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Addition/Correction

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Correction to Comparison of Two Simple Models for High Frequency Friction: Exponential versus Gaussian Wings

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In *J. Phys. Chem. B* **2009**, *113*, 5528−5536, we compared two models for the normalized fluctuating force autocorrelation function $C(t) = \langle \tilde{F}(t)\tilde{F}\rangle_0/\langle \tilde{F}^2\rangle_0$ for vibrational energy relaxation (VER) in liquids. These are the Gaussian model $C_{ga}(t) = \exp([-1/2(t^2/\tau^2)]$ and the model $C_{se}(t) = \mathrm{sech}(t/\tau)$ where $\tau = [\langle \dot{\tilde{F}}^2\rangle_0/\langle \dot{\tilde{F}}^2\rangle_0]^{1/2}$. We were concerned with their friction kernels $\beta(\omega) = (\langle \tilde{F}^2\rangle_0/kT)\int_0^\infty \cos\,\omega t\;C(t)\mathrm{d}t$, since these when evaluated at the frequency ω_l of the relaxing normal mode are proportional to its inverse VER time T_1^{-1}. Note that $\beta_{ga}(\omega)$ has Gaussian wings given by $\lim_{\omega\to\infty}\beta_{ga}(\omega) = (\langle F^2\rangle_0/k_BT)\exp[(-1/2)\omega^2\tau^2]$ while $\beta_{se}(\omega)$ has exponential wings given by $\lim_{\omega\to\infty}\beta_{se}(\omega) = (\langle \tilde{F}^2\rangle_0/kT)\pi\tau\,\exp(-\pi\omega\tau/2)$. Then on the basis of theoretical arguments we concluded that $C_{ga}(t)$ is unphysical and thus that Gaussian not exponential wings are physical. In agreement with the calculations of Egorov and Skinner,[1] we have now reversed our conclusion.

Our initial conclusion was based on the assumption (correct) that if $\lim_{\omega\to\infty}\beta_{se}(\omega)$ arises from the long time tail of $C_{se}(t)$ then the latter is unphysical. Our "proof" that this is true arises in part, from a Fourier transform argument based on Figure 4 of the paper. Namely, from Figure 4 in the 0−200 fs "head" region of the $C(t)$'s, $C_{ga}(t)$ is "narrower" than $C_{se}(t)$, apparently implying that $\beta_{ga}(\omega)$ would be "broader" than $\beta_{se}(\omega)$ if the heads dominated the $\beta(\omega)$'s. This further apparently implies that, if the heads dominated, $\beta_{ga}(\omega)$ would be larger than $\beta_{se}(\omega)$, and hence, $T_{1,ga}^{-1} > T_{1,se}^{-1}$. However, since

$$\lim_{\omega_l\to\infty}\beta_{se}(\omega_l) \sim \exp\left(-\frac{\pi\omega_l\tau}{2}\right) \gg \lim_{\omega_l\to\infty}\beta_{ga}(\omega_l) \sim \exp\left(-\frac{1}{2}\omega_l^2\tau^2\right)$$

actually $T_{1,ga}^{-1} \ll T_{1,se}^{-1}$. Thus we concluded that the tail of $C_{se}(t)$ determines $T_{1,se}$, invalidating $C_{se}(t)$.

This "proof" is flawed. The flaw is that, at sufficient high ω, $\beta_{ga}(\omega) < \beta_{se}(\omega)$ even if the head dominates the Fourier transforms, thus permitting $\lim_{\omega\to\infty}\beta_{se}(\omega)$ to properly derive from the head of $C(t)$.

In ref 2 we derived molecular formulas for $\langle F^2\rangle_0$ and τ and then embedded them into $C_{ga}(t)$. The above comments do not invalidate these formulas since they can equally well be imbedded in a model $C(t)$ which gives a $\beta(\omega)$ with exponential wings.

REFERENCES

(1) Egorov, S. A.; Skinner, J. L. *J. Chem. Phys.* **1996**, *106*, 7047.
(2) Adelman, S. A.; Ravi, R.; Muralidhar, R.; Stote, R. H. *Adv. Chem. Phys.* **1993**, *84*, 73.