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Title	Analysis of polymer melts confined between nanoscale gap
Researchers	Takeshi Aoyagi, Tatsuya Shoji, Fumio Sawa, Hiroo Fukunaga, Jun-ichi Takimoto and Masao Doi
Purpose of this study	To clarify the mechanism of the specific behaviors of polymer melts confined between nanoscale gap, which is observed experimentally.
System (Material)	Poly-isoprene thin film confined between mica plate. (3nm-100nm gap)
Program (including analysis)	COGNAC v1.0, 2.0 Trajectory analysis utility (self diffusion, normal modes etc.)
Method & Some important input parameters	(Method) Coarse-grained molecular dynamics with bead-spring polymer chain model. (Inputs) Bead-spring model: degree of polymerization, number of molecule interaction potential: bead-bead, bead-wall simulation conditions: temperature, density, time step etc.
Advance & Problem	(Advance) The thickness of the surface layer, estimated from the analysis of the static polymer structure, is about 1.0–1.5 times the radius of gyration *Rg* in the bulk, and is independent of the distance between the walls and the wall–polymer interaction. The relaxation time of the polymers, obtained from the autocorrelation of normal modes, increases with increasing the strength of the wall–polymer interaction and with decreasing the distance between the walls. These wall effects are observed at a distance much larger than *Rg*. This result is in agreement with the recent dielectric measurements of *cis*-polyisoprene confined between mica surfaces. (Problem) The result of normal force is not consistent with the previous literature, where repulsive force has been reported for polymer adsorbing walls. A possible reason for this discrepancy is that we used a structureless wall potential, which allows the adsorbed polymers to slide freely along the surface, while real polymers are pinned on the surface.
References	[Manuscript] J.Chem.Phys. **115**(1) 552 (2001) [Presentation at conferences (Meetings)] Polymer preprint Japan, **48**(13), 3562 (1999) 47th Rheology tohronkai, p265 (1999)
KeyWords (in English)	confined system, isoprene, mica, nanoscale gap, nanorheology, coarse grained molecular dynamics, bead-spring model

Results (Remarks)

＜Simulation results＞

The component of radius of gyration perpendicular to the wall (Fig.3(a) in ref.) and the relaxation time τ_R(Fig.6 in ref.) as a function of the distance between wall Z.
τ_R slows down around the distance Z=30~40（1/Z=0.025~0.033）. $<Rg^2>^{1/2}$ of this polymer chain model is about 3.2.

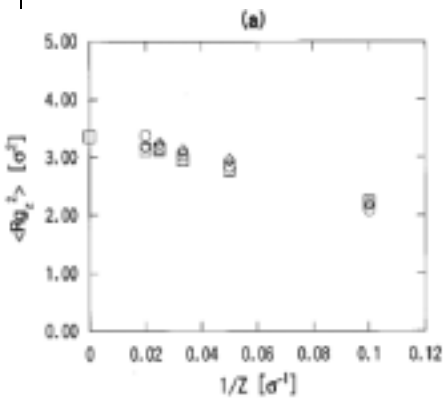

FIG. 3. Component of $\langle R_z^2 \rangle$ as a function of the distance between the walls, Z. (a) Component perpendicular to the wall and (b) component parallel to the wall, plotted *vs* 1/Z. The results of the bulk simulation are shown at 1/Z=0. ϵ^*=5.0ε (circles), ϵ^*=1.0ε (squares), and ϵ^*=1.0ε with a cutoff at 1.0σ (diamonds).

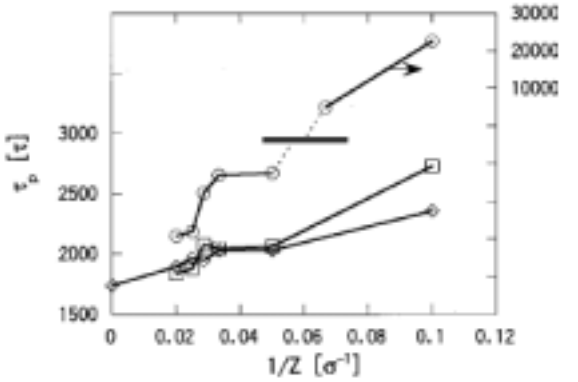

FIG. 6. Relaxation time $\tau_{p=1}$ as a function of Z. The results of the bulk simulation are shown at 1/Z=0. ϵ^*=5.0ε (circles), ϵ^*=1.0ε (squares), and ϵ^*=1.0ε with the cutoff at 1.0σ (diamonds).

<Example of experimental results>
Y.Cho, H.Watanabe and S.Granick, J.Chem.Phys., **110**, 9688 (1999)
Dielectric relaxation of polyisoprene confined between mica plate.

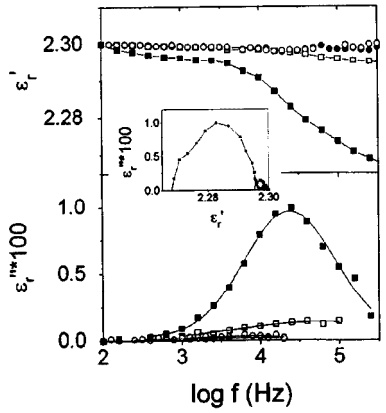

FIG. 7. Comparison of measurements made in parallel-plate geometry concerning spin-coated films of *cis*-polyisoprene (M_n=6000 g mol^{-1}, M_w/M_n =1.04) confined between atomically smooth muscovite mica. The normalized responses in phase with the electric field [$\epsilon_r'(f)$, the top panel] and 90° out of phase [$\epsilon_r''(f)$, the bottom panel], are plotted against Hertzian frequency, *f*, after normalization using Eqs. (8) and (9). The data concern films of macroscopic thickness (closed squares), 572 A thickness (open squares), 285 A thickness (closed circles), and 64 A thickness (open circles). Thickness was determined by multiple beam interferometry. The inset shows $\epsilon_r''(f)$ plotted against $\epsilon_r'(f)$, i.e., a Cole–Cole plot.