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Supporting Information for

Rheology and Structure of Model Smectite Clay: Insights from Molecular Dynamics

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Introduction

This supplementary file includes a brief description of the Gay-Berne potential used to describe clay interaction in our model. We have also included four tables on all the fitting parameters used in the data analysis.

Text S1.

Gay-Berne Potential

The Gay-Berne potential is used to describe the interaction between clay platelets with shape and energy anisotropy. Each clay platelet is treated as an effective oblate ellipsoid. Then the pair potential is in the form (Coussaert and Baus, 2002; Gay and Berne, 1981; Luckhurst and Simmonds, 1993):

$$V(\boldsymbol{r}_{12}, \boldsymbol{u}_1, \boldsymbol{u}_2) = \epsilon_0 \epsilon(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}}_{12}) \times \varphi(\frac{r_{12}}{\sigma_0} + 1 - \sigma(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}}_{12})) \quad \text{(S1)}$$

where $\hat{\boldsymbol{r}}_{12}$ is the unit vector along the center-to-center vector $\mathbf{r}_{12}$ between two particles, $r_{12} = |\boldsymbol{r}_{12}|$. $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ are unit vectors along the symmetry axis of particle 1 and 2. ϵ_0 and σ_0 set the energy and length scale. $\varphi(y) = y^{12} - y^6$ is the dimensionless 12-6 Lennard-Jones potential.

Each function in Eq. (S1) is chosen as:

$$\sigma(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}}_{12}) = \left\{\left(\frac{1+\chi}{1-\chi}\right) w(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}}_{12}; \chi)\right\}^{-1/2} \tag{S2}$$

$$w(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}}_{12}; \chi) = 1 - \frac{\chi}{2}\left\{\frac{\left(\hat{\boldsymbol{r}}_{12}\cdot(\boldsymbol{u}_1+\boldsymbol{u}_2)\right)^2}{1+\chi\boldsymbol{u}_1\cdot\boldsymbol{u}_2} + \frac{\left(\hat{\boldsymbol{r}}_{12}\cdot(\boldsymbol{u}_1-\boldsymbol{u}_2)\right)^2}{1-\chi\boldsymbol{u}_1\cdot\boldsymbol{u}_2}\right\} \tag{S3}$$

$$\epsilon(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}}_{12}) = \{1 - \chi^2(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)^2\}^{-\upsilon/2} \times w(\boldsymbol{u}_1, \boldsymbol{u}_2, \hat{\boldsymbol{r}}_{12}; \chi')^{\mu} \tag{S4}$$

The zeros of the potential are determined by Eqs. (S2) and (S3). The anisotropy of the Gay-Berne potential is captured by the powers of υ and μ in Eq. (S4), where the first factor on the right-hand side favors alignment in the direction parallel to the symmetry axis.

For discotic molecules, we follow the convention to use υ = 2 and μ = 1 (Caprion et al., 2003; Cienega-Cacerez et al., 2014; Coussaert and Baus, 2002). The aspect ratio $\kappa = \sigma_{ff}/\sigma_{ee}$ is the ratio of particle thickness (face-to-face) to particle diameter (end-to-end), $\kappa < 1$ corresponds to a discotic molecule and $\kappa = 1$ corresponds to spherical molecule. The energy ratio $\kappa' = \epsilon_{ee}/\epsilon_{ff}$ is the ratio of the corresponding well depth between the end-to-end configuration and the face-to-face configuration, then:

$$\chi = \frac{\kappa^2-1}{\kappa^2+1}, \chi' = \frac{\kappa'-1}{\kappa'+1}, \epsilon_0 = (1-\chi^2)\epsilon_{ee}, \sigma_0 = \sigma_{ff} = \kappa\sigma_{ee} \tag{S5}$$

The system considered in this work are mixtures of three type of particles A, B and C with the same thickness and different diameter, corresponding to aspect ratio κ of 1/5, 1/6 and 1/7. The slight polydispersity is introduced to avoid crystallization in mono-dispersed system. The type with the smallest aspect ratio (1/5) is used as a reference component with mass $m_A = 1$ and diameter $\sigma_{A,ff} = \sigma_0 = 1$. The energy ratio $\kappa' = 1/5$ is used for all particles.

For interaction between different particle types, the following mixing rule is used after Cienega-Cacerez et al. (2016):

$$\epsilon_{ij} = \sqrt{\epsilon_i\epsilon_j}, \sigma_{ij} = \frac{\sigma_i+\sigma_j}{2} \tag{S6}$$

Table S1. Fitting parameters of the Herschel-Bulkley model of shear stress dependence on strain rate in Figure 5a.

Table S2. Fitting parameters of the exponential model of PaRDF peak dependence on distance, an example at normal stress P = 5.62MPa and strain rate $\dot{\gamma} = 6.93\times10^8$ /s in Figure 7b.

Table S3. Fitting parameters of the exponential model of stacking size dependence on shear strain at normal stress P=5.62MPa in Figure 7c.

Table S4. Fitting parameters in Equation (7) at normal stress P = 5.62 MPa in Figure 8.