Transition paths are hot – supporting information

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I. CALCULATION OF THE SECOND MOMENT OF VELOCITIES

We evaluate the second moment of velocities explicitly for the equilibrium distribution, in order to illustrate our definition of an effective temperature. The calculation is straightforward: based on the flux-weighted velocity distribution

$$P^{\mathrm{eq}}(v) \propto |v| \exp\left(-mv^2/2k_{\mathrm{B}}T\right), \tag{1}$$

we can write

$$\left\langle v^2(x_0)\right\rangle = \frac{\int_{-\infty}^{\infty} dv v^2 \,|v| \exp\left(-mv^2/2k_{\mathrm{B}}T\right)}{\int_{-\infty}^{\infty} dv \,|v| \exp\left(-mv^2/2k_{\mathrm{B}}T\right)} \tag{2}$$

$$= \frac{\int_{0}^{\infty} dv v^3 \exp\left(-mv^2/2k_{\mathrm{B}}T\right)}{\int_{0}^{\infty} dv v \exp\left(-mv^2/2k_{\mathrm{B}}T\right)} \tag{3}$$

$$= \frac{2(k_{\mathrm{B}}T/m)^2}{k_{\mathrm{B}}T/m} = 2k_{\mathrm{B}}T/m. \tag{4}$$

Thus,

$$k_{\mathrm{B}}T = \frac{1}{2} m \left\langle v^2(x_0)\right\rangle. \tag{5}$$

II. ESTIMATION OF THE EFFECTIVE INITIAL TRANSITION PATH TEMPERATURE FOR SMALL MASSES

In this section, we present an approximative argument, supporting the numerical observation that also for small mass the initial effective temperature of transition paths is higher than the equilibrium temperature.

We estimate the effective temperature by assuming a flat potential $U = 0$, i.e. free diffusion. The solution $x(t)$ of the corresponding Langevin equation with an initial condition $v(0) = v_0$, $x(0) = x_{\mathrm{A}}$ obeys

$$\langle x(t)\rangle = x_{\mathrm{A}} + \frac{m}{\gamma}\left(1 - \exp\left\{-\frac{\gamma}{m}t\right\}\right) v_0, \tag{6}$$

$$\langle v(t)\rangle = \exp\left\{-\frac{\gamma}{m}t\right\} v_0. \tag{7}$$

Hence, for $t \gg \tau_m = m/\gamma$ we obtain

$$\langle x(t) \rangle = x_\mathrm{A} + \frac{m}{\gamma} v_0, \tag{8}$$

$$\langle v(t) \rangle = 0 \tag{9}$$

and the motion becomes purely diffusive.

Starting from this position, the probability to exit the interval at x_B is given by the splitting probability

$$\phi_\mathrm{B} = \frac{\langle x(t) \rangle - x_\mathrm{A}}{x_\mathrm{B} - x_\mathrm{A}} = \frac{m v_0}{\gamma \left(x_\mathrm{B} - x_\mathrm{A} \right)} \equiv \phi_\mathrm{B}(v_0), \tag{10}$$

which obviously depends on the initial velocity v_0. Hence, in this approximation, the probability to be on a transition path is the product of the probability to enter the interval with a velocity v_0, which is given by the flux-weighted equilibrium distribution, times the probability to exit at x_B, i.e.

$$P^\mathrm{TP}(v_0) = P^\mathrm{eq}(v_0) \phi_\mathrm{B}(v_0). \tag{11}$$

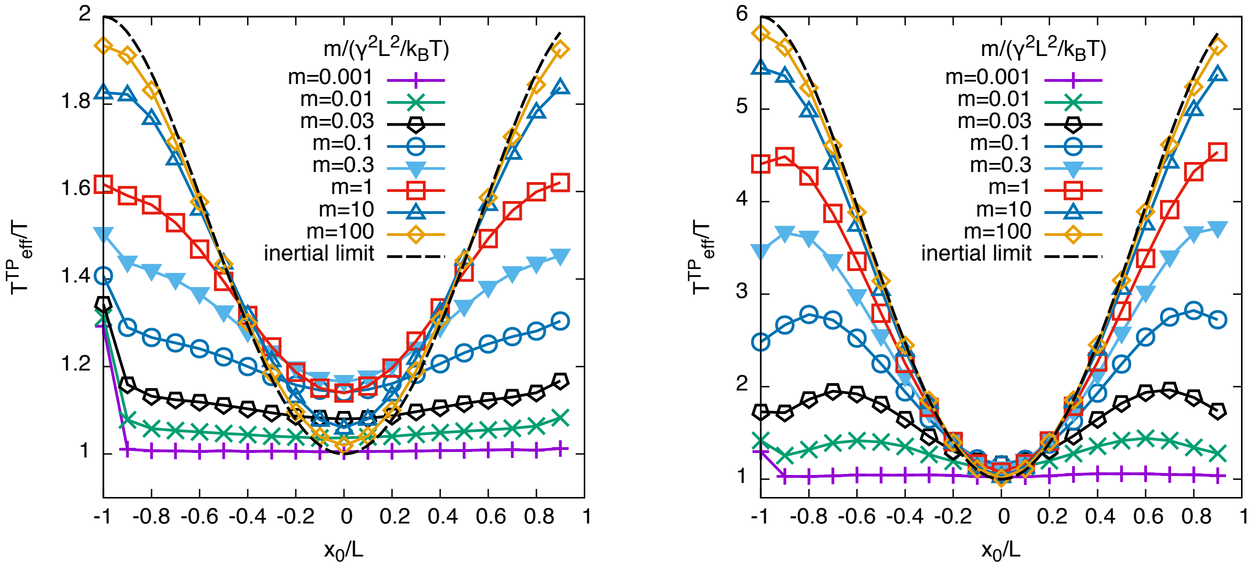
Thus, we can directly compute the flux-weighted average of the squared velocity of transition paths at the initial position x_A

$$\left\langle v^2(x_\mathrm{A}) \right\rangle^\mathrm{TP} = \frac{\int dv\, v^2 P^\mathrm{TP}(v)}{\int dv\, P^\mathrm{TP}(v)} = \frac{\int dv\, v^4 \exp\left\{-mv^2/2\right\}}{\int dv\, v^2 \exp\left\{-mv^2/2\right\}} = \frac{3 k_\mathrm{B} T_\mathrm{eff}}{m} = \frac{3}{2} \left\langle v^2(x_\mathrm{A}) \right\rangle, \tag{12}$$

where eq. (5) was used in the last step. Therefore we conclude

$$T_\mathrm{eff}/T \approx \frac{3}{2}. \tag{13}$$

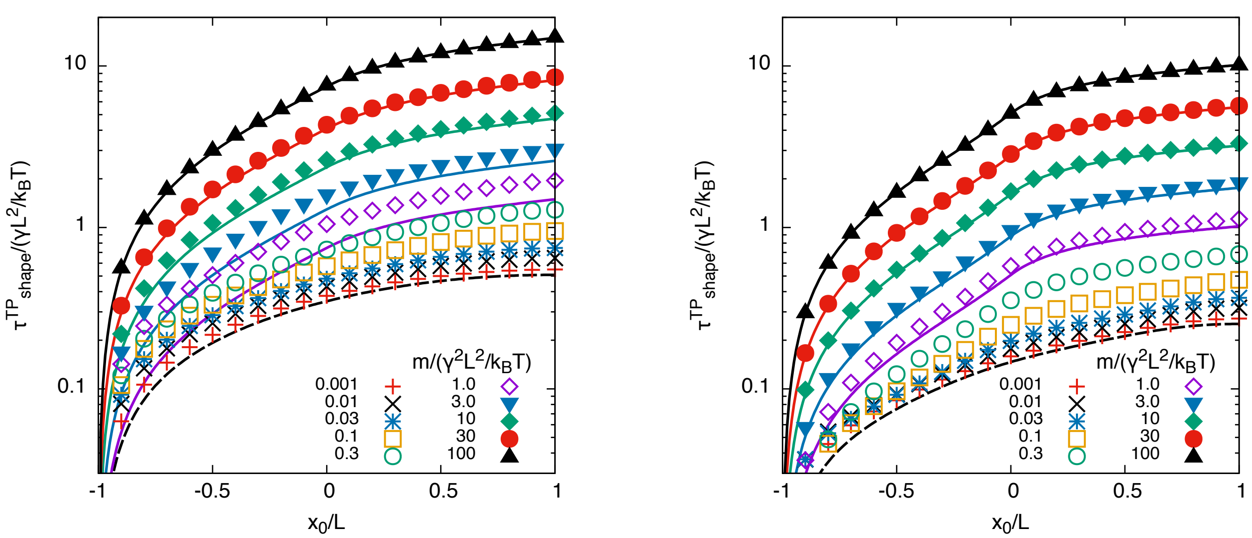
The result is somewhat larger than the actual value from the simulation $T_\mathrm{eff}/T \approx 1.3$, which is presumably caused by the drastic approximations employed in deriving eq. (13). On the other hand, the calculation provides insight into how the distribution shifts even in the case of a small mass and suggests that the overdamped limit $m \to 0$ is singular.



(a) $U_0 = 1\,k_\mathrm{B}T$

(b) $U_0 = 5\,k_\mathrm{B}T$

FIG. 1. (color online) Effective transition path temperature $T_\mathrm{eff}^\mathrm{TP}$ as a function of position x_0 for different masses at fixed barrier heights of (a) $U_0 = 1\,k_\mathrm{B}T$ and (b) $U_0 = 5\,k_\mathrm{B}T$. The data points are connected by lines to guide the eye. The inertial limit is shown as a dashed line.



(a) $U_0 = 1\,k_\mathrm{B}T$

(b) $U_0 = 5\,k_\mathrm{B}T$

FIG. 2. (color online) Mean transition path shapes $\tau_\mathrm{shape}^\mathrm{TP}(x_0|x_\mathrm{A})$ for the barrier heights (a) $U_0 = 1\,k_\mathrm{B}T$ and (b) $U_0 = 5\,k_\mathrm{B}T$ as a function of the position x_0 for different masses m. The overdamped limit is included as a dashed line, the inertial limit is shown as solid lines.