



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Computer Physics Communications 169 (2005) 262–266

Computer Physics
Communications

www.elsevier.com/locate/cpc

Molecular modeling of shear-induced alignment of cylindrical micelles

Gaurav Arya, Athanassios Z. Panagiotopoulos *

Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, USA

Available online 8 April 2005

Abstract

This paper presents results from Monte Carlo (MC) and molecular dynamics (MD) simulations on the shear-induced long-ranged alignment of cylindrical micelles in thin films. The surfactant is represented on a lattice and the shear flow is simulated via incorporation of a shear-induced potential energy term within the acceptance criteria in the MC simulations. The MD simulations are conducted on a coarse-grained, off-lattice surfactant while the shear flow is imposed in thin films by sliding confining walls in opposite directions. It is shown that the two methods lead to different steady state orientations of micelles. We also discuss several problematic issues concerned with incorporating shear or dynamics within MC schemes.

© 2005 Elsevier B.V. All rights reserved.

PACS: 83.80.Qr; 81.16.Dn; 82.35.Jk

Keywords: Self-assembly; Micelles; Shear; Alignment; Monte Carlo; Molecular Dynamics

1. Introduction

It is well known that surfactants and block copolymers self-assemble and phase separate into a striking array of microphases which may be spherical, cylindrical-, lamellar- or gyroid-shaped [1]. The coarsening process through which these microphases form long-ranged order at equilibrium is generally very slow (e.g., consider thin films of block copolymer cylinders which coarsen with time (t) with a scaling of $t^{1/4}$ above their glass transition temperature [2]).

A common ad-hoc strategy for speeding up the coarsening process as well as controlling the orientation of the microdomains involves subjecting the material to a steady or oscillatory shear. Indeed, experiments have demonstrated that shear orients block copolymer lamellae either parallel or transverse to the shearing direction [3], and aligns micellar and block copolymer cylinders in the direction of shear [4]. Recent experiments have shown that long-ranged alignment of block copolymer cylinders may also be attained in thin films, which has enormous potential applications in the lithography and semiconductor industry [5]. Though speculations on the possible mechanisms of alignment in lamellae and cylinders exist [3,4], detailed molecular-

* Corresponding author.

E-mail address: azp@princeton.edu (A.Z. Panagiotopoulos).

level understanding is still lacking. Clearly, molecular simulation approaches are called for in order to probe the dynamics of the self-assembly process under shear.

In this paper we present one such approach, namely a “nonequilibrium” version of the lattice Monte Carlo (MC) technique, and review some key results from its recent application to thin films of cylindrical micelles [6]. Next, we show that the idea of incorporating shear within MC, though potentially powerful, suffers from a lack of theoretical rigor which results in incorrect structural and thermodynamic properties. Finally, we discuss some preliminary findings on the behavior of cylindrical micelles under shear via more conventional molecular dynamics (MD) techniques.

2. Monte Carlo: Methodology, application and critique

An equilibrium canonical Monte Carlo (MC) approach involves conducting a random walk through phase space, where the probability of accepting another state is given by $\min[1, \exp(-\Delta U_0/k_B T)]$, where ΔU_0 is the potential energy difference between the two states. In our nonequilibrium MC (NEMC) approach, first proposed by Xu et al. [7], this acceptance criteria is modified by incorporating within it an additional term associated with the drag force experienced by the surfactant due to the shear flow. For Couette flow, the new acceptance probability becomes

$$P_{\text{acc}} = \min \left[1, \exp \left(- \left(\Delta U_0 - \Gamma \sum_{i=1}^N \bar{y}_i \Delta x_i \right) / k_B T \right) \right] \quad (1)$$

where Γ is a parameter characterizing the magnitude of shear, Δx_i is the displacement of surfactant bead i in the shear direction while \bar{y}_i is its average position in the velocity gradient direction, and N is the total number of beads within the surfactant (see Refs. [6,7] for more details). The above acceptance criteria hence ensures that the displacements of the surfactant is always biased in the flow direction.

In our previous study [6], the surfactant was modeled as a lattice surfactant on a cubic lattice. Thin films of cylinder-forming surfactants were simulated using NEMC with the criteria equation (1) within impenetrable walls in one direction and periodic boundary

conditions in the others. The main results from this investigation are as follows. In the case of a monolayer-thick surfactant film, the micelles align parallel to the shearing direction. The mechanism of this alignment, was shown to involve rotation and/or breakup of cylinders perpendicular to the shearing direction and their subsequent growth in the direction of shear, which agrees well with that hypothesized earlier [4]. For thicker films, the micelles adopted a finite tilt with respect to the shearing direction in the velocity–velocity gradient plane. The tilt angle decreases with the film thickness, but clearly remains non-zero for the thicknesses considered in the study.

Though the idea of incorporating shear within a Monte Carlo framework sounds very appealing, it has several shortcomings which are discussed in some depth next. One immediately perceivable drawback is that the “pseudo” potential energy associated with shear (the second term inside the exponential in Eq. (1)) is nonconservative due to its dependence on the y coordinate of the molecule. This means that the energy change experienced by a molecule in going from one position to another depends on the path it traverses. A second drawback arises due to the fact that our MC scheme samples from a distribution function which is essentially canonical superimposed with the pseudopotential due to shear. As pointed out by Evans et al. [8], such a distribution cannot be valid arbitrarily far from equilibrium as it represents a local equilibrium distribution that has not relaxed to its true nonequilibrium state. The NEMC method hence suffers from a lack of rigorous statistical mechanical basis, and one should expect differences between the thermodynamics/structure of fluids sheared with this method and those sheared with the more rigorous nonequilibrium molecular dynamics (NEMD) technique. Such a comparison between the two methods is described below.

The model fluid is chosen to be liquid n -butane at $T = 300$ K and $\rho = 0.6$ g/cm³ modeled using the united atoms approach with fully flexible internal degrees of freedom. The NEMD simulations were conducted using the standard Sllod algorithm [9] with Lees Edwards periodic boundary conditions (LEP-BCs) [10]. The forcefield and the integration algorithm were followed from Ref. [11]. The temperature was maintained constant with a Nosé–Hoover chains thermostat [12] coupled to each individual molecule

in the simulation box. In the case of NEMC simulations, sampling was obtained via three types of moves on the molecules: isotropic translational displacements, rotations about the center of masses, and regrowth moves consisting of “cutting” and regrowing molecules using the configurational bias method [13]. The relative frequency of the three moves was taken to be equal to 0.82 : 0.179 : 0.001, respectively. This particular mix of moves ensured that the *ratio* of the timescales corresponding to the translational diffusion, rotation, and average Gauche-Trans transitions remained roughly similar to that obtained from MD simulations at equivalent conditions. This then set a physical time of roughly 2.6×10^{-5} ps for one MC step, consistent with the three types of molecular motions. The shear rate ($\dot{\gamma}$), controlled via the parameter Γ , was estimated by measuring the slope of the velocity profile at the center of the simulation box.

An issue that requires some attention concerns the boundary conditions employed in NEMC simulations. It was noticed that standard periodic boundary conditions (PBCs) gave rise to “boundary” effects at the simulation box faces normal to the velocity gradient (y -faces), which results in non-linear velocity profiles (see Fig. 1). This is evidently due to interaction between oppositely flowing fluid layers at these boundaries (due to action of PBCs) resulting in a reduction of their streaming velocities. These undesired bound-

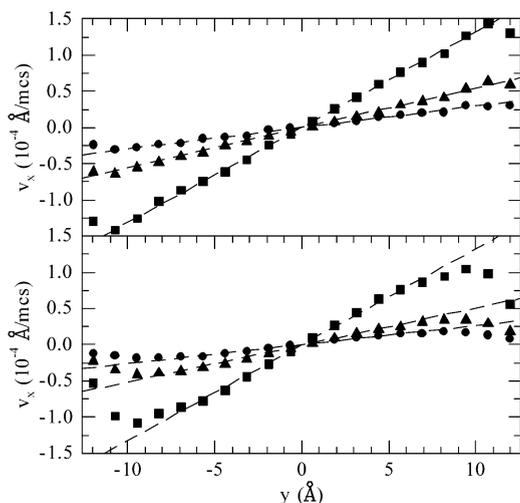


Fig. 1. Velocity profiles at different shear rates from NEMC simulations with (top) and without (bottom) LEPBCs. Dashed lines are linear fits to the data within $|y| < 7.5 \text{ \AA}$.

ary effects may be minimized by employing LEPBCs as is normally done in NEMD simulations. The correct rate of displacement of the image boxes with respect to the central simulation box in LEPBCs may be obtained self-consistently by matching it to the shear rate in the interior of simulation box. We found that though the incorporation of LEPBCs managed to substantially decrease boundary effects (see Fig. 1), other adverse effects crept into our simulations. For molecules positioned midway across the y -faces, the LEPBCs tended to pull apart the two portions of molecules on either sides resulting in abnormal bond length and angle distributions. This was especially severe for large shear rates and simulations where the regrowth moves (which help in relaxing the internal degrees of freedom of the molecules) were attempted infrequently. Increasing the frequency of regrowth moves resolved this problem but then resulted in a Trans-Gauche transition rate which was inconsistent with MD simulations. Due to these reasons, results from simulations with LEPBCs are less meaningful than those without it.

Fig. 2 compares the NEMC method against the “benchmark” NEMD method in terms of the intermolecular component of internal energy and pressure, and the orientational order parameter at different shear rates. The intramolecular components of the energy and pressure were found to be very sensitive to our choice of thermostat and were thus excluded. The order parameter λ was obtained from the order tensor using standard approaches [14]. The figure clearly indicates that the energy, pressure and structure of fluids sheared using the NEMC method do not match those obtained with the NEMD technique, these deviations being especially severe at large shear rates. The largest deviation seems to be in the orientation order of molecules between the two types of simulations. This analysis thus confirms the drawbacks of using synthetic shear within an inherently static MC method.

3. Molecular dynamics: Preliminary results

Given the frailty of the NEMC method earlier used by us to study the shear-induced alignment of micelles [6], we now revisit the micellar alignment problem, this time using an MD approach where the surfactants

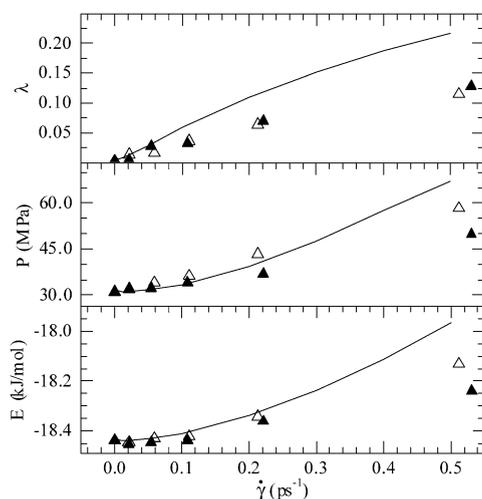


Fig. 2. Variation of the intermolecular part of the potential energy and pressure, and the alignment order parameter versus shear rate. Solid lines represent NEMD results, while the solid (open) symbols represent NEMC results with (without) LEPBCs.

are modeled as in Ref. [15]. Briefly, our H_4T_4 surfactant is a chain composed of coarse-grained head (H) and tail (T) beads, where the beads are held together by a finitely extensible nonlinear elastic (FENE) springs. All beads interact via the repulsive Weeks–Chandler–Anderson potential while the T–T interaction contains an additional attractive tail to promote phase separation. The spring constant and its maximum extension, and the range of the attractive tail were fixed to values of $30 \epsilon / \sigma^2$, 1.5σ and 1.5σ , respectively. At a temperature of $k_B T = 1$, the attractive tail depth ϕ was chosen to be equal to 1.6ϵ , large enough to lead to the formation of well-formed micelles but small enough to prevent their crystallization. In the case of thin film simulations, the surfactants were enclosed within repulsive atomic walls and sheared by sliding the walls at constant speed in the opposite directions. The bulk simulations were performed using LEPBCs along with a profile-unbiased Nosé–Hoover thermostat [11,16].

Fig. 3 summarizes some preliminary results obtained from these simulations. For thin films composed of a monolayer of micelles (see Fig. 3(a)), it is observed that the micelles orient perpendicular (or at other non-zero angles in some cases) with respect to the shearing direction above a certain shear rate where they exhibit a “log-rolling” behavior, in contrast to our earlier NEMC results [6] where the micelles aligned

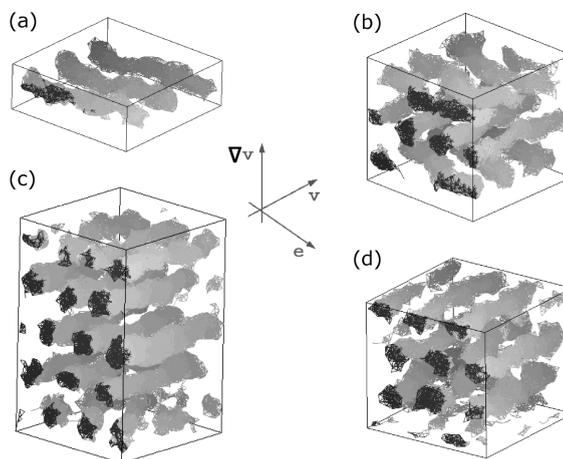


Fig. 3. Isometric view of the micelles after shearing them via molecular dynamics in thin films of different thicknesses (a–c), and in the bulk (d). The light grey regions correspond to the core of the micelles while the dark-grey represent the crosssection of micelles along the faces of the simulation box. The corona of micelles have been omitted for clarity.

parallel to the shearing direction. The log-rolling behavior, though observed in nematic molecules previously [17], has not been observed in micelles till now. A convincing explanation for such deviant behavior is currently being formulated, which we believe is related to the interactions between the sliding walls and the surfactant, since micelles within the interior of thicker films (Fig. 3(b) and (c)) or in the bulk (Fig. 3(d)) once again tend to align parallel to the shearing direction. These observations in thick films and in the bulk are consistent with experiments [4] but differ from our NEMC results where the micelles assume a finite tilt with respect to the shearing direction within the velocity–velocity gradient plane. This behavior was also observed in larger system sizes (not shown). Clearly, a more thorough investigation of the effect of boundary conditions and thermostats on the behavior of surfactant/block copolymer microphases (especially in monolayer-thick films) with molecular dynamics is required.

4. Conclusions

This study focuses on molecular-level modeling of shear-induced alignment of surfactant/block copolymer microphases using Monte Carlo and molecular

dynamics approaches. It has been demonstrated here that even though the incorporation of shear via synthetic means within Monte Carlo leads to correct qualitative behavior of cylindrical micelles in thin films, it is not a reliable and theoretically rigorous approach for studying such problems. Instead, the nonequilibrium molecular dynamics method using profile-unbiased thermostats constitutes a more convincing and rigorous approach to studying such shear-driven phenomena. A few preliminary results from applying this method to cylindrical micelles both in the bulk and in thin films have been presented in this study.

Acknowledgements

This work was supported by the NSF (MRSEC program) through the Princeton Center for Complex Materials (Grant No. DMR 0213706). Additional support has been provided by the Department of Energy (Grant No. FG02-01ER15121) and the ACS-PRF (Grant No. 38165-AC9). We also thank Paul Chaikin, Richard Register and Mark Tuckerman for useful discussions.

References

- [1] M.W. Matsen, F.S. Bates, *Macromolecules* 29 (4) (1996) 1091–1098.
- [2] Z.C.C. Harrison, S. Sethuraman, D.A. Huse, P.M. Chaikin, D.A. Vega, J.M. Sebastian, R.A. Register, D.H. Adamson, *Phys. Rev. E* 66 (1) (2002) 011706.
- [3] Z.-R. Chen, A.M. Issain, J.A. Kornfield, S.D. Smith, J.T. Grothaus, M.M. Satkowski, *Macromolecules* 30 (23) (1997) 7096–7114.
- [4] D.B. Scott, A.J. Waddon, Y. Lin, F.E. Karasz, H.H. Winter, *Macromolecules* 25 (16) (1992) 4175–4181.
- [5] D.E. Angelescu, J.H. Waller, D.H. Adamson, P. Deshpande, S.Y. Chou, R.A. Register, P.M. Chaikin, *Adv. Mater.* (2004), in press.
- [6] G. Arya, A.Z. Panagiotopoulos, *Phys. Rev. E* 70 (3) (2004) 031501.
- [7] G. Xu, J. Ding, Y. Yang, *J. Chem. Phys.* 107 (10) (1997) 4070–4084.
- [8] D.J. Evans, D.J. Searles, W.G. Hoover, C.G. Hoover, B.L. Holian, H.A. Posch, G.P. Morriss, *J. Chem. Phys.* 108 (10) (1998) 4351–4352.
- [9] D.J. Evans, G.P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids*, Academic, London, 1990.
- [10] A.W. Lees, S.F. Edwards, *J. Phys. C* 5 (15) (1972) 1921–1929.
- [11] G. Arya, E.J. Maginn, H.-C. Chang, *J. Chem. Phys.* 113 (6) (2000) 2079–2087.
- [12] G.J. Martyna, M.L. Klein, M. Tuckerman, *J. Chem. Phys.* 97 (4) (1992) 2635–2643.
- [13] D. Frenkel, G.C.A. Mooij, B. Smit, *J. Phys.: Condens. Matter* 4 (12) (1992) 3053–3076.
- [14] L.I. Kioupis, E.J. Maginn, *Chem. Eng. Sci.* 74 (1–2) (1999) 129–146.
- [15] H. Guo, K. Kremer, *J. Chem. Phys.* 119 (17) (2003) 9308–9320.
- [16] D.J. Evans, G.P. Morriss, *Phys. Rev. Lett.* 56 (20) (1986) 2172–2175.
- [17] A. Romo-Uribe, A.H. Windle, *Macromolecules* 29 (19) (1996) 6246–6255.