ,  $\tau(\langle S^2 \rangle)$  which support the scaling theory. It should be noted in this connection that statistical results on oligomers are quite useful since many polymeric products in certain applications, e.g., in coatings, are applied as oligomers rather than true high polymers.

Our MC studies of the static configurational properties of continuum chains subject to the intermolecular potential given by Eq. (1) were carried out by employing modifications of the reptation MC algorithm used by Wall et al. [6, 7]. In our technique, following Webman et al. [16], the "head" or "tail" of a chain is reptated with equal probability (to satisfy detailed balance), to achieve the desired equilibrium configurations of the system. Details of the procedure can be found elsewhere [10], but chains with chain lengths of 5, 10, 20, 32, 50, and 70 units were studied, either as single chains without solvent atoms at a chain density of 0.001 or as multichain systems (without solvent, i.e., as melts) at densities of 0.3 and 0.5. The equilibrium properties were independent of the starting space lattice configuration employed or the number of chains of fixed chain length used to obtain these results.

We found [10] that solvent compressed somewhat the dimensions of shorter chains (e.g.,  $N = 5$ ). In Table 2 we summarize the density and  $N$ -dependence of  $\langle R^2 \rangle$ ,  $\langle S^2 \rangle$  and the mean-square bond length observed in our studies [10] of chains with  $N = 20, 32, 50,$  and  $70$ . The exponent 1.07 for the multichain configurational at higher densities was obtained from a lattice model by De Vos and Bellemans [17]. The extent of chain overlap (defined through the overlap of the chain ellipsoids whose principal axes are those of their moment of inertia tensor), as expected, saturates with increasing chain length and density [10]. Further work is under way on both the static

TABLE 2  
MC Configurational Properties (Distance in Units of  $\sigma$ )

Reduced density	$\langle R^2 \rangle$	$\langle S^2 \rangle$	Mean-square bond length
0.001	$(1.44 \pm 0.22) \langle N-1 \rangle^{1.22 \pm 0.05}$	$(0.23 \pm 0.03) \langle N-1 \rangle^{1.22 \pm 0.03}$	1.42
0.3	$(1.83 \pm 0.15) \langle N-1 \rangle^{1.07 \pm 0.02}$	$(0.31 \pm 0.02) \langle N-1 \rangle^{1.07 \pm 0.02}$	1.39
0.5	$(1.50 \pm 0.20) \langle N-1 \rangle^{1.09 \pm 0.04}$	$(0.26 \pm 0.02) \langle N-1 \rangle^{1.08 \pm 0.02}$	1.35

results (extending the range of parameters employed, e.g., the chain density), as well as chain mixtures (long and short chains, the latter with degrees of polymerization larger or smaller than the square root of the degree of polymerization of the longer chain) and dynamic properties such as the correlation functions and self-diffusion. Ultimately, we hope to obtain estimates of chain mechanical relaxation times and melt viscosities.

In conclusion, it is noteworthy how well certain static configurational properties are reproduced by studies on widely different models, e.g., off or on lattices. In view of this and the large number of possibilities which need to be investigated to carry out meaningful comparisons with scaling theory it would be very desirable to find a continuing mechanism, such as a specialized annual meeting devoted to cross comparisons of polymer computer simulation results.

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