Comparison of two simple models for high frequency friction: Exponential vs. Gaussian wings

STEVEN ADELMAN, Purdue University — We describe new methods for ruling out unphysical forms for the high frequency friction \( \lim_{\omega \to \infty} \beta(\omega) \) needed to compute vibrational energy relaxation times. These are based on the fluctuating force autocorrelation function \( (f \cdot f)(t) = \langle \tilde{\mathbb{I}}_2 \rangle - \langle \tilde{\mathbb{I}}_2 \rangle \) needed to compute vibrational energy relaxation times. These are based on the fluctuating force autocorrelation function \( (f \cdot f)(t) = \langle \tilde{\mathbb{I}}_2 \rangle - \langle \tilde{\mathbb{I}}_2 \rangle \), which is proportional to the Fourier transform of \( \beta(\omega) \). Here we compare two model \( (f \cdot f)(t) \)’s

\[
C_{\text{se}}(t) = \text{sech} \left( \frac{t}{\tau} \right) \quad \text{and} \quad C_{\text{ga}}(t) = \exp \left[ -\frac{1}{2} \left( \frac{t}{\tau} \right)^2 \right].
\]

These give respective high frequency frictions which have incompatible exponential and Gaussian forms. We apply our procedures to eliminate \( C_{\text{se}}(t) \). We do this by showing from \( \beta_{\text{se}}(\omega) \equiv \frac{\langle \tilde{\mathbb{I}}_2 \rangle}{k_B T} \int_0^\infty \cos \omega t C_{\text{se}}(t)dt \) that \( \lim_{\omega \to \infty} \beta_{\text{se}}(\omega) \) derives from the long time “tail” of \( C_{\text{se}}(t) \). We then note that \( C_{\text{se}}(t) \) is built only from short time quantities, rendering the form of this “tail” artifactual. Thus the exponential form of \( \lim_{\omega \to \infty} \beta(\omega) \), is also artifactual.