Electronic Supporting Information (ESI) for: Shear heating, flow, and friction of confined molecular fluids at high pressure

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Atomic Mass Density Profiles

Atomic mass density profiles are shown for the symmetrical (Fig. S1) and unsymmetrical (Fig. S2) systems at 0.5 and 1.0 GPa, 5 and 100 m s^{-1}. At both pressures, fluid layering extends less than 1 nm from the solid slabs. This means that no confinement-induced viscosity increase is expected and thus the systems are representative of thicker films (see refs. 32-34).

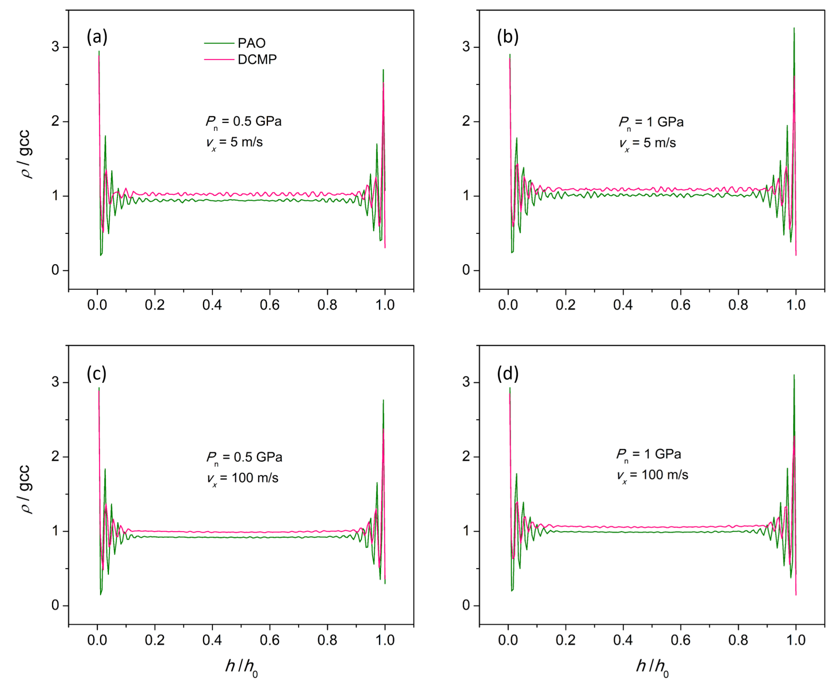

Figure S1: Spatially resolved atomic mass density profiles for PAO and DCMP at 0.5 and 1.0 GPa, 5 and 100 m s^{-1}. Symmetrical systems - both slabs thermostat coupling time is 0.1 ps. Note that h is normalized.

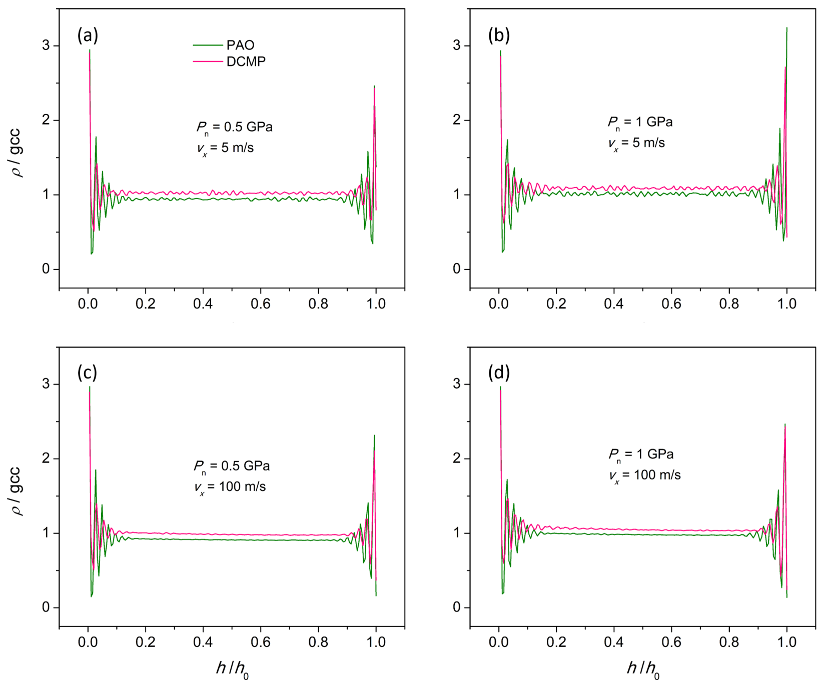

Figure S2: Spatially resolved atomic mass density profiles for PAO and DCMP at 0.5 and 1.0 GPa, 5 and 100 m s^{-1}. Unsymmetrical systems - bottom slab thermostat coupling time of 0.1 ps, top slab 100 ps. Note that h is normalized.

Average Fluid Density

The change in average fluid density, $\bar{\rho}_{\mathrm{f}}$, calculated from the center 10 nm of fluid, with pressure, P and shear rate, $\dot{\gamma}$, is shown in Fig. S3. As expected, $\bar{\rho}_{\mathrm{f}}$; i) is higher for DCMP compared to PAO, ii) increases with increasing P, and iii) decreases with increasing $\dot{\gamma}$. There is only a slight change between the symmetrical and unsymmetrical systems, despite the larger ΔT_{f} for the latter.

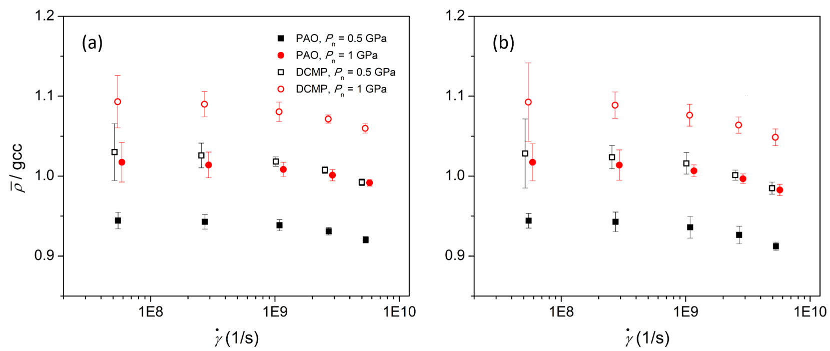

Figure S3: Change in average fluid density, $\bar{\rho}_{\mathrm{f}}$ with logarithmic shear rate, $\dot{\gamma}$, for (a) symmetrical and (b) unsymmetrical systems.

Additional Temperature Profiles

As mentioned in the main text, the entire liquid domain was divided into spatial bins (with an interval of 0.5 Å) along the film thickness, in which the average T was calculated. The peculiar momenta kinetic energy was used, which is computed relative to the imposed streaming velocity. A representative spatially resolved T-profile from NEMD is shown in the main text. The NEMD profiles were fit with a quadratic function, $T = ah^2 + bh + c$, where h is the film thickness, a, b, and c are the fitting parameters. According to the Fourier law of heat conduction, a correlation can be established between the fitting parameter (the prefactor of the leading order term) and the fluid thermal conductivity, λ_f:

$$a = \frac{\bar{\tau}\dot{\gamma}}{2\lambda_\mathrm{f}}, \tag{1}$$

where $\bar{\tau}$ is the mean shear stress and $\dot{\gamma}$ the shear rate. A more detailed derivation can be found in ref. 24. The thus derived λ_f (for the symmetric cases) are shown in the main text.

Additional T profiles for the other thermostat coupling times considered (1-10 ps) are shown in Fig. S4.

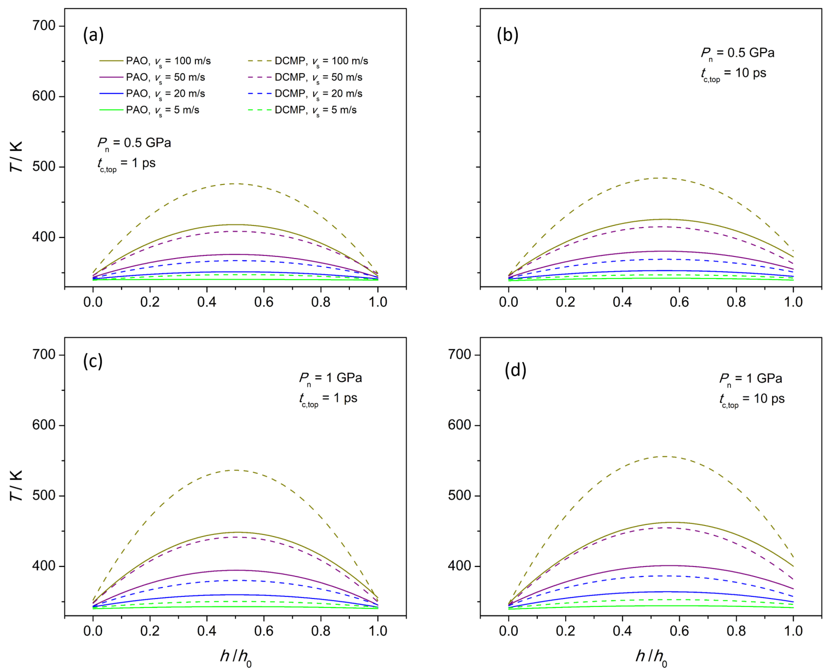

Figure S4: Quadratic fits of the spatially resolved $T(z)$ profiles for PAO and DCMP at 0.5 GPa and 1.0 GPa for the different values of v_{s} considered. Bottom slab thermostat coupling time of 0.1 ps, top slab 1-10 ps. Note that h is normalized.

Additional Flow Profiles

Additional flow profiles for the other values of v_s considered are shown in Fig. S5.

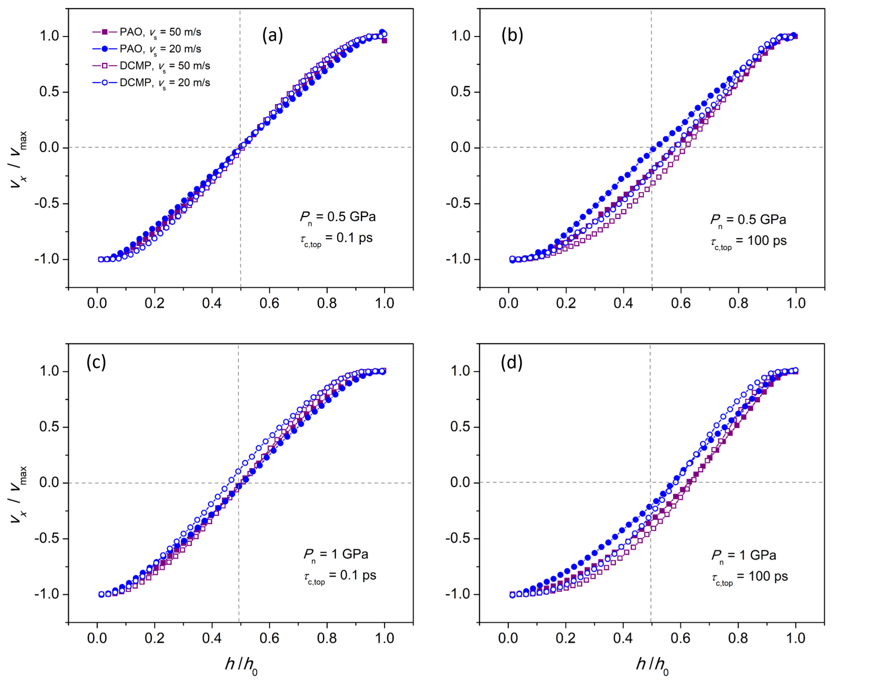

Figure S5: Spatially resolved flow, $v_x(z)$, profiles for PAO and DCMP at 0.5 GPa and 1.0 GPa and 20 m s^{-1} and 50 m s^{-1} (other v_s in main text). Symmetrical and unsymmetrical systems shown. Note that h and v_s are normalized.

Relating Temperature Rise and Flow

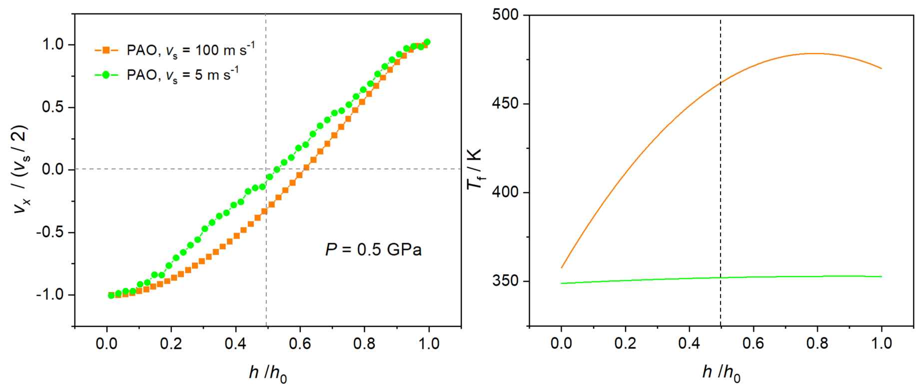

Figure S6: Examples of spatially resolved flow and temperature profiles for an unsymmetrical system (PAO at 0.5 GPa) at high and low sliding velocity.