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Note on the number dependence of nonequilibrium molecular dynamics simulations of the viscosity of structured molecules

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Note on the number dependence of nonequilibrium molecular dynamics simulations of the viscosity of structured molecules

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In a recent comment about the number dependence of nonequilibrium molecular dynamics (NEMD) simulations of structured molecules, Chynoweth *et al.*[1] reported a "significant number dependence" at lower shear rates. This dependence on system size was found by comparison of their *n*-butane simulations using 468 molecules to the results previously published by Edberg *et al.*[2] on a 64-molecule system. Because we have also reported NEMD simulations of *n*-butane viscosities,[3] we considered it important to test the purported number dependence. In our previous work, simulations were performed on systems of 125 particles; here we report simulations on a system of 512 particles. For ease of discussion, we refer to the Chynoweth *et al.* paper as paper 1, the Edberg *et al.* paper as paper 2, the Rowley and Ely paper as paper 3 and this note as paper 4.

Just as paper 1 reports results at the same condition as reported in paper 2 but with a larger number of particles, this note reports results at conditions identical to that reported in paper 3 but with a larger system size. Paper 1 suggests two aspects of the purported number dependence. First, the simulated viscosities were in general smaller for the larger system size. This was particularly true at low shear rates. Second, the larger system appeared to show a linear behavior of η^* with respect to $\gamma^{*1/2}$ over the entire domain $0<\gamma^{*1/2}<1.5$, whereas the smaller system appeared to have two different linear regions within this domain. In paper 2, this behavior was attributed to two different rheological behaviors. A similar break in linearity was reported in paper 3. Saturation of shear induced molecular alignment was found in paper 3 to be the cause of this change in rheology.

It is useful to keep in mind the similarities and differences between these four studies. All of them used equivalent four-site models for *n*-butane interacting with the same Lennard-Jones site–site parameters. However, paper 1 includes stretching and angular bending potentials about the equilibrium values, while the other three studies used rigid bond lengths and angles fixed at the equilibrium values of 0.153 nm and 109.47°, respectively. The comparison between papers 1 and 2 is between 64- and 468-particle systems at $T^*=kT/\epsilon=4.05$ and $\rho^*=N\sigma^3/V=0.365$; the comparison between papers 3 and 4 is between 125- and 512-particle systems at $T^*=1.871$ and $\rho^*=0.463$.

The same procedures reported in paper 3 were used to perform the 512-particle simulations reported here. Figure 1 shows the results obtained in this study in comparison with the 125-particle system. The open symbols are the 125-particle results, the uncertainty bars show the range of values obtained from block averages, and the solid line represents the weighted least-squares fit of the data previously reported. Of particular importance is the considerable reduction in the scatter of values obtained from block averages when the larger system is used. The range of values for three to six 20 000-time-step block averages were smaller than the symbols used in Fig. 1. Table I shows the average values obtained and the range of the block averages as a function of shear rate. This suggests that larger systems may be used to compensate for the large noise level of simulated values at lower shear rates. This might be particularly important at very high densities where the nonlinear region is shifted to lower shear rates.[3]

Paper 2 also reports large uncertainty bars for simulations performed at lower shear rates. In view of the above comments, one would in fact expect the large uncertainty bars for those 64-particle simulations. The comparison made in paper 1 does not include the uncertainty bars on the 64-particle data, but it appears that the reported discrepancy could be accounted for entirely in terms of the

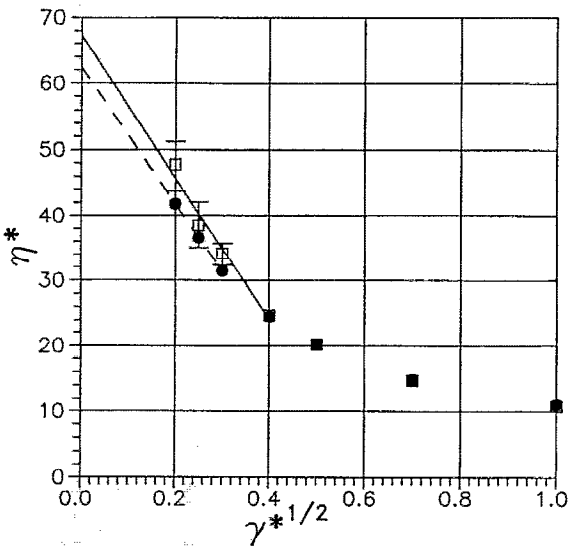

FIG. 1. Simulated values of η^* for the 125-particle system (□, with accompanying block average range) and for the 512-particle system (●). Lines show extrapolation to zero shear (solid: 125 particles; dashed: 512 particles).

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TABLE I. Results for the 512- and 125-particle simulations.

γ^*	$\eta^*(512)$	Range of η^* from block averages	$\eta^*(125)$
0.04	41.79	40.57 – 42.18	47.76
0.0625	36.61	36.50 – 36.72	38.52
0.09	31.47	31.27 – 31.76	34.58
0.16	24.49	24.26 – 24.73	24.70
0.25	20.17	19.92 – 20.28	20.18
0.49	14.88	14.72 – 15.05	14.73
1.00	10.99	10.91 – 11.07	10.72

previously reported uncertainty at the lower shear rates. One cannot conclude however that there is no number dependence. All of the η^* values for the 468-particle system were larger than the corresponding 64-particle values in the low shear region. This same behavior is also observed in Fig. 1, indicating that there is indeed a small number dependence on the viscosity. The larger relative discrepancy reported in paper 1 than that of Fig. 1 leads us to believe that most of the reported number dependence is due to the extremely small size of the 64-particle system used in paper 2. Even with the uncertainties in the 125-particle values shown in Fig. 1, the results of the linear extrapolation are within the uncertainties stated in paper 3. We obtain $\eta^* = 67.28$ for the 125-particle system and $\eta^* = 62.42$ for the one containing 512 particles. It is interesting to note that the slopes of the lines fitted to the data are the same for both systems.

Unlike the result reported in paper 1, we still see a break in the linear behavior of η^* with $\gamma^{*1/2}$ at values of $\gamma^{*1/2}$ larger than about 0.5, independent of the system size. This is similar to the results reported in both papers 2 and 3. This change in rheology is in fact a real phenomenon attributable to saturation of molecular alignment modes as

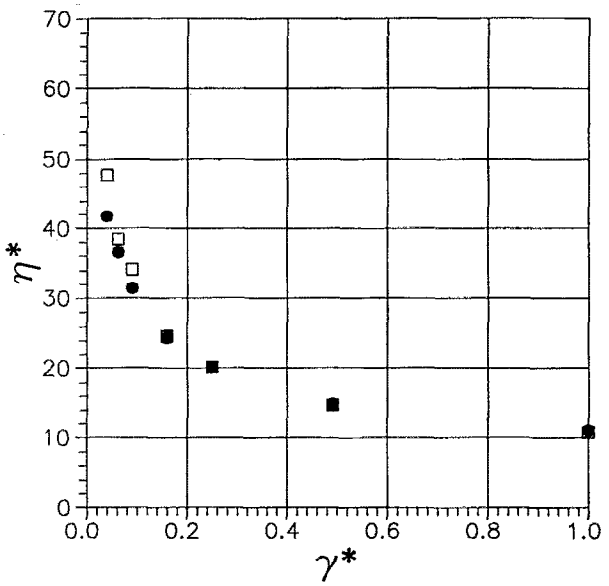

FIG. 2. Simulated values of η^* for the 125-particle system (□) and for the 512-particle system (●) vs γ^*.

suggested in paper 3, not a number-dependent artifact. One might interpret the discussion in paper 2 as an indication that there is a sharp break in the linear region at some value of γ^*, but the change in rheology is in fact a continuous one as the shear-thinning behavior decreases with γ^*. This is conveniently seen in a plot of η^* vs γ^*, as in Fig. 2.

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