Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

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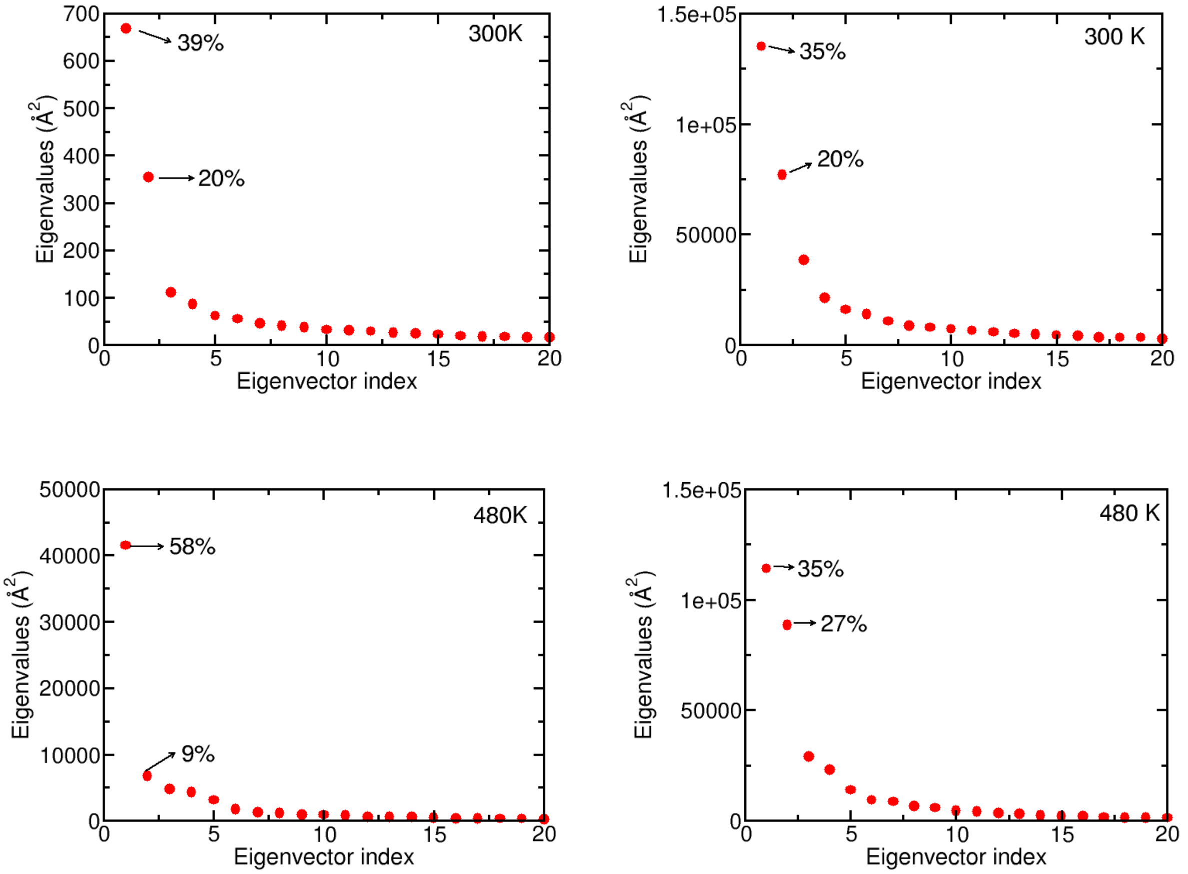

FIG. S-1: The eigenvalues obtained from the covariance matrix at (top) 300 and (bottom) 480 K for (LHS) $h = 0.05$ and (RHS) $h = 0.25$ g_{water}/g_{lignin}.

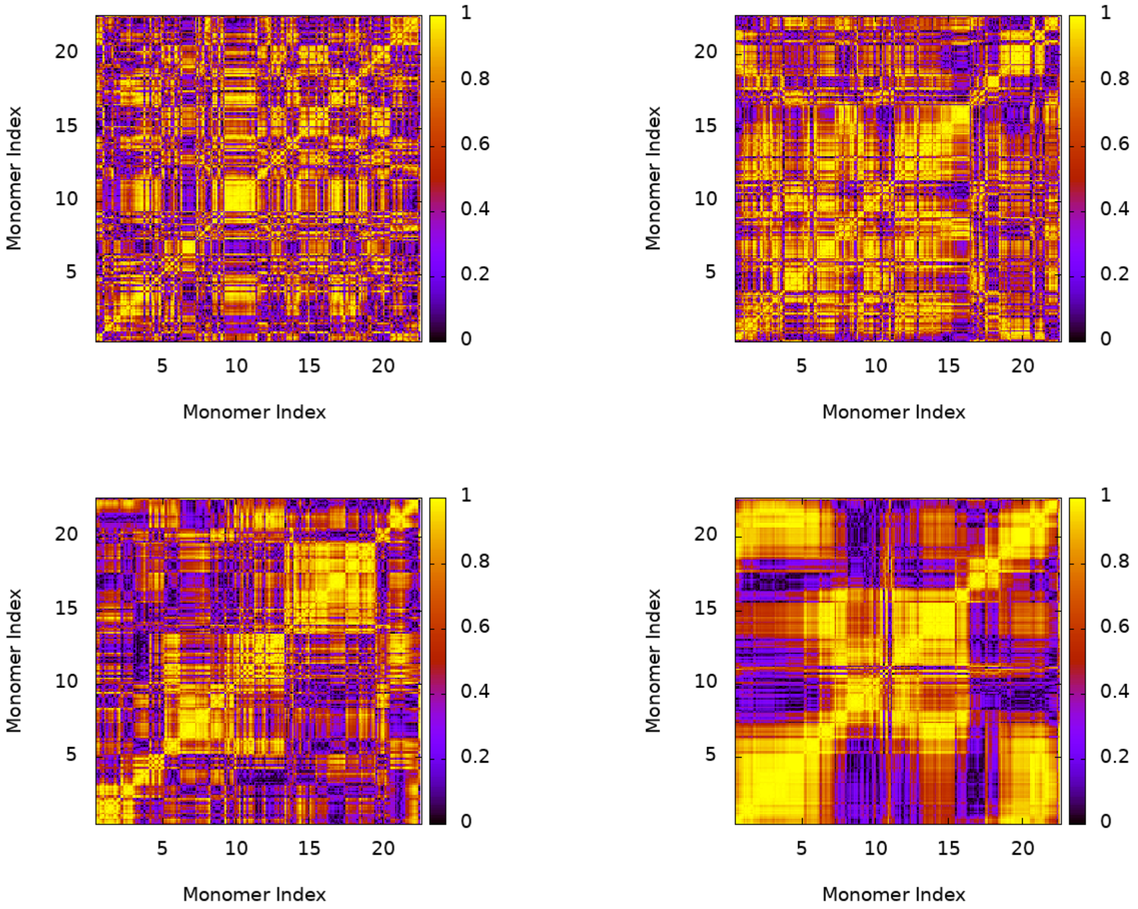

FIG. S-2: Correlation of each monomer of a single lignin molecule at (top) 300 and (bottom) 480 K for (LHS) $h = 0.05$ and (RHS) $h = 0.25$ g_{water}/g_{lignin}. Correlation is calculated as $C_{ij} = v_{1,i}v_{1,j}/|v_{1,i}||v_{1,j}|$, where $v_{1,i}$ is the first eigenvector of carbon i.

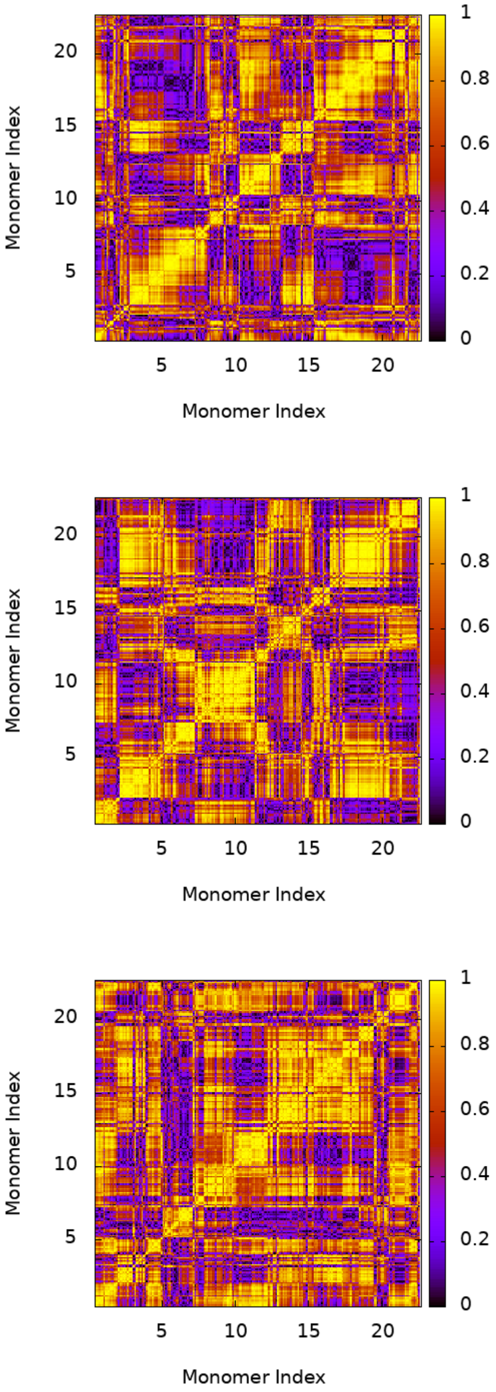

FIG. S-3: Correlation of each monomer of a single lignin molecule (for other three lignin molecules) at 480 K for $h = 0.05\ g_{water}/g_{lignin}$. Correlation is calculated as $C_{ij} = v_{1,i}v_{1,j}/|v_{1,i}||v_{1,j}|$, where $v_{1,i}$ is the first eigenvector of carbon i.

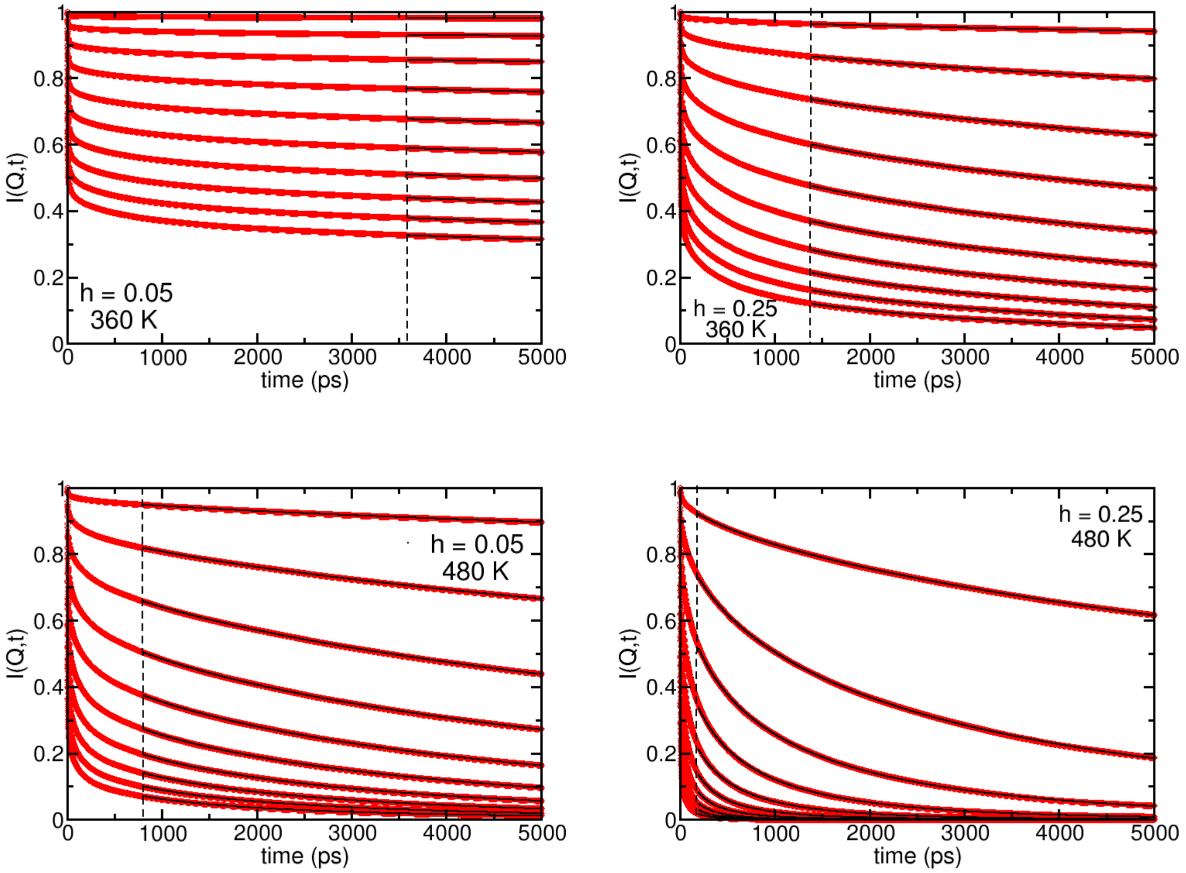

FIG. S-4: Incoherent intermediate scattering function $I(Q,t)$ for lignin at 360 and 480 for $0 < t < 5$ ns calculated from the second half of a 150-ns MD simulation (red open circles). The solid lines are the fits of $I_{KWW(}Q,t)$ to $I(Q,t)$. (LHS) $h = 0.05$ and (RHS) $h = 0.25$ g_{water}/g_{lignin}. From top to bottom the Q values are 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2 Å^{-1}. Here, β is the free fitting parameter.

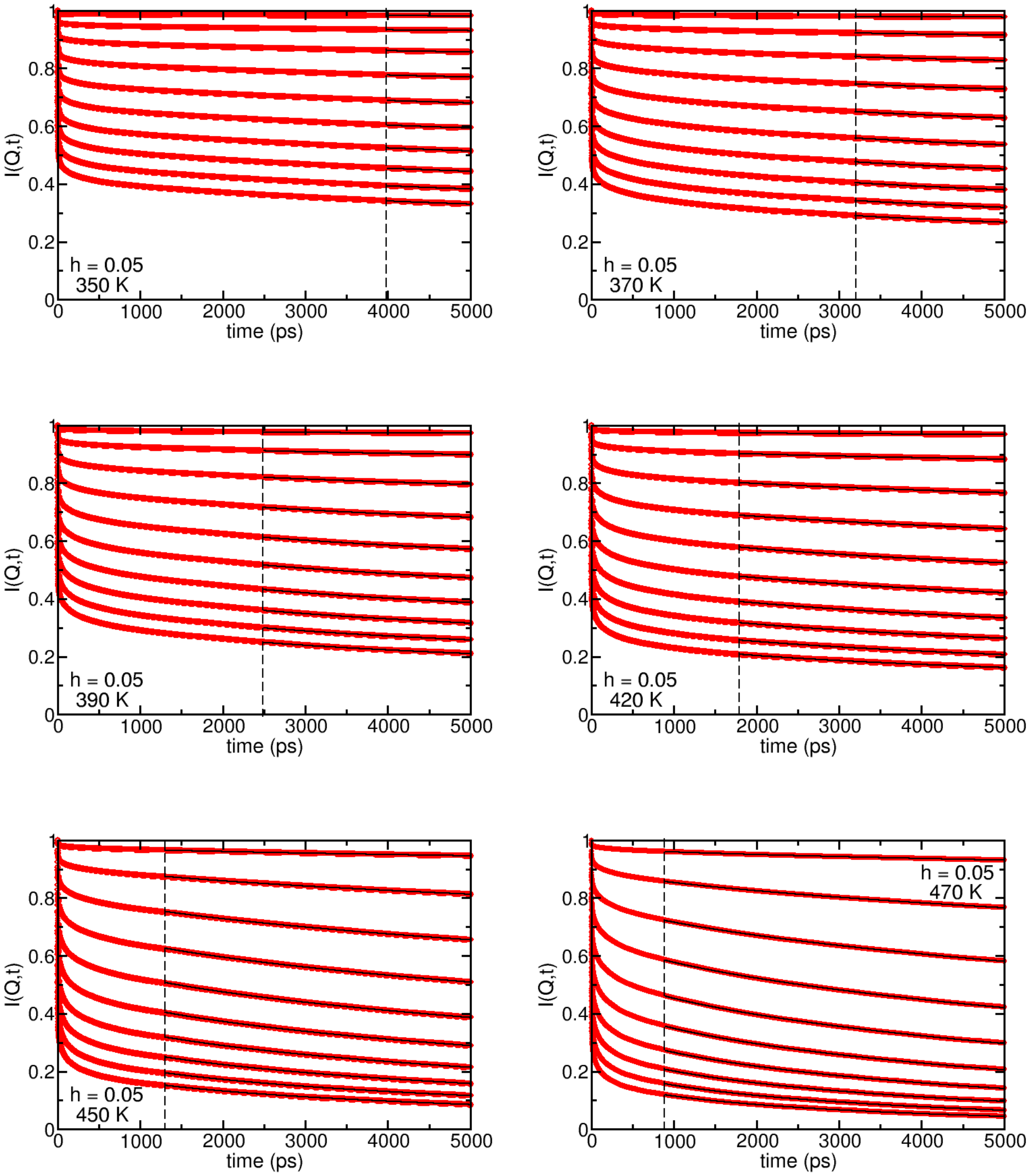

FIG. S-5: Incoherent intermediate scattering function $I(Q,t)$ for lignin at 350, 370, 390, 420, 450 and 470 for $h = 0.05$ g_{water}/g_{lignin}(red open circles). The solid lines are the fits of $I_{KWW}(Q,t)$ to $I(Q,t)$. From top to bottom the Q values are 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2 Å^{-1}.

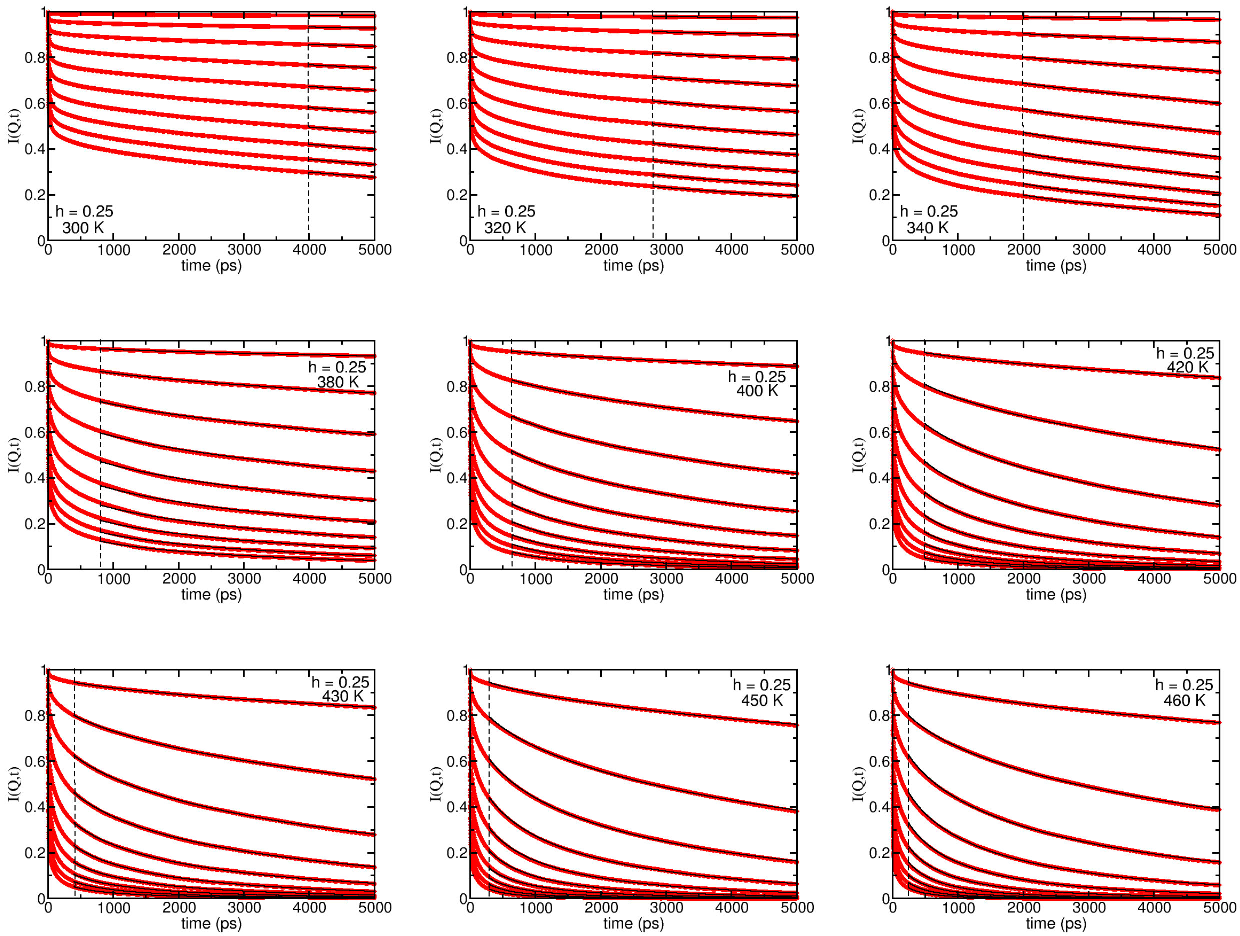

FIG. S-6: Incoherent intermediate scattering function $I(Q,t)$ for lignin at 300, 320, 340, 380, 400, 420, 430, 450 and 460 for $h = 0.25$ g_{water}/g_{lignin}(red open circles). The solid lines are the fits of $I_{KWW}(Q,t)$ to $I(Q,t)$. From top to bottom the Q values are 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2 Å^{-1}.

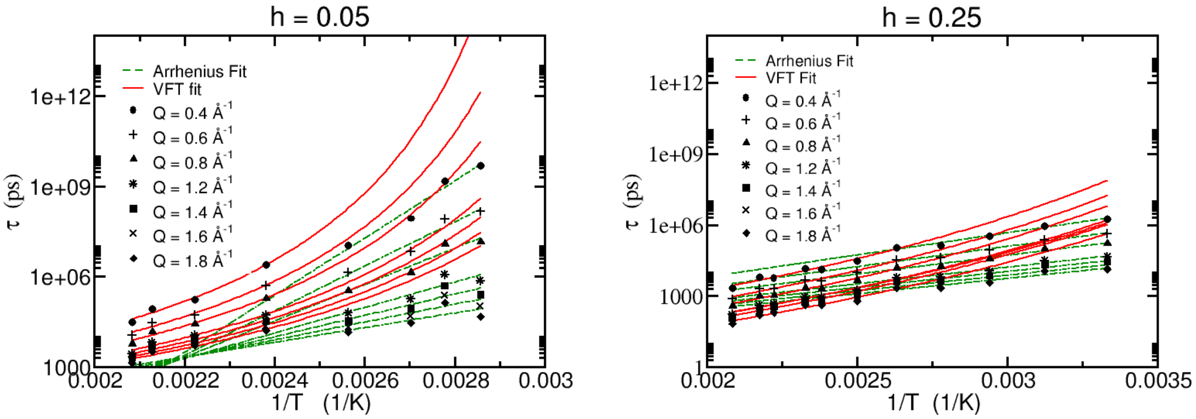

FIG. S-7: τ versus temperature. The solid lines represent the fit of the VFT and the dashed line the fit of the Arrhenius function to τ for the Q-value : 0.4, 0.6, 0.8, 1.2, 1.4, 1.6 and 1.8 Å^{-1}. (LHS) $h = 0.05$ and (RHS) $h = 0.25$ g_{water}/g_{lignin}.

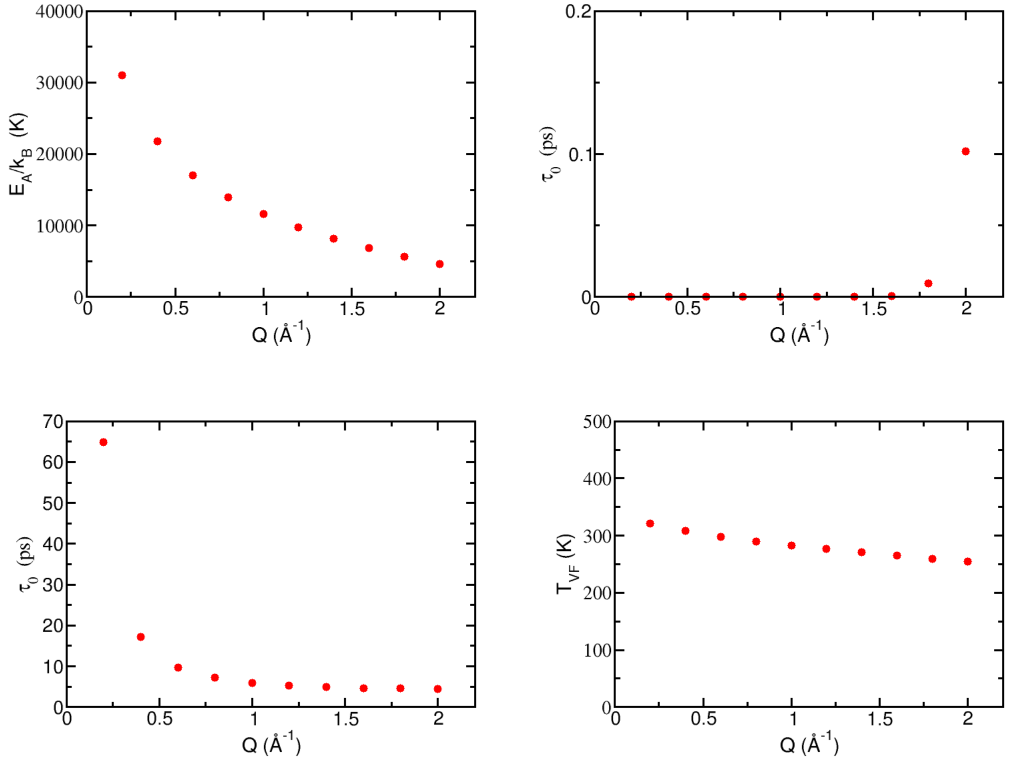

FIG. S-8: Fitting parameter for the Arrhenius ($T < 400$ K) and VFT ($T > 400$ K) fits to τ for $h = 0.05$ g_{water}/g_{lignin}. For VFT fit, B parameter was fixed a constant value $B = 1325$ K at $Q = 0.1$ Å^{-1}.

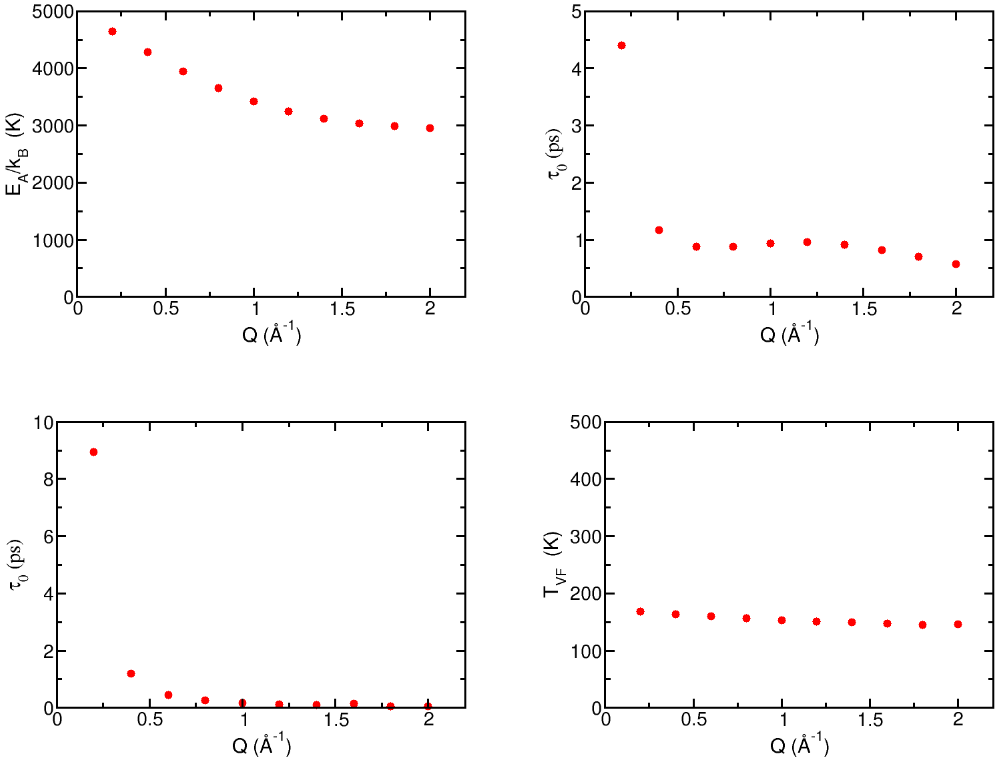

FIG. S-9: Fitting parameter for the Arrhenius ($T < 360$ K) and VFT ($T > 360$ K) fits to τ for $h = 0.25\ g_{water}/g_{lignin}$. For VFT fit, B parameter was fixed a constant value $B = 2443$ K at $Q = 0.1$ Å^{-1} .

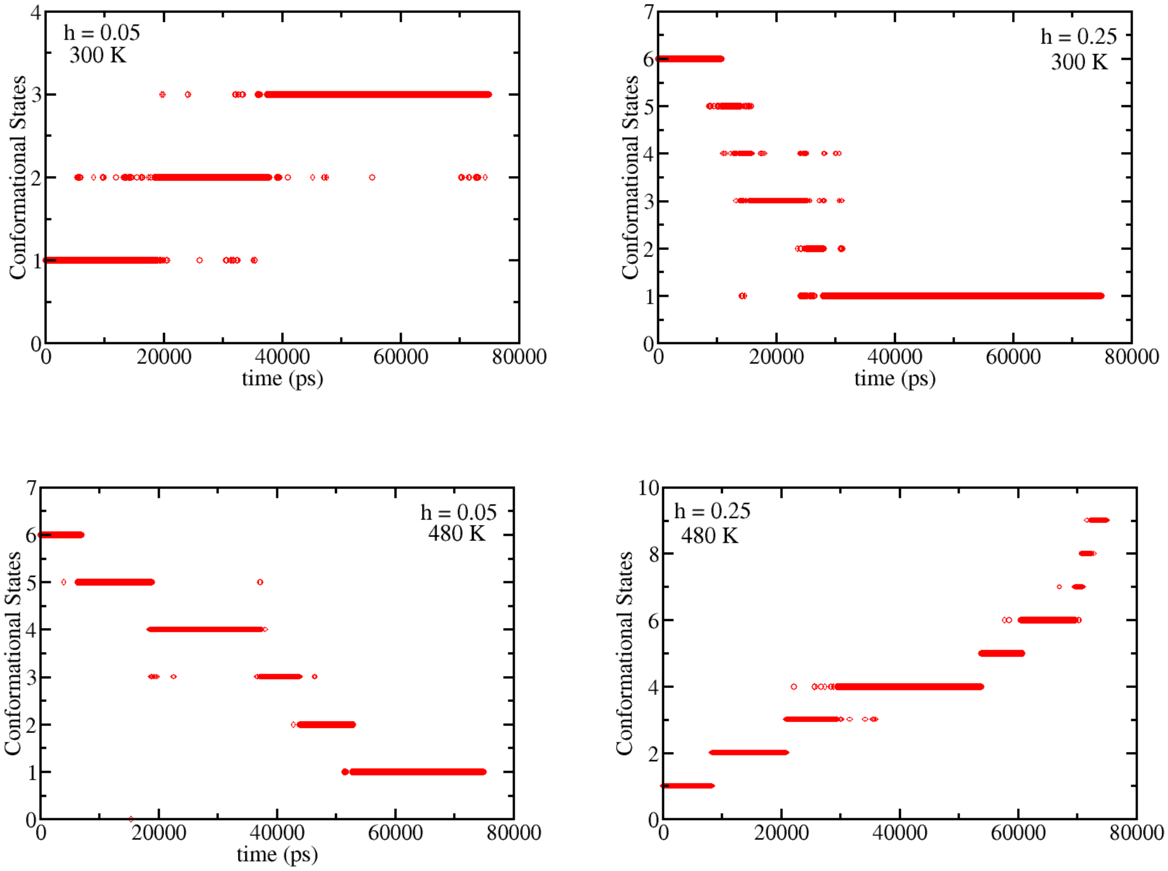

FIG. S-10: Time series of transitions between conformational states (top) 300 and (bottom) 480 K for (LHS) $h = 0.05$ and (RHS) $h = 0.25$ g_{water}/g_{lignin}.

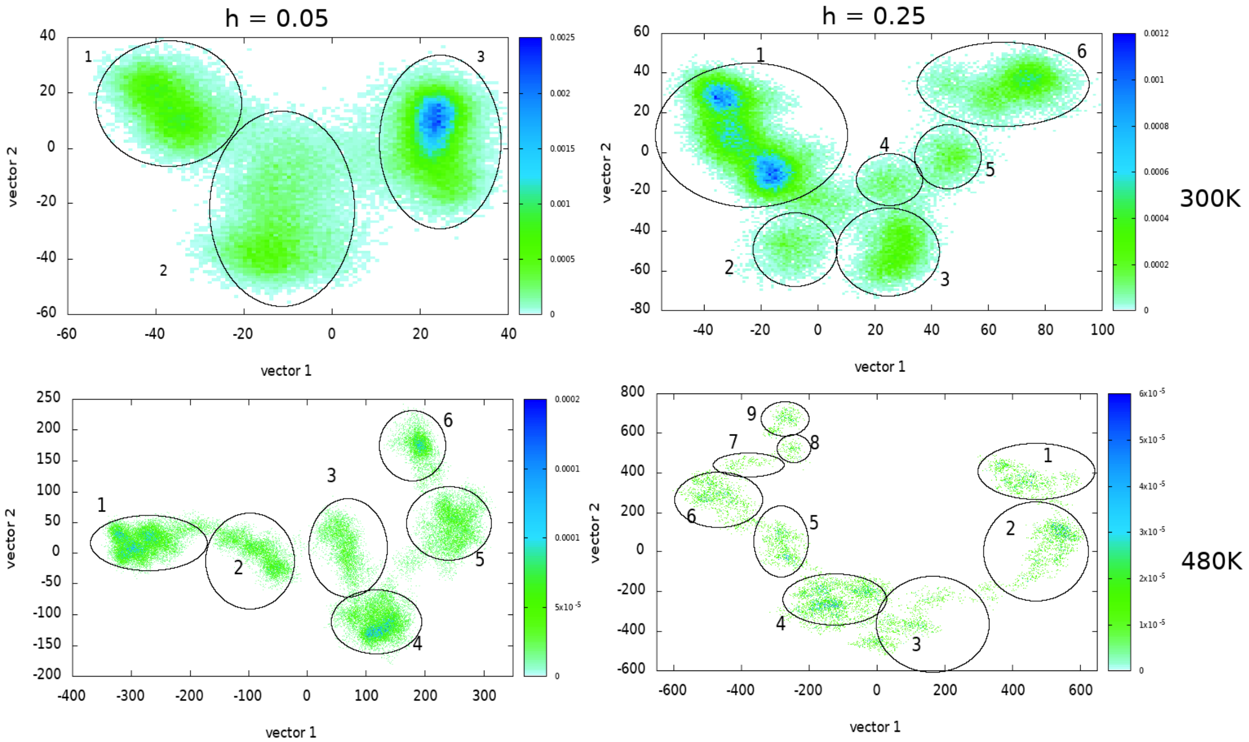

FIG. S-11: The projection of the lignin trajectory onto v_1 (first principal component) and v_2 (second principal component) at (top) 300 and (bottom) 480 K for (LHS) $h = 0.05$ and (RHS) $h = 0.25$ g_{water}/g_{lignin}. z-axis represents the probablility.

TABLE S-1: The primary sequence of the first lignin molecule

monomers	linkages
S	
S	βO4L
G	βO4R
G	β5L
G	βO4R
S	βO4L
G	β5R
G	βO4L
G	βO4R
S	βO4L
G	βO4R
G	β5L
G	βO4R
S	βO4L
G	βO4R
G	βO4L
G	βO4R
S	βO4L
G	β5R
G	βO4L
G	βO4R
G	$\beta\beta$

TABLE S-2: The primary sequence of the second lignin molecule

monomers	linkages
S	
S	βO4L
G	βO4R
G	βO4L
G	βO4R
S	βO4L
G	βO4R
G	βO4L
G	βO4R
S	βO4L
G	βO4R
G	β5L
G	βO4R
S	βO4L
G	βO4R
G	β5L
G	βO4R
S	βO4L
G	β5R
G	β5L
G	β5R
G	$\beta\beta$

TABLE S-3: The primary sequence of the third lignin molecule

monomers	linkages
S	
S	βO4L
G	βO4R
G	βO4L
G	βO4R
S	βO4L
G	βO4R
G	β5L
G	β5R
S	βO4L
G	β5R
G	βO4L
G	βO4R
S	βO4L
G	βO4R
G	βO4L
G	βO4R
G	β5L
S	βO4R
G	βO4L
G	βO4R
G	$\beta\beta$

TABLE S-4: The primary sequence of the fourth lignin molecule

monomers	linkages
S	
G	β5L
G	βO4R
G	βO4L
G	β5R
S	βO4L
G	βO4R
G	βO4L
G	βO4R
S	βO4L
G	βO4R
G	β5L
G	βO4R
S	βO4L
G	βO4R
G	βO4L
G	βO4R
S	βO4L
G	βO4R
S	βO4L
G	β5R
G	$\beta\beta$

A. The Q-dependence of relaxation time τ

The Kohlrausch-Williams-Watts (KWW) stretched exponential function,

$$I(Q,t) \sim exp(-(t/\tau)^{\beta_I}) \tag{S-1}$$

and in the Gaussian approximation, the intermediate scattering function is

$$\begin{aligned} I(Q,t) &\sim exp(-Q^2\langle r^2\rangle) \\ &\sim exp(-Q^2\langle t^{\beta_m}) \end{aligned} \tag{S-2}$$

where $\langle r^2\rangle \sim t^{\beta_m}$. From Eq. (S-1) and Eq. (S-2),

$$\begin{aligned} exp(-(t/\tau)^{\beta_I}) &\sim exp(-Q^2 t^{\beta_m}) \\ (\frac{t}{\tau})^{\beta} &\sim Q^2 t^{\beta} \\ \tau &\sim Q^{-2/\beta} \\ \tau &\sim Q^{-2/\beta_\tau} \end{aligned} \tag{S-3}$$

where $\beta = \beta_\tau = \beta_I = \beta_m$.