Macromol. Symp. **2006**, 237, 69–72 DOI: 10.1002/masy.200650508

Thermodynamic Limitations of the Reptation Model

Nail Fatkullin,[1] *Rainer Kimmich*[2]

Summary: The paper deals with the question whether the tube/reptation model of polymer chain dynamics is compatible with general laws of statistical physics. Based on a relation between the mean squared fluctuation of the number of segments in a given volume element and the isothermal compressibility of the polymer system, it follows straightforwardly that the tube/reptation model predicts fluctuations larger than permitted by thermodynamics on the time scale $t \gtrsim \tau_R$, where τ_R is the Rouse relaxation time.

Keywords: chain dynamics; fluctuations; polymer melts; reptation; thermodynamics

Introduction

The reptation concept was introduced by de Gennes [1] with the aim to explain thermal motions of a long polymer chain in the presence of fixed obstacles. The ‘‘tube’’ was suggested by Edwards as an interpretation of the enhanced modulus of rubber.[2] The unification of the two formalisms by Doi and Edwards led to the ‘‘tube/reptation’’ model [3], which nowadays is considered as the standard phenomenological description of polymer chain dynamics.

The tube/reptation model appears to be quite persuasive and can be explained using relatively simple mathematics. Qualitatively it gives reasonable explanations for several experimental findings. On the other hand, substantial discrepancies between certain model predictions and experimental observations must be stated. Examples can be found in a recent review article and in the literature cited in it[4].

Actually, one faces a situation similar to the phenomenological van der Waals equation of state for dense gases and liquids. The reasoning leading to the van der Waals equation is also easily understood. The formalism is based on simple mathematics and qualitatively renders the main features of the gas-to-liquid phase transition. Nevertheless, apart from dilute gases no real system can precisely be described by the van der Waals equation. Keeping this rather rough, but meaningful analogy in mind, the purpose of the present study is to find a time region, where the tube/reptation model can provide a more accurate description of reality.

Results

n the following, all formulae and notations for the reptation model are taken from the classical book by Doi and Edwards[5]. Consider a polymer melt of macromolecules of molecular mass $N \gg N_c$ measured in units of Kuhn segments. N_c corresponds to the critical molecular mass. The treatment is to refer to a volume $V \simeq R_F^3$ in the melt, where $R_F = bN^{1/2}$ is the Flory radius of the macromolecules, and b is the Kuhn segment length. The average number of Kuhn segments inside this volume can be estimated as

$$\langle N_V \rangle = \rho_s V \simeq \rho_s b^3 N^{3/2}, \qquad (1)$$

where ρ_s is the number density of Kuhn segments.

The tube/reptation model postulates, that a polymer chain starts to reptate inside

---

[1] Kazan State University, Physics Department, 420008, Kazan, Russia/Tatarstan
E-mail: Nail.Fatkullin@ksu.ru
[2] Universität Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany
E-mail: Rainer.Kimmich@uni-ulm.de

its own tube in the time limit $t \gg \tau_e = \tau_s N_e^2$ where τ_e is so-called entanglement time, τ_s is the segmental relaxation time, and $N_e = N_c/2$ is the number of segments between two successive entanglements corresponding to the tube diameter $d = bN_e^{1/2}$. The number of tubes, n_t, having one end inside the considered volume V, and the other outside is equal to the number of polymer chains with this property, and can be estimated by

$$n_t \simeq \langle N_V \rangle / N = \rho_s b^3 N^{1/2}. \tag{2}$$

In the limit $t \gg \tau_R$, polymer chains are coherently displaced curvilinear distances $s(t)$ along their tubes, where $\tau_R = \tau_s N^2$ is the Rouse relaxation time. Since thermal fluctuations of polymer chains are strongly restricted in the tubes, the number of segments leaving their old tubes, $n(t)$, is of the order of the number of segments contained in the tube section of the curvilinear length $s(t)$. That is,

$$\frac{n(t)}{N_e} = \frac{s(t)}{bN_e^{1/2}} \quad \text{or} \quad n(t) = \frac{s(t)}{b} N_e^{1/2}. \tag{3}$$

Reptation of polymer chains causes fluctuations of the number of segments in the considered volume $V \simeq R_F^3$. Motions of different chains inside their own tubes are independent of each other. The mean squared fluctuation of segments in V at time t can be estimated as

$$\left\langle (\delta N_V)^2 \right\rangle_{rep} \simeq n_t \langle n^2(t) \rangle, \tag{4}$$

where the brackets indicate an average over all stochastic processes connected with reptation of the chains. Combining Eqs (2) to (4) we have

$$\left\langle (\delta N(t))^2 \right\rangle_{rep} \simeq \rho_s b \langle s^2(t) \rangle N^{1/2} N_e. \tag{5}$$

On the other hand, the total mean squared fluctuation of segments in a volume V obeys the known thermodynamic relation (see for example[6])

$$\left\langle (\delta N_V)^2 \right\rangle = k_B T \rho_s \kappa_N \langle N_V \rangle, \tag{6}$$

where $k_B T$ is the Boltzmann constant multiplied by the absolute temperature, and κ_T is the isothermal compressibility of the system. It is clear that the inequality

$$\left\langle (\delta N_V(t))^2 \right\rangle_{rep} \le \left\langle (\delta N_V)^2 \right\rangle \tag{7}$$

should be valid at any time.

Based on Eqs (1), (5), (6) and (7), the mean squared curvilinear segment displacement is limited according to the inequality

$$\langle s^2(t) \rangle \le \rho_s k_B T \kappa_T b^2 N N_e^{-1}. \tag{8}$$

The tube length is of the order

$$L_t \simeq bNN_e^{-1}. \tag{9}$$

The comparison of expressions (8) and (9) suggests that the thermodynamically permitted displacements by reptation along the tubes are much shorter than the tube length:

$$\langle s^2(t) \rangle^{1/2} \le (\rho_s k_B T \kappa_T b^2 N N_e^{-1})^{1/2} \ll L_t \simeq bNN_e^{-1}. \tag{10}$$

Inequality (10) means, that, solely based on reptation modes, polymer chains cannot diffuse over distances comparable with their linear sizes. In other words, reptation motions would cause fluctuations much larger than thermodynamically permitted in times long enough.

To express inequality (10) in terms of time scale limitations for the compatibility of the tube/reptation model with thermodynamics, it is necessary to use explicit expressions for the mean squared displacement $\langle s^2(t) \rangle$ along the tubes. In the limit $\tau_e \ll t \ll \tau_R$ (regime II), the mean squared curvilinear displacement varies with time as

$$\langle s^2(t) \rangle \simeq \frac{2}{3\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2}. \tag{11}$$

Inserting expression (8) leads to

$$t \lesssim \frac{9\pi^3}{4} \left[\frac{\rho_s k_B T \kappa_T}{N_e} \right]^2 \tau_R. \tag{12}$$

For times in the limit $\tau_R \ll t \ll \tau_1 = 3\tau_s N^3 N_e^{-1}$ (regime III), where τ_1 is the terminal relaxation time predicted by the reptation model, the mean squared curvilinear displacement obeys

$$\langle s^2(t)\rangle \simeq \frac{2}{3\pi^2} b^2 \frac{t}{N\tau_s}. \tag{13}$$

Inserting inequality (8) again, suggests the following restriction:

$$t \lesssim \frac{3\pi^2}{2} \rho_s k_B T \kappa_T \tau_R N_e^{-1}. \tag{14}$$

Discussion

Expressions (12) and (14) represent the main results of this study. They specify the time scales on which density fluctuations produced by reptation in polymer melts are thermodynamically allowed. The formalism is based on Eq (6) following from equilibrium statistical physics, and on expression (5) predicted by the reptation model for the dynamical fluctuations of the segment number in $V = R_F^3$. If it is accepted that polymer melts are ergodic systems, i.e. time averaging is equivalent to ensemble averaging, expression (8) is correct and follows straightforwardly from basic laws and the assumptions intrinsic to the tube/reptation model.

Inequality (12) is the consequence of expression (8) for the limit $\tau_e \ll t \ll \tau_R$. It is clear that for molecular masses large enough the inequality

$$\tau_e \ll t \ll \frac{9\pi^2}{4}\left[\frac{\rho_s k_B T \kappa_T}{N_e}\right]^2 \tau_R \leq \tau_R \tag{15}$$

can be obeyed in any case. That is, thermodynamics allows for reptation motions in this particular limit.

The expression (14) was obtained for longer times corresponding to $\tau_R \ll t \ll \tau_1 = 3\tau_s N^3 N_e^{-1}$. Typically the isothermal compressibility of condensed systems in general and polymers melts in particular is rather small, and it holds $\rho_s k_B T \kappa_T \simeq 10^{-2}$. As usual one expects, that

$$\frac{9\pi^2}{4}\left[\frac{\rho_s k_B T \kappa_T}{N_e}\right]^2 \tau_R \leq \tau_R. \tag{16}$$

On a time scale of the order or longer than the Rouse relaxation time, $t \geq \tau_R = \tau_s N^2$, thermodynamics does therefore not permit reptational motions.

The key point in the derivation of this result was expression (4), which is a mathematical consequence of the basic postulate for tube/reptaton motions: Chains in entangled polymer melts are assumed to move independently of each other in their own tubes formed by all other chains. Such uncorrelated motions unavoidably lead to large fluctuations of segment numbers in different space regions of a characteristic linear size of the order R_F.

Conclusion

An intrinsic discrepancy between the postulates of the standard tube/reptation model leading to contradiction with the thermodynamic laws was revealed: On the one hand, interactions between the probe chain and neighboring chains are extremely important. Chain motions are supposed to be extremely anisotropic and restricted to tubes for times $t \ll \tau_1$. This can only be the consequence of *strong* interchain interactions. On the other hand, macromolecules are supposed to move in a diffusive way inside their own tubes without any essential mutual correlation, which anticipates *weak* intermolecular interactions. Obviously, in order to reach more realistic polymer dynamics models, dynamical correlations of different polymer chains must be taken into account. The same conclusion can be drawn from the recently discovered and qualitatively explained "corset effect" [7,8], which also reveals the importance of intermolecular dynamical correlations in polymer melts even between chains separated by distances much larger than the Flory radius.

Acknowledgements: This work was supported by the Volkswagen-Stiftung (1/74602), and CRDF REC-007.

[1] P.G. de Gennes, J.Chem.Phys. **1971**, 55, 572

[2] S.F. Edwards, Proc.Phys.Soc. **1967**, 92, 9

[3] M. Doi, S.F. Edwards, J.Chem.Soc.Faraday Trans. II, **1978**, 74, 1789

[4] R. Kimmich, N. Fatkullin, Advan. Polym. Sci. **2004**, 170, 1

[5] M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics*, 1986, Clarendon, Oxford

[6] R. Balesku, *Equilibrium and Nonequilibrium Statistical Mechanics*, 1975, Wiley, New York

[7] C. Mattea, N. Fatkullin, E. Fischer, U. Beginn, E. Anoardo, M. Kroutieva, R. Kimmich, *Appl.Magn.Res.* **2004**, 27, 371

[8] N. Fatkullin, R. Kimmich, E. Fischer, C. Mattea, U. Beginn, M. Kroutieva, *New Journal of Phys.* **2004**, 6, 46