CrossMark

REGULAR ARTICLE

A coarse-grained model based on core-oftened potentials for anomalous polymers[†]

RONALDO J C BATISTA[a], EVY A SALCEDO TORRES[b], ALAN BARROS DE OLIVEIRA[a] and MARCIA C B BARBOSA[c,*]

[a]Departamento de Física, Universidade Federal de Ouro Preto, Ouro Preto, MG 35400-000, Brazil
[b]Coordenadoria Especial de Física, Química e Matemática, Universidade Federal de Santa Catarina, Rua Pedro João Pereira, 150, Araranguá, SC 88900-000, Brazil
[c]Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS 91501-970, Brazil
E-mail: marcia.barbosa@ufrgs.br

Abstract. Starting from an anomalous monomeric system, where particles interact via a two-scale core-softened potential, we investigate how the system properties evolve inasmuch as particles are put together to form polymers whose chain size varies from 4 up to 32 monomers. We observed that the density and diffusion anomaly regions in the pressure versus temperature phase diagram of the monomeric system is smaller in the monomeric system when compared with the polymers. We also found that the polymers do not fold into themselves to form solid spheres instead they tend to maximize the chain-fluid contact. Also, Rouse and Reptation models can be employed to describe the polymers diffusive behaviour. But, in contrast to results of simulations where mere interacts via Lennard-Jones potentials, our results shown a much shorter entanglement length of at most 8 monomers.

Keywords. Polymers; anomaly; water.

1. Introduction

Traditional solids and liquids are made of atoms and molecules at the very smallest scales and physical and chemical behaviors of these systems are governed by the characteristic of these small scales. Complex fluids even thought are also made of atoms and molecules, form larger structures that are responsible for many of their properties. This is the case of the water that due to its hydrogen bonds forms tetramers and octamers which lead to the presence of more than seventy anomalies.[1] These phenomena are governed by the transient clusters formed by water whose origin are the hydrogen bonds. But water is not unique. Other materials (i.e., Se_xTe_{1-x}, $Ge_{15}Te_{85}$ and liquid sulfur) display unusual behaviour in which system expansion upon cooling is observed.[2–11] Such anomaly, called density anomaly, is not an isolated case. Anomalous behaviour in compressibility, refractive index, speed of sound, solubility, heat conductivity and many others have been observed for liquid water.[1]

Thanks to the fact that the anomalies in these materials—and in particular in water—are related to length scales larger than the usual atomistic or molecular distances, the use of coarse-grained models to study these systems becomes an interesting tool. In the case of complex water-like systems two characteristic length scales are present: an open structure and a closed structure. Consequently, these anomalous systems are modeled by core-softened shoulder potentials.[12–26] These models produced pressure versus temperature phase diagrams which reproduce the anomalies present in the tetrahedral liquids. They also suggest a mechanism behind the anomalies.[16,17]

In addition to water and to the tetrahedral fluids mentioned above, polymers are also complex fluids. They are made of atoms and molecules which are organized to form larger structures. The behavior of the polymeric materials can be explained by taking into account these intermediate scales of organization and therefore the use of coarse-grained methods becomes an interesting strategy to study polymers. In principle just one length scale would be necessary. In the case of homopolymers, the monomer-monomer interaction would represent this length scale. However, there are a number of polymers in which just one length scale would not be able to account

---

for the complexity of the system. An example of complex fluid of this type is the star polymer. A star polymer consists of several linear polymer chains connected to a central core, forming a core-brush structure. The interaction between two neighbor star polymers depends on two length scales: the core-brush interaction (that can be a van der Waals potential) and the brush-brush (soft repulsive) contribution energy. Then, we can raise the question whether a system made of star polymers with the interactions represented by core-softened potentials would exhibit the same anomalies present in water.

In this work we address this question by studying the pressure versus temperature phase diagram of polymers interacting through a core-softened potentials. Density and diffusive anomalies are investigated as a function of polymers length. In addition, we test the ability of the standard diffusive models (Rouse and Reptation models) in describing the dynamics of anomalous polymeric fluids. The paper is organized as follows. In the Sec. 2 the simulations are described, Sec. 3 results and discussions are presented and conclusions are shown in the Sec. 4.

2. Simulation details

Molecular dynamics simulations were performed as implemented in the LAMMPS package.[27] Each polymer is modeled as N monomers with the same mass (m) and diameter (σ), connected through springs with constant $k = 3000$ in units of force/length and equilibrium distance σ. Non-bonded monomers from the same polymer or belonging to a different polymer interact through a soft-core potential developed by da Silva *et al.*,[25] given by

$$\frac{U(r)}{\varepsilon} = 4\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$
$$+ a\exp\left[-\frac{1}{c^2}\left(\frac{r-r_0}{\sigma}\right)^2\right]$$
$$+ b\exp\left[-\frac{1}{d^2}\left(\frac{r-r_1}{\sigma}\right)^2\right], \qquad (1)$$

while bonded monomers have such an interaction turned off. Here, ε is the interaction energy strength which turns to be the energy unit in this work. Note the first term in the potential is the well-known Lennard-Jones potential, and the remaining two terms are gaussians with a = 5.0, r_0/σ = 0.7, c = 1.0, r_1/σ = 3.0, b = −0.5, and d = 0.5. The resulting potential shape with these parameters can be seen in Figure 1.

The temperature was kept constant by means of the Nosé-Hoover thermostat with time constant 0.1 and timestep 0.001 (both given in terms of $\sigma\sqrt{m/\varepsilon}$). A total of 2×10^6 steps were carried out, from which the first half was discarded in order to ensure the equilibrium of the system in the production stage.

Different degrees of polymerization were considered, in which 256 chains composed by N = 4, 8, 16, and
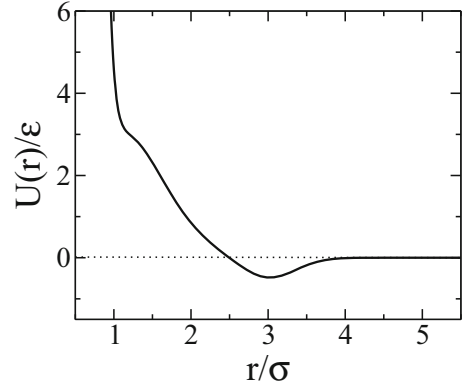
Figure 1. Pair potential as a function of particle distance used in this work.

32 monomers were used. Thermodynamic quantities are expressed in terms of the unit of length, σ, energy, ε, and the Boltzmann constant, k_B, so they become dimentionless. For example, pressure, temperature, and force are given in terms of ε/σ^3, ε/k_B, and ε/σ, respectively.

3. Results and Discussion

First, we verify the state of the solution. The radial distribution function was studied for temperatures $T^* = 0.2-4.0$ and densities $\rho^* = 0.1-0.7$ showing a characteristic behavior of liquid state, therefore our system was liquid for all the temperatures analyzed.

Next, we studied how each polymer is structured in its liquid solution. In order to do that, we analyzed the radius of gyration. According to the Flory's mean field approach,[28,29] the radius of gyration scales with N^ℓ, where N is the degree of polymerization and ℓ is a coefficient that determines the quality of the solvent in which the chain is immersed. The radius of gyration is calculated as follows:

$$R_G^2 = \frac{1}{N}\left\langle\sum_{i=1}^{N}\left(\overrightarrow{r} - \overrightarrow{r}_{cm}\right)^2\right\rangle, \qquad (2)$$

where the summation runs over the monomers of a single chain. For a simple polymer in which the spring is the only interaction, $\ell = 1/2$ and the polymer is in the coil state. At low temperature and for a bad solvent, the polymers assume a solid-like form and $\ell = 1/3$. For a good solvent and at high temperatures, the polymer becomes extended form and $\ell = 3/5$.

The figure 2 shows the radius of gyration as a function of the degree of polymerization for a system at temperature $T^* = 2$ and number density $\rho^* = n/V = 0.4$, where n is the total number of monomers in the solution and V is the simulation box volume. It is possible to see that a curve $R_G \propto N^{3/5}$ fits well the points
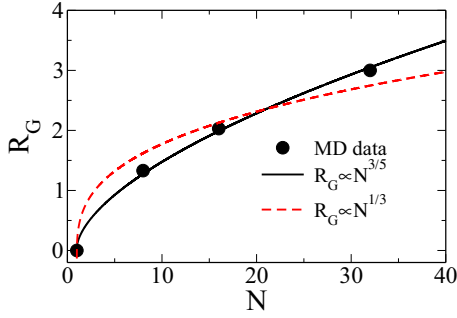
Figure 2. Radius of gyration as a function of the degree of polymerization N for $T^* = 2$ and number density $\rho^* = n/V = 0.4$, where n is the total number of monomers and V is the simulation box volume. It is possible to see that the curve with the coefficient 3/5 fits well the calculated values of R_G showing that the polymers chains do not form coils. For a matter of comparison we have also plotted the curve with coefficient 1/3.

Figure 3. Pressure versus temperature phase diagram for the monomeric case (N = 1) and polymers with chain size of 4, 8, 16 and 32 monomers showing the density anomalous region, i.e., the TMD loci for different degree of polymerization.

obtained through simulations, in contrast with the curve $R_G \propto N^{1/3}$. This means that in our simulations the polymers are in the extended state

Next, we address the question if this core-softened polymer exhibits in some region of pressures and temperatures the density anomaly as the anomaly present in liquid water. The density anomaly, as explained in the Introduction, is the property in which liquids expand under cooling. This anomaly in monomeric systems can be modeled by core-softned potentials and, therefore, it is natural to expect that a polymer with these competing forces would exhibit this type of anomaly. In order to confirm this assumption we studied the isochores of the polymer solution. Thermodynamic identities show that the temperature of minimum pressure at constant density (isochores) locates the temperature of maximum density at constant pressure. Therefore, Figure 3 shows the pressure-temperature phase diagram for polymeric systems with different degrees of polymerization illustrating the temperature of the minimum pressure along different isochores. The additional points at the isochores are not show for clarity. All the polymers show the presence of maximum density. The region in pressures in which the anomaly is present increases nonlinearly with the degree of polymerization. This is consistent with the results from the monomeric[25] and the dimeric systems.[24] In the case of the monomeric system, the size of the density anomaly region is at least one order of magnitude smaller than that of the fluid with $N = 4$. In contrast, the fluids with $N = 16$ and $N = 32$ presents similar density anomaly regions size. This is also consistent with the observations in dimeric systems for different sizes in which the larger structures
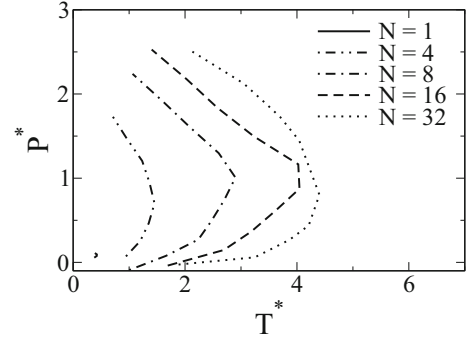
implies additional degrees of freedom . This, however, reaches a limit what is observed in the $N = 16$ and $N = 32$ cases

Polymers fluids exhibit a diffusion which sharply differs from that of ordinary Newtonian fluids. Such distinct behaviour is due to the entanglement between polymers chains that constrains the monomers movement.

One of the first models to describe polymers fluids dynamics was proposed by P. E. Rouse,[30] which assumes that monomers are points that interacts only through harmonic potential and all complicated interactions are absorbed into a monomeric friction and a coupling with a heat bath. Such a model correctly predicts the long-time diffusion for polymers shorter than the entanglement length. Within such model the mean-square displacement is proportional to: $t^{1/2}$ and t for subsequent time scales.

The Figure 4 shows the mean-square displacement as a function of time for the polymers with $N = 4$ and 32 (the other sizes were not presented for simplicity). We observed that the polymers with the chain length $N = 4$ are described by the Rouse model. However, the polymers with chain length larger than 8 monomers cannot be described by the Rouse model. In the Figure 4 for $N = 32$ it is possible to see that there are more than 3 distinct behaviours of $\langle R^2 \rangle$ as a function of time. Here we illustrate for this long polymer times that are short to full observe the linear behavior. Longer simulations and simulations for $N = 16$ shows the same linearity.

The presence of a conventional polymer fluid whose chains are larger than the entanglement length, the Reptation model[29,31] shows that the diffusion exhibit more than three regimes. The Reptation model predicts that the mean-square displacement is proportional to: $t^{1/2}$, $t^{1/4}$, $t^{1/2}$, and t for subsequent time scales. Our results shown in the Figure 4 that the same is true for anomalous
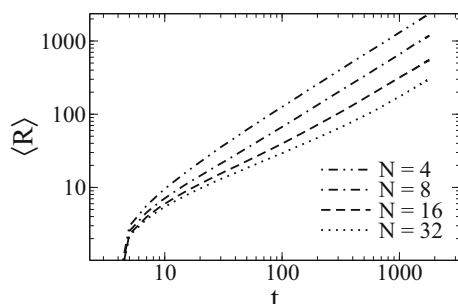
Figure 4. Mean-square displacement versus time for polymers with different degrees of polymerization N for $\rho^* = 0.4$ and $T^* = 2.0$. We note the changing behavior with increasing degree of polymerization. For $N = 4$ the mean square displacement scales linearly with time for intermediate times. This is not true for $N = 32$, for example (see Figure 5). The transition length seems to be about $N = 8$, which is called the entanglement length.
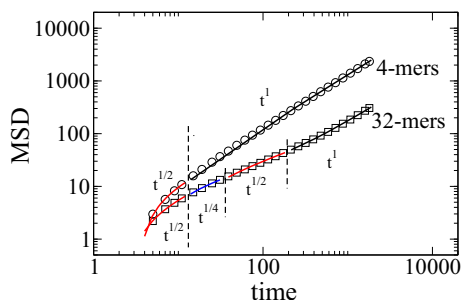

Figure 5. Mean-square displacement versus time for polymer fluids with chains smaller ($N = 4$) and bigger ($N = 32$) than the entanglement length ($N = 8$). The points were fitted by Rouse and Reptation models. Density and temperature were 0.4 and 2.0 for all cases, respectively.

polymer fluids. Our analysis suggests that the reptation regime is reached for a degree of polymerization, $N \approx 8$, much smaller than that of conventional polymer fluids.[29,31]

Finally, we address the question if the core-softened polymer exhibits the diffusion anomaly present in water. In water and other tetrahedral liquids as the density increases the diffusion coefficient grows, what it is know as diffusion anomaly. In order to answer to this question the diffusion coefficient versus density was computed for a number of temperatures. We observe that for a large range of temperatures the diffusion has a maximum and a minimum locating a region in which the diffusion is anomalous.

The Figure 6 illustrates the pressure versus temperature phase diagram in which the location of the
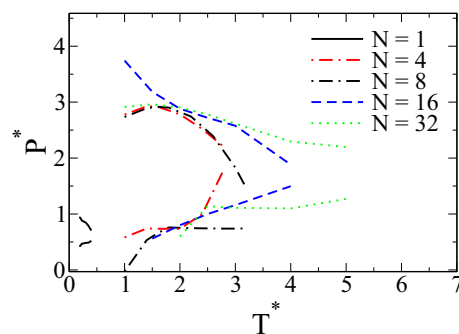
Figure 6. Pressure versus temperature phase diagram for polymers with chain size of 4, 8, 16 and 32 monomers showing the diffusion anomalous region.

maximum diffusion (upper lines) and minimum diffusion coefficients (lower lines) are located. The range in temperatures for the dynamic anomalous regions increases with the increase of the polymer size. This is probably related to collective effects.

4. Conclusion

In summary we presented results of simulations of polymeric fluids whose monomers interacts via two-scale core-softened pair potentials capable of describing anomalous fluids. We found that investigated polymer systems display density and diffusion anomalies. The size of anomalies regions depends on the chain size in special for very short chain lengths. Rouse and Reptation models can describe the diffusion. However, the predict entanglement length is very short in comparison to previous studies on ordinary polymer fluids indicating a possible relation between short entanglement length and diffusion anomaly.

References

1. Chaplin M 2016 Anomalous properties of water http://www1.lsbu.ac.uk/water/water_anomalies.html Date accessed: October 2016
2. Angell C A, Finch D E and Bach P 1976 Spin-echo diffusion coefficients of water to 2380 bar and -20°C *J. Chem. Phys.* **65** 3063

3. Thurn H and Ruska J Change of bonding system in liquid $Se_x Te_{1-1}$ alloys as shown by density measurements *J. Non-Cryst. Solids* **22** 331

4. Sauer G E and Borst L B 1967 Lambda transition in liquid sulfur *Science* **158** 1567

5. Kennedy S J and Wheeler J C 1983 On the density anomaly in sulfur at the polymerization transition *J. Chem. Phys.* **78** 1523

6. Tsuchiya T 1991 The anomalous negative thermal expansion and the compressibility maximum of molten Ge–Te alloys *J. Phys. Soc. Jpn.* **60** 227

7. Angell C A, Bressel R D, Hemmatti M, Sare E J and Tucker J C 2000 Water and its anomalies in perspective: tetrahedral liquids with and without liquid–liquid phase transitions *Phys. Chem. Chem. Phys.* **2** 1559

8. Sharma R, Chakraborty S N and Chakravarty C 2006 Entropy, diffusivity, and structural order in liquids with waterlike anomalies *J. Chem. Phys.* **125** 204501

9. Shell M S, Debenedetti P G and Panagiotopoulos A Z 2002 Molecular structural order and anomalies in liquid silica *Phys. Rev. E* **66** 011202

10. Poole P, Hemmati M and Angell C A 1997 Comparison of thermodynamic properties of simulated liquid silica and water *Phys. Rev. Lett.* **79** 2281

11. Sastry S and Angell C A 2003 Liquid-liquid phase transition in supercooled silicon *Nat. Mater.* **2** 739

12. Franzese G, Malescio G, Skibinsky A, Buldyrev S V and Stanley H E 2001 Generic mechanism for generating a liquid–liquid phase transition *Nature (London)* **409** 692

13. Netz P A, Raymundi J F, Camera A S and Barbosa M C 2004 Dynamic anomalies of fluids with isotropic doubled-ranged potential *Phys. A* **342** 48

14. Balladares A L and Barbosa M C 2004 Density anomaly in core-softened lattice gas *J. Phys. Condens. Matter* **16** 8811

15. de Oliveira A B and Barbosa M C 2005 Density anomaly in a competing interactions lattice gas model *J. Phys. Condens. Matter* **17** 399

16. de Oliveira A B, Netz P A, Colla T and Barbosa M C 2004 Thermodynamic and dynamic anomalies for a three dimensional isotropic core-softened potential *Chem. Phys.* **124** 084505

17. de Oliveira A B, Netz A, Colla T and Barbosa M C 2006 Thermodynamic and dynamic anomalies for a three dimensional isotropic core-softened potential *J. Chem. Phys.* **125** 124503

18. Netz P A, Buldyrev S V, Barbosa M C and Stanley H E 2006 Thermodynamic and dynamic anomalies for dumbbell molecules interacting with a repulsive ramp-like potential *Phys. Rev. E* **73** 061504

19. Franzese G and Stanley H E 2002 Liquid–liquid critical point in a Hamiltonian model for water: analytic solution *J. Phys. Condens. Matter* **14** 2201

20. Franzese G and Stanley H E 2007 Widom line of super-cooled water *J. Phys. Condens. Matter* **19** 205126

21. de Oliveira A B, Netz P A and Barbosa M C 2008 Which mechanism underlies the water-like anomalies in core-softened potentials? *Euro. Phys. J. B* **64** 481

22. de Oliveira A B, Franzese G, Netz A P and Barbosa M C 2008 Water-like hierarchy of anomalies in a continuous spherical shouldered potentia *J. Chem. Phys.* **128** 064901

23. de Oliveira A B, Netz P A and Barbosa M C An ubiquitous mechanism for water-like anomalies *Europhys. Lett.* **85** 36001

24. de Oliveira A B, Neves E B, Gavazzoni C, Paukowski J Z, Netz P A and Barbosa M C 2010 Liquid crystal phase and water-like anomalies in a core-softened shoulder-dumbbells system *J. Chem. Phys.* **132** 164505

25. da Silva J N, Salcedo E, de Oliveira A B and Barbosa M C 2010 Effects of the attractive interactions in the thermodynamic, dynamic and structural anomalies of a two length scale potential *J. Chem. Phys.* **133** 244506

26. Gallo P and Sciortino F 2012 Ising universality class for the liquid–liquid critical point of a one component fluid: a finite-size scaling test *Phys. Rev. Lett.* **109** 177801

27. Plimpton S 1995 Fast Parallel Algorithms for Short-Range Molecular Dynamics *J. Comp. Phys.* **117** 1

28. Flory P J 1953 *Principles of Polymer Chemistry* (New York: Cornell University Press)

29. de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca and London: Cornell University Press)

30. P E Rouse 1953 A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers *J. Chem. Phys.* **21** 1272

31. de Gennes P G 1971 Reptation of a Polymer Chain in Presence of Fixed Obstacles *J. Chem. Phys.* **55** 572