

Supplementary Information

Characterizing the resistance generated
by a molecular bond as it is forcibly separated¹

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¹These notes are intended to accompany an article with the same title. References are included in that article and are not reproduced here.

Thermodynamic basis for the governing equations

A distribution of states represented by $\rho(x, t)$ is considered to evolve over time within a one-dimensional energy landscape expressed as a time-dependent spatial profile $\mathcal{U}(x, t)$. The states are noninteracting and, microscopically, each state evolves as a random walk. The extent of the distribution is $x_1 < x < x_2$ and evolution begins at $t = 0$. The entropy per state of the “ideal gas” distribution is $kT \ln[\rho(x, t)/\rho_0]$ where ρ_0 is a reference density at which entropy is zero; the actual value of this parameter is inconsequential in the present context. Adoption of the continuum description presumes that, typically, many steps are required before any particular state escapes from the bond well. The total free energy of the system is then

$$\mathcal{E}(t) = kT \int_{x_1}^{x_2} \rho(x, t) \left[\mathcal{U}(x, t) + \ln \frac{\rho(x, t)}{\rho_0} \right] dx \quad (1)$$

at constant temperature T , where k is the Boltzmann constant. As this expression implies, the interaction energy \mathcal{U} is expressed in multiples of kT .

In order to determine the forces at play in driving evolution of this distribution, form the total time derivative of system free energy. Assuming the endpoints to be independent of time, this rate is

$$\dot{\mathcal{E}}(t) = kT \int_{x_1}^{x_2} \left\{ \partial_t \rho(x, t) \left[\mathcal{U}(x, t) + \ln \frac{\rho(x, t)}{\rho_0} + 1 \right] + \rho(x, t) \partial_t \mathcal{U}(x, t) \right\} dx. \quad (2)$$

It should be noted that if there would be a flux of states, say $j(x_2, t)$ through the boundary at $x = x_2$, then the energy rate would be augmented by an additional term of the form

$$-j(x_2, t) kT \left[\mathcal{U}(x_2, t) + \ln \frac{\rho(x_2, t)}{\rho_0} + 1 \right] \quad (3)$$

to account for loss of energy from within $x_1 < x < x_2$ associated with the flux through the boundary. The same would be true of the boundary at $x = x_1$.

Suppose that the time dependence of the energy landscape derives from the fact that an external constraint imposes a deterministic translation in some way. This translation is represented by $x = y(t)$. A specific case of this type is treated in the accompanying paper. The landscape is then time-dependent only through the time dependence of $y(t)$ so that

$$\partial_t \mathcal{U}(x, t) = \dot{y}(t) \partial_{y(t)} \mathcal{U}(x, t). \quad (4)$$

The energy rate expression then takes the form

$$\dot{\mathcal{E}}(t) = kT \int_{x_1}^{x_2} [\mu(x, t) \partial_t \rho(x, t) dx + \dot{y}(t) f(t)] dx \quad (5)$$

where $\mu(x, t) = \mathcal{U}(x, t) + \ln[\rho(x, t)/\rho_0] + 1$ is the chemical potential for the distribution in units of kT per state and

$$f(t) = -kT \int_{x_1}^{x_2} \rho(x, t) \partial_{y(t)} \mathcal{U}(x, t) dx \quad (6)$$

is the external applied force acting on the distribution that is work conjugate to $y(t)$. The local gradient in chemical potential drives the evolution of the distribution within the energy landscape, and the landscape itself is time-dependent due to the external force.

Suppose the local flux of states during evolution is represented by $j(x, t)$ with physical dimensions of number per unit depth (perpendicular to the plane of view) per unit time. Then, local conservation requires that

$$\partial_t \rho(x, t) + \partial_x j(x, t) = 0, \quad x_1 < x < x_2. \quad (7)$$

A common linear constitutive equation for the flux presumes that it is proportional to the local gradient in chemical potential,

$$j(x, t) = -D \rho(x, t) \partial_x \mu(x, t) \quad (8)$$

where the system constant D , the diffusivity, has physical dimensions of length²/time. In the present instance, this transport equation reduces to

$$j(x, t) = -D [\partial_x \rho(x, t) + \rho(x, t) \partial_x \mathcal{U}(x, t)]. \quad (9)$$

Combination of (7) and (9) through elimination of $j(x, t)$ leads to a partial differential equation for the density, commonly known as the Smoluchowski equation.

The transport equation (9) is next inverted to express the distribution $\rho(x, t)$ in terms of the flux and the energy landscape profile. To effect this inversion, write the density in terms of an auxiliary function $r(x, t)$ as $\rho(x, t) = r(x, t) e^{-\mathcal{U}(x, t)}$. Following substitution and some manipulation, (9) then becomes

$$j(x, t) = -D e^{-\mathcal{U}(x, t)} \partial_x r(x, t).$$

The result is readily integrated to find $r(x, t)$ in terms of $j(x, t)$ and $\mathcal{U}(x, t)$, from which it follows that

$$\rho(x, t) = D^{-1} e^{-\mathcal{U}(x, t)} \int_x^{x_2} j(\xi, t) e^{\mathcal{U}(\xi, t)} d\xi + C_2 e^{-\mathcal{U}(x, t)} \quad (10)$$

where C_2 is a constant of integration to be determined from the physics of the configuration. For example, if $|\mathcal{U}(x_2, t)| < \infty$ and $\rho(x_2, t) = 0$ (as at a “sink”) then $C_2 = 0$.

Asymptotic analysis

The survival probability of the bond $R(t)$ is the fraction of all bonds in the ensemble which remain intact after elapsed time t . In terms of the density of states,

$$R(t) = \int_{x_1}^{x_+} \rho(x, t) dx. \quad (11)$$

If the above expression (10) for density of states is integrated over the range indicated in (11), then

$$R(t) = D^{-1} \int_{x_1}^{x_+} e^{-\mathcal{U}(x, t)} \int_x^{x_2} j(\xi, t) e^{\mathcal{U}(\xi, t)} d\xi dx. \quad (12)$$

The integrand of the integral over $x_1 < x < x_+$ has a distinct peak at $\xi = x_-$ so that the integral is well suited for approximate evaluation by the Laplace method. The result of doing so is

$$R(t) \approx D^{-1} \sqrt{\frac{2\pi}{\mathcal{U}_{11}(x_-, t)}} \int_{x_-}^{x_2} j(\xi, t) e^{\mathcal{U}(\xi, t)} d\xi \quad (13)$$

where \mathcal{U}_{11} represents the second derivative of \mathcal{U} with respect to its first argument. Likewise, the integrand of the remaining integral over $x_- < \xi < x_2$ has an exponential peak at $x = x_+$; asymptotic evaluation of this integral leads to

$$R(t) \approx \frac{j(x_+, t)}{D} \frac{2\pi e^{\mathcal{U}(x_+, t) - \mathcal{U}(x_-, t)}}{\sqrt{|\mathcal{U}_{11}(x_-, t)| |\mathcal{U}_{11}(x_+, t)|}}. \quad (14)$$

As is noted in the manuscript, the quantity $j(x_+, t)$ can be identified as $-\dot{R}(t)$, thereby giving rise to a rate equation for determination of the survival probability. For the case of constant rate loading with $y(t) = vt$, the rate

equation can be integrated in terms of the error function with the result that

$$R(t) = e^{-\frac{D(16c_b^2 - a^4 \kappa^2)}{8av\kappa\sqrt{\pi c_b kT}}} \left[\operatorname{erf}\left(\sqrt{\frac{c_b}{kT}} \frac{(4c_b + a^2 \kappa)}{\sqrt{16c_b^2 - a^4 \kappa^2}}\right) - \operatorname{erf}\left(\sqrt{\frac{c_b}{kT}} \frac{(4c_b + a^2 \kappa - 2atv\kappa)}{\sqrt{16c_b^2 - a^4 \kappa^2}}\right) \right]. \quad (15)$$

For purposes of calculating the force $f(t)$, we substitute the expression (10) for density of states (with $C_2 = 0$) into the defining expression (6) to obtain

$$f(t) = \frac{kT}{D} \int_{x_1}^{x_2} e^{-\mathcal{U}(x,t)} \partial_{y(t)} \mathcal{U}(x,t) \int_x^{x_2} j(\xi,t) e^{\mathcal{U}(\xi,t)} d\xi dx. \quad (16)$$

Successive applications of the Laplace method to this expression, proceeding as above, leads to the result that

$$f(t) \approx \frac{j(x_+,t)}{D} \frac{2\pi e^{\mathcal{U}(x_+,t) - \mathcal{U}(x_-,t)}}{\sqrt{|\mathcal{U}_{11}(x_-,t)| |\mathcal{U}_{11}(x_+,t)|}} \left(kT \partial_{y(t)} \mathcal{U}(x_-,t) \right) = R(t) \varphi(t) \quad (17)$$

where $\varphi(t) \equiv kT \partial_{y(t)} \mathcal{U}(x_-,t)$. This yields an expression that is useful for calculating the force corresponding to a prescribed translation.

We recognize $-\dot{R}(t)$ as the fraction of states leaving the well per unit time, and $\dot{\varphi}(t)$ is the change in force per state per unit time. Because both measures are *total* derivatives, the ratio $-\dot{R}(t)/\dot{\varphi}(t)$ is the fraction of states per unit force leaving the bond well. Consequently, a graph of $-\dot{R}(t)/\dot{\varphi}(t)$ versus $\varphi(t)$, parametric in time, provides a description of this measure in terms of specific choices of microscopic system parameters. When expressed in terms of force φ as the independent variable instead of time t , this quantity is known as the force probability distribution $P(\varphi)$.

Quality of the asymptotic approximation

In order to develop some sense of the quality of the asymptotic approximation used above, we have evaluated the integral

$$I(t) = \int_{x_1}^{x_+} e^{-\mathcal{U}(x,t)} \int_x^{x_2} e^{\mathcal{U}(\xi,t)} d\xi dx \quad (18)$$

by means of standard numerical methods as a basis for comparison. The interaction energy $\mathcal{U}(x, t)$ is chosen as in the manuscript. The comparison is carried out for parameter values $kT = 4$, $v = 1$, $\kappa = 2$, $a = 1$ and a range of values of c_b , all in consistent units. The result of asymptotic approximation by means of the Laplace method for values of c_b/kT that are large in some sense is

$$I_a(t) \approx \frac{2\pi e^{\mathcal{U}(x_+,t)-\mathcal{U}(x_-,t)}}{\sqrt{\mathcal{U}_{11}(x_-,t)|\mathcal{U}_{11}(x_+,t)|}} = \frac{2\pi a^2 kT}{\sqrt{16c_b^2 - a^4 \kappa^2}} e^{\frac{c_b(4c_b + a\kappa(a-2vt))^2}{kT(16c_b^2 - a^4 \kappa^2)}}. \quad (19)$$

This expression is readily evaluated for any choice of parameter values.

Comparison of the asymptotic approximation to $I(t)$ obtained for values of c_b/kT that are large compared to one with the results of accurate numerical evaluation of the definite integrals is illustrated in Figure 2 for two values of c_b/kT . Figure 2 shows the comparison for $c_b/kT = 5$ in the form of discrete values – red for asymptotic and blue for numerical – at slightly offset values in time. It is evident that the two sets of points represent values more or less falling on a single curve, that is, the two results are virtually indistinguishable over the full range of t of interest for the underlying parameter set.

Figure 3 shows a similar comparison between numerical and asymptotic results for $c_b/kT = 3$. Even for this relatively small value of c_b/kT (on the scale of molecular bond strengths), the difference between the two results is small and probably inconsequential for any practical point of view. The conclusion to be drawn from these and other similar comparisons is that the results of asymptotic evaluation of the integral representations of physical quantities of interest in studies of debonding are reliable indicators of system behavior.

Sensitivity of force probability distribution to stiffness κ

The sensitivity of bond response to changes in the stiffness κ of the loading apparatus and/or of the molecules themselves can be demonstrated by considering changes in the force probability distribution $P(\varphi)$ due to changes

in stiffness with all other parameters, both those associated with loading and those associated with response, held fixed. An example is shown in the figure for the parameters given in Eq. 16 of the manuscript, except for the value of κ which is varied significantly from that reference value.

Figure Captions

1. An example of bond interaction energy. The function $\mathcal{U}(x, t)$ represents an energy landscape to which possible states of the bond are confined. In general, this landscape evolves over time as a result of external constraints.
2. Comparison of asymptotic and numerical results of integral evaluation. The blue points represent the results of accurate numerical evaluation of the definite integral defined in Eq. 18 at discrete values of time, whereas the red points represent the results of asymptotic evaluation for “large” values of c_b/kT . The results show the asymptotic result to be very accurate for values of c_b/kT as small as 5.
3. Same as Figure 2 but for $c_b/kT = 3$.
4. Sensitivity of force probability distribution to system stiffness κ . Plot is based on relationship in Eq. 17 in the manuscript and on Eq. 15 above.







