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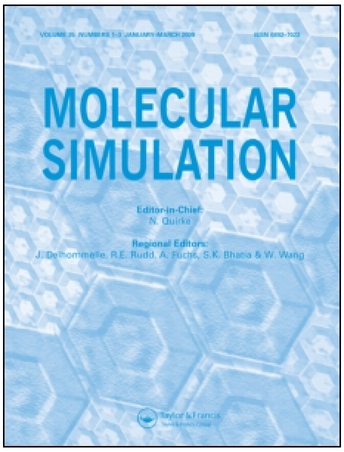

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Dynamics of Selenium Chain Melts by MD Simulation

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DYNAMICS OF SELENIUM CHAIN MELTS BY MD SIMULATION

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A molecular dynamics (MD) study of liquid selenium modelled by linear chains is presented. The simulated thermodynamic state corresponds to the experimental density of 3570 Kg m^{-3} at 873 K. We have studied melts with chains of different lengths, varying in the range of 10–80 atoms, just up to the limit where the melts relax in the temporary and spatial length window (10^1 ns and 28.6 A) of the numerical experiment. The flexibility of the chains at the thermodynamic state considered enabled us the observation of different spatio temporal dynamics regimes, which can be described by the Rouse model for dense polymer solutions.

KEY WORDS: Selenium, chain melts, Rouse model

1 INTRODUCTION

There has been a long standing interest in the molecular structure and dynamics of liquid and amorphous selenium [1]. From the present available evidence it can be concluded than the actual disorder phases of selenium show a complex chain structure. Although a temperature dependence of the length of the chains can be observed, at the temperature of this study 873 K, an average length in the range of 10^2–10^3 atomic units has been estimated [2]. Accordingly, a melt of monodisperse linear atomic chains atoms seems to be a first approach to modelling the dynamics of that system. A preliminary study with chains of 40 atoms has already appeared (in References 3), and we showed the capability of the model for describing the measured structural and dynamical properties of liquid selenium. In this work we consider the effect of changing the length of the chains from 10 up to 80 atoms according a compromise in between the length of the chains, the sample size and relaxation time accessible to present days MD studies.

The computer simulation studies of polymer melts can be classified into two groups according to whether their main interests is to reflect global [4–5] or local properties [6–8]. The origin of such a division is the wide spatial and time scales, spanning many orders of magnitude, implicit in the physics of polymers, and only reachable by standard simulation techniques from models where the chain is described by string of independent 'blobs' [5, 9]. On the other hand full atomic models of polymers have been mainly applied to short chains of linear hydrocarbon compounds, where the $-CH_2$ units are fused in an interacting particle. But the restricted flexibility of those chains implies the use of enormous amount of computer resources to observe the global spatial and temporary scale behavior of melts with more than two tenths of $-CH_2$ units chains [8]. Given that limitation these previous simulations have centered its attention mainly in structural and thermodynamics properties, and the fast relaxation process of the chains. Therefore another aim of this paper is to present large scale MD simulations of a melt of linear atomic chains of different lengths, which offer us the possibility of following the crossover of the dynamics of atoms from microscopic short range to large global system dynamics behavior. The simulation of liquid selenium is an interesting benchmark for that purpose since, according with the comments given above is mainly formed by linear chains, and given the higher flexibility of it a few atomic units could be enough for defining polymeric blobs, and a few decades of atoms could to disturb the Rouse behavior in the melt [10].

The sketch of the paper is as follows, in section 2 we briefly describe the model, and the simulation method, as well as thermodynamic properties of the liquid. Section 3 accounts for the structural properties. Section 4analyzes the dynamics of the melts. Section 5 finally contains the main conclusions.

2 CHAIN MODEL AND SIMULATION METHODOLOGY

We have carried out MD simulations of selenium chains in the microcanonical ensemble [11] using a partial flexible model, bending and torsional motions are modelled. The simulation cubic box contains 640 atoms. The thermodynamic state studied was defined in terms of the experimental density at $T = 873\,\mathrm{K}$, $3570\,\mathrm{Kg\,m^{-3}}$ [12].

There is a general consensus on the bond length and bond angle of the chain from neutron diffraction measurements [13]. Spectroscopic measurements, lattice dynamics and 'first principles' calculations [14] provide enough information for establishing the force constants of atoms in the chain (see table 1). Pairs of atoms belonging to different chains or belonging to the same chain but separated by more than three bonds interact through a Lennard–Jones (LJ) potential, with $\varepsilon/k_B = 200\,\mathrm{K}$ and $\sigma = 3.3\,\text{Å}$. This potential was truncated spherically at $R_c = 2.5\sigma$.

The equations of motion were integrated using the *leap-frog* algorithm [15]. The time-step used was $\Delta t = 4.542\,\mathrm{fs}$. The covalent bond distance 2.373 Å was maintained according the *shake* procedure [11]. The total energy was accurately conserved and no drifts appeared in the simulation runs of short chains, although for longer chains with simulation runs beyond 10 ns small fluctuations of the total energy have been observed. The initial configuration was created by fixing bonds over an atomic LJ system, and by simulating a completely flexible chain model. Obviously such a procedure leads to extremely high values in the bending terms of the intramolecular energy, however the length of the chains allow a fast interchange of energy between the different degrees of freedom, which let the system to equilibrium. The atomic velocities were scaled during the equilibration time in order to get the required temperature. In order to monitor the equilibration process, attention was paid to the relaxation of bond angles, radius of gyration and end to end distances of the chains (see definitions in Section III), total energy and the different contributions to the potential energy. The convergence of the *molecular translational* temperature to the value of the *atomic* temperature (fixed by the scaling of velocities) was another check in monitoring the equilibration.

3 STRUCTURE AND THERMODYNAMICS

Table 1 shows the value of bond and torsion angles obtained from time averaging the internal coordinates along the simulated trajectory. The system is stable and the modelled chains are compatible with the experimental information about the selenium chains. The general shape of the chain can be described in terms of the mean square end-end distances

$$\langle R^2 \rangle = \langle (\mathbf{r}_N - \mathbf{r}_0)^2 \rangle \tag{1}$$

where $\mathbf{r}_N$ and $\mathbf{r}_0$ denote the position of the first and the last atom of the chain and $\langle\ \rangle$ denotes a time average over chains. From the results showed in table 2, we can observe as $\langle R^2 \rangle$ follows the scale law $\langle R^2 \rangle \propto N^{\beta}$, with $\beta = 1.141$. This scaling is in between the ideal gaussian value of $\beta = 1$, and the excluded volume value $\beta = 1.176$ [10]. The chains are so short for screening the intramolecular short range repulsions, and excluded volume effects influence the global shape of the chains in the melts. Another standard shape parameter of the polymer is the radius of gyration R_g [10], given by the average

$$\langle R_g^2 \rangle = 1/(1+N) \sum_{i=0}^{N} \langle (\mathbf{r}_i - \mathbf{R}_G)^2 \rangle \tag{2}$$

where $\mathbf{R}_G$ is the position of the center of mass of the chain,

$$\mathbf{R}_G = 1/(1+N) \sum_{i=0}^{N} \mathbf{r}_i \tag{3}$$

Table 1 Force field and Geometric Parameters

	Simulation	*t-Se*	*M-Se*
$R(\mathring{A})$	2.373	2.373	2.337
$\langle\theta(deg)\rangle$	102.9	103.1	102.1
$\langle\phi(deg)\rangle$	92.9	100.6	74.7
$u_{\text{bend}} = \frac{k_c}{2}(\cos\theta - \cos\theta_0)^2$	$k_c = 433\ \text{kJ mol}^{-1}$	$\theta_0 = 103.0\ \text{deg}$	
$u_{\text{tors}} = k_t(\cos\phi - \cos\phi_0)^2$	$k_t = 6.65\ \text{kJ mol}^{-1}$	$\theta_0 = 90.0\ \text{deg}$	

The subscripts "*bend*" and "*tors*" correspond to *bond-bending* and *bond-torsion* contributions to the total energy. *t*-Se and M-Se are solid phases results of selenium [14].

Table 2 Total time of the runs, mean squared end-end distance $\langle R^2 \rangle$ and the radius of gyration $\langle R_g^2 \rangle$. Here $N+1$ is the number of atoms and N_c the number of chains.

$N+1/N_c$	T/ps	$\langle R^2 \rangle / A^2$	$\langle R_g^2 \rangle / A^2$
10/64	200.	84.	13.7
20/32	1000.	195.	32.
40/16	12000.	446.	72.
80/8	10000.	1001.	161.

The values of $\langle R_g^2 \rangle$ are showed in table 2, and the ratios R/R_g are slightly larger than the corresponding ratio for an ideal chain 6 [10].

In Figure 1 we show the log plot of the intramolecular structure factor, which has been obtained by calculating $S(q)$ for individual polymer chains of 10 and 40 atoms. We see that the three different spatial regimes assumed in polymer structural studies for this kind of function [10]. At short wavelengths, $q > 2\pi/\xi$, where ξ is the correlation length a faster varying and oscillatory behavior could be observed, according the local atomic structure. At larger wavelengths, in the intermediate range $2\pi/R_g < q < 2\pi/\xi$ a universal power law of $S(q) \propto q^\beta$ is predicted, and must be independent of the chain length. The exponent is dependent by the medium where we have the polymeric chain. In melts if the screening is expected the polymers follow the gaussian exponent $\beta = -2$. We observe this behavior for values of q less than $0.8\,\text{Å}^{-1}$, which implies a correlation length ξ around of 8 Å. According to the geometry of the chain this distance corre-

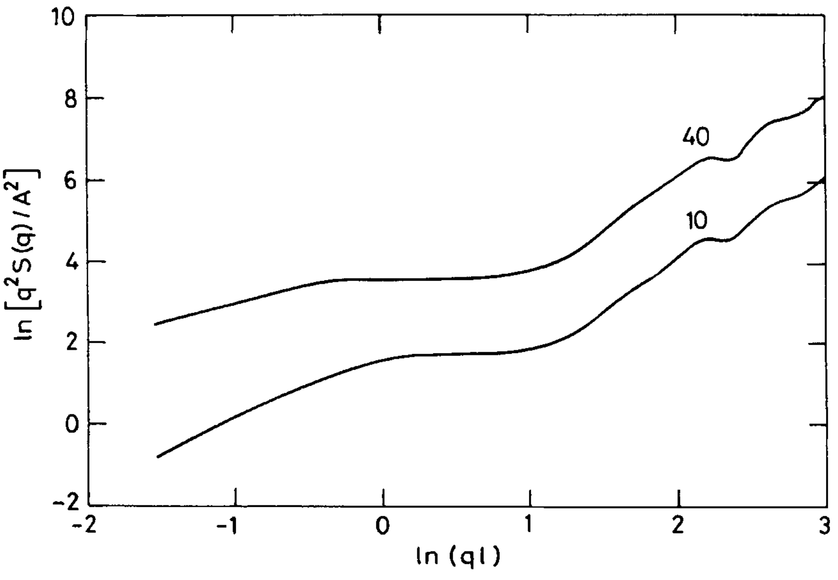

Figure 1 Intramolecular structure factor $q^2 S(q)$ of chains vs. ql for 10 and 40 atoms chain melts. The three region defined by theoretical polymer predictions can be observed, $q < 2\pi/R_g$, $q > 2\pi/\xi$ and in between.

Table 3 Thermodynamic Results(1).

$N+1$	*10*	*20*	*40*	*80*
$U^{\mathrm{LJ}}_{\mathrm{inter}}/(\varepsilon N_c)$	-39.94	-73.2	-137.3	-259.7
$U^{\mathrm{LJ}}_{\mathrm{intra}}/(\varepsilon N_c)$	-2.75	-10.0	-27.4	-69.1
$U_{\mathrm{bend}}/(\varepsilon N_c)$	17.57	41.1	86.9	172.9
$U_{\mathrm{tors}}/(\varepsilon N_c)$	10.78	26.4	57.2	118.2
$p\sigma^3/\varepsilon$	4.11	3.25	2.75	2.34
$(kT/\varepsilon)_{\mathrm{atom}}$	4.29	4.46	4.45	4.35
$(kT/\varepsilon)_{\mathrm{molec}}$	4.30	4.46	4.45	4.35

(1) Energies are in reduced units per atom:
$\varepsilon/k_B = 200\,\mathrm{K}$, $\varepsilon = 1663\,\mathrm{J/mol}$; $\varepsilon/\sigma^3 = 76.8\,\mathrm{MPa}$.

sponds approximately to the separation of 1–7 atoms of the chain, and is the average number of atoms that exists within a sphere of diameter ξ. The chain can be visualized as a string of 'blobs' of size ξ [9]. Inside one blob the atomic correlations arise from the same chain, and are mostly defined by excluded volume interactions. For short wave length vectors, up to $q \simeq 1.4\,\text{Å}^{-1}$, the power law decreases reflecting excluded volume effects at short distances. For $qR_g < 1$ we found a global size chain dependent behavior, which follows the gaussian chain structure factor function [10] often approximated by

$$N/S(q) = 1 + q^2 R_g^2/2 \tag{4}$$

this is the traditional tool for measuring the size of the chains from scattering techniques. Plotting this function we have obtained the same R_g than reported previously. In spite of the shortness of the chains studied, they reflect the three structural regimes of structure factor predicted for polymers.

Thermodynamic properties are given in table 3. Pressure is evaluated in an atomic description, and decreases with the length of the chain, according the existence of more free volume for the long chain systems. Long range interactions were included in the calculationf of the energy and pressure assuming that the atomic pair distribution function $g(r) = 1$, for $r > R_c$.

4 DYNAMICS

In Figure 2 we show the relaxation of the chain conformation through the normalized-correlation functions of $\langle R^2 \rangle$ defined as

$$AR(t) = \frac{\langle R^2(t)R^2(0)\rangle - \langle R^2\rangle^2}{\langle R^4\rangle - \langle R^2\rangle^2} \tag{5}$$

The functions show an exponential relaxation behavior, and the relaxation times follow the scalling law $\tau_{AR} \propto N^2$. The universal behavior of that function confirms the Rouse prediction for the scaling of the largest relaxation time of the chains, $\tau_N \propto N\langle R^2\rangle$ [5].

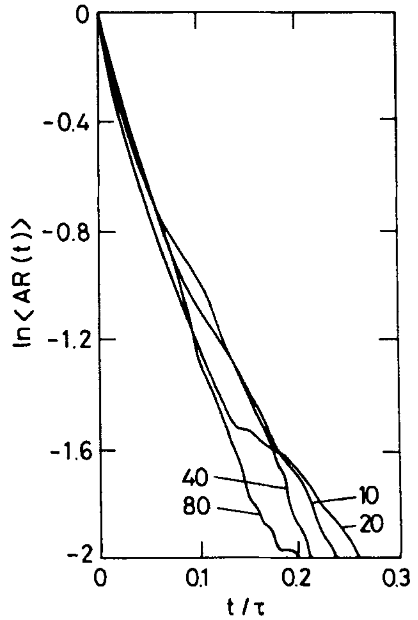

Figure 2 Time correltion function of R^2 for 10, 20, 40 and 80 atoms chain melts. The time has been scaled by τ, the time necessary for observing parallel behavior of $g_1(t)$ and $g_{1\mathrm{CM}}(t)$ functions.

The type of atomic motion observed in a experiment on melts of linear chains will be essentially determined by the spatial an time window of the used technique [10]. Fortunately for us in our melts has been possible to observe at least three different dynamic scales: The 'quasi-hydrodynamics' or long time behavior, where we observe mainly the motion of the chains as a whole, responding to very soft interchain interactions and with atomic cross-links as constraints; the 'universal' or intermediate regime where the dynamics of the chain segments is not affected neither by the molecular size nor by the chemical structure of the chain; and finally by the 'local' or atomic scale, where the motion of atoms responds to intramolecular constraints, bonds and angles, and the presence of neighboring atoms, which defines strong excluded volume interactions (i.e. inter and intramolecular repulsive Lennard Jones interactions). We therefore will try to identify those scales, although very often given the shortness of our chains we must observe a mixture of them and for the longest run of 40 chains the 'quasi-hydrodynamics' regime shows some complexity because could be the result of coupling of different global dynamics process.

The translational displacements of an atom or the center of mass CM of the chains over the time duration of the simulation, averaged over all particles, is the simplest time dependent property that we can investigate. In terms of the atom-atom positions $\mathbf{r}(t)$, the atomic mean square displacement function $g_1(t)$ is given by

$$g_1(t) = \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle \tag{6}$$

where $\mathbf{r}(t)$ means the atom position at time t, and $\langle\ \rangle$ stands for the average of different time origins of the trajectory and all particles of the system, and in terms of the center of mass position $\mathbf{r}_{\mathrm{cm}}(t)$ the motion of the center of mass $g_{1_{\mathrm{cm}}}(t)$ is given by

$$g_{1\,\mathrm{cm}}(t) = \langle [\mathbf{r}_{\mathrm{cm}}(t) - \mathbf{r}_{\mathrm{cm}}(0)]^2 \rangle \tag{7}$$

where the ensemble average $\langle\ \rangle$ is carried out as an average over different chains and time origins. After a fast motion of the atoms, when the mean square displacements of the atoms are nearly to the square end-end distances, the atomic and center of mass mean square displacements grow parallel,

$$g_1(t) = 2\langle R_g^2 \rangle + g_{1\,\mathrm{cm}}(t) \tag{8}$$

which means that at this time scale the dynamics of the atoms are governed by the global motion of the chain. In table 4 we show the approximate time τ necessary for avoiding internal motions influence on $g_1(t)$. At least for short chains, up to 40 atoms, $\tau \propto N^2$, although for 80 atoms chain the relaxation of the shape of chain increase faster as a product of a more complex dynamics. In Figure 3 we show these quantities obtained from the analysis of the overall trajectories, for the chains of 10 and 40 atoms. In the former a linear variation with time is established beyond $\tau \simeq 50$ ps for atomic displacements and fractions of ps for the CM. The behavior of 40 atoms chains is more complex, the atomic displacement shows the same slope that the CM beyond $\tau \simeq 1000$ ps., and both functions show a non linear time behavior which leads to introduce a time diffusion constant. In Table 4 we show the length and time dependence of the CM diffusion coefficient, when the length of the chain increases we have identified different dynamics regimes, with slopes that show the same scaling law $D_{\mathrm{CM}}(t) \propto N^{-1}$ if we observe up 20 ps, or in the range of $t \simeq \tau$. A third regime has been identified in 40 atoms chain system, in the range of 4000–8000 ps, but the shortness of the trajectory on 80 atoms chain can not visualize this regime. The Rouse model explains the motion of polymer chains at infinite dilution according with the chain connectivity and absorbing the rest of the interactions of the monomer in terms of a friction constant and a coupling to a heat bath [16]. Each monomer models a 'blob', composed by several chemical repeated units. The mean square displacement of

Table 4 Chain length and time dependence of the diffusion coefficient. $[t_0, t_1]$ is the time range considered for obtaining $D(t)$, DN is the Rouse prescription of the length dependence of D, τ is the relaxation time necessary for observing $g_1(t) - g_{1\mathrm{CM}}(t) = 2\langle R_g^2 \rangle$.

N	$[t_0, t_1]/ps$	$D(t)/A^2 ps^{-1}$	DN	τ/ps
10	0, 20	0.24	2.2	50.
	20, 200	0.20	1.8	
20	0, 20	0.11	2.1	260.
	50, 400	0.068	1.3	
40	0, 20	0.061	2.3	1000.
	100, 1500	0.035	1.4	
	4000, 8000	0.019	0.74	
80	0, 20	0.20	2.1	> 7000.
	100, 2000	0.017	1.3	

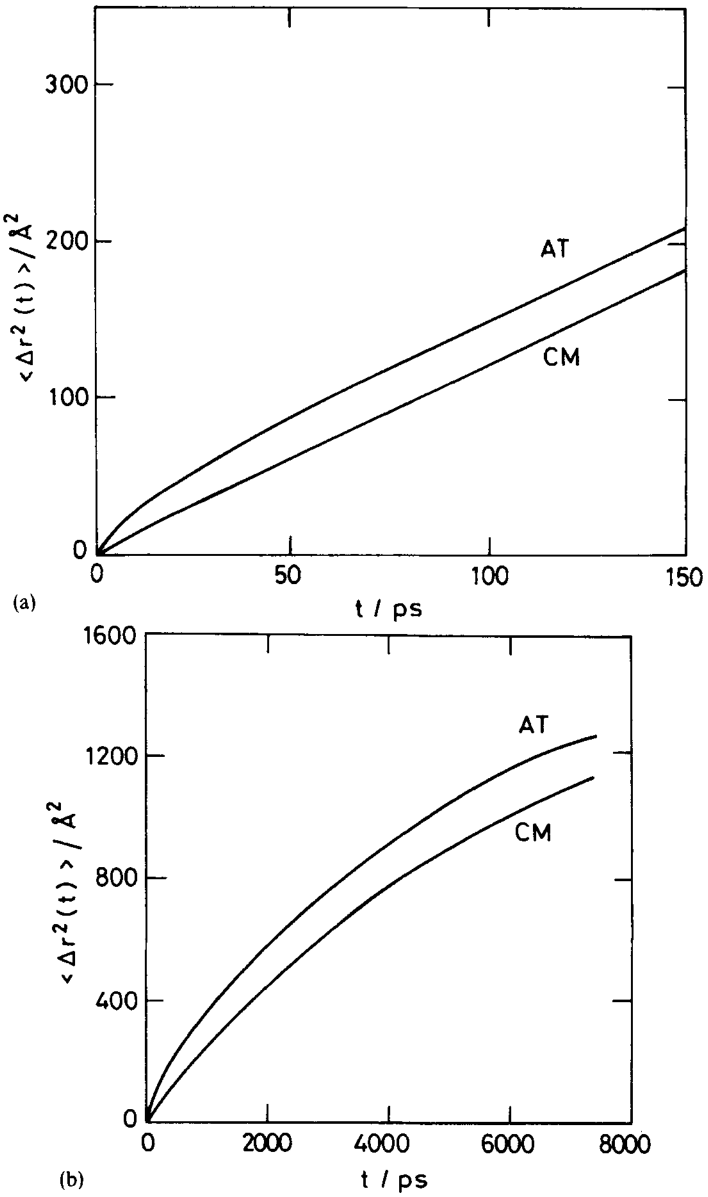

Figure 3 Mean square displacement of the atoms $g_1(t)$ and the center of mass $g_{1\mathrm{CM}}(t)$ (lower curves): (a) 10 atoms chain. (b) 40 atoms chain.

a monomer in this model shows the following power law behavior

$$g_1(t) \propto \begin{array}{ll} t^1 & t < \tau_0, g_1(t) < l_{\mathrm{eff}}^2 \\ t^{1/2} & \tau_0 < t < \tau_N, g_1(t) < \langle R^2 \rangle \\ t^1 & t > \tau_N, g_1(t) > \langle R^2 \rangle \end{array} \tag{9}$$

$$g_{1\mathrm{cm}}(t) \propto t^1 \tag{10}$$

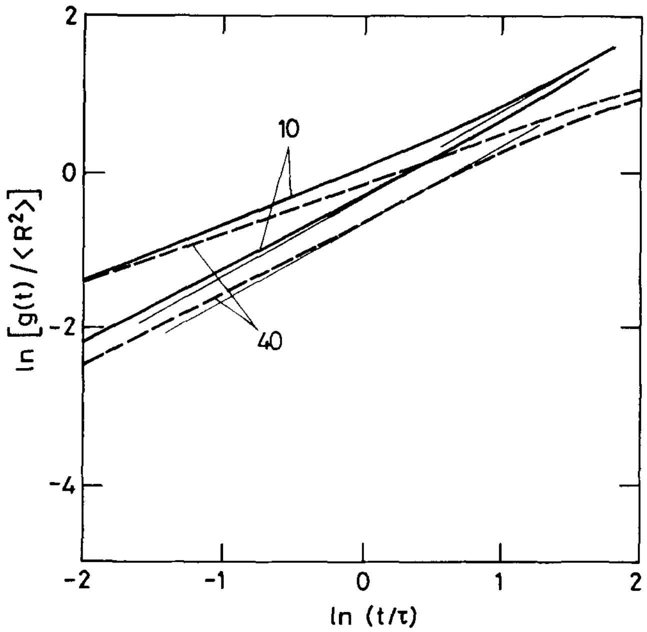

Figure 4 Log plot of $g_1(t)$ and $g_{1CM}(t)$ against t for the 10 and 40 atoms chain melts. The results are plotted in reduced units, t/τ and $g(t)/\langle R^2 \rangle$. Thin lines show the t^1 behavior.

It is assumed that this model works for melts of short chains [4]. The equation 9 shows different dynamic regimes for the monomer diffusion, local, universal regime and diffusive motion with different time power laws. In figure 4 we show the log plots of the mean square displacement for selenium atoms and the CM of the chains, which correspond in the atomic case to the last two regimes shown by Eq. 9. The data follow qualitatively the Rouse description. The exponent of the universal regime is greater than 0.5, around 0.61 and 0.71 for the 40 and 10 atoms chain. This kind of exponent has been observed by Schieber *et al.* [16], from a reanalysis of diffusion data on a concentrated polystyrene solution using forced Rayleigh scattering technique. This regime is extended to τ and a mean square displacement of the atoms nearly to the R^2 value. After this behavior the Fickian regime appears in the 10 atoms chain system corresponding to the center of mass diffusive behavior. The overall curve for the center of mass of that system follows the Rouse prescription. However the results for the 40 atoms chain are more complex, after a 'quasi' Fickian regime at τ, the exponent goes down which leads us to think in a new dynamic regime originated in the restrictions imposed by neighboring chains. Unfortunately the runs have not arrived to the Fickian regime and the exponent of the curves are always below one.

CONCLUSIONS

We have performed an extensive molecular dynamics simulations of melts of linear polymer chains of different lengths aiming to model liquid selenium at high temperatures. The high flexibility of the chains at the studied thermodynamic conditions, can offer us different structural and dynamic regimes mostly predicted by the current polymer theoretical approaches. The shape parameter show excluded volume effects, although the intramolecular structure factor shows gaussian decays in the universal range of wave vectors. The internal modes of the chains relax according the Rouse scaling las $\tau \propto (N-1)^2$ at least for the range of 10 to 40 atoms chain. The mean square displacement of the particles show a clearly time dependent diffusion constant, which can be scaled according the Rouse length dependence prediction. For the longest chains, up 80 atoms chain, the total length of the run, larger than 10 ns., is not enough for observing the hydrodynamics limit.

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