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ORIGINAL PAPER

A Molecular-Scale Analysis of Pressure-Dependent Sliding Shear Stresses

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Abstract

Stress-modified activated processes are analyzed using a model first proposed by Evans and Polanyi that uses transition-state theory to calculate the effect of some perturbation, described by an intensive variable, I, on the reaction rate. They suggested that the rate constant depended primarily on the equilibrium between the transition state and the reactant, which, in turn, depends on the effect of the perturbation I on the Gibbs free energy, $G = U - TS + IC$, where C is a variable conjugate to I. For example, in the case of a hydrostatic pressure P, the conjugate variable is the volume, $-V$. This allows a pressure-dependent rate to be calculated from the equilibrium constant between the reactant and transition state. Advantages to this approach are that the analysis is independent of the pathway between the two states and can simultaneously include the effect of multiple perturbations. These ideas are applied to the Prandtl–Tomlinson model, which analyses the force-induced transition rate over a surface energy barrier. The Evans–Polanyi analysis is independent of the shape of the sliding potential and merely requires the locations of the initial and transition states. It also allows the effects of both normal and shear stresses to be analyzed to identify the molecular origins of the well-known pressure-dependent shear stress: $\tau = \tau_0 + \mu_L P$, where τ_0 is a pressure-independent stress. The analysis reveals that μ_L depends on the molecular corrugation of the potential and that τ_0 is velocity dependent, in accord with an empirical equation proposed by Briscoe and Evans.

Keywords Evans–Polanyi perturbation theory · Stress-induced processes · Pressure-induced shear stress · Thermodynamic analysis

1 Introduction

Identical physical principles underpin all stress-activated processes, for example, the Prandtl–Tomlinson model for friction [1–5], the Eyring model for viscosity [6, 7], and models for mechano- or tribochemical reaction rates [8]. They involve an applied force modifying the potential energy surface (PES) for the system, therefore changing the reaction and transition-state energies. This, in turn, changes the reaction activation energy and, as a result, influences the rate [9]. This central concept, in principle, allows the molecular mechanisms that describe macroscale phenomena such as friction, wear [10], viscosity, or mechanochemistry [8] to be identified. Such theories are invariably framed in terms of a reaction pathway linking the transition-state to the reactant. This pathway can be either in the form of a simple analytical function, often just a sinusoid [1–4, 7, 8, 11–14], or can be derived from a force-modified potential energy surface (FMPES) [15–19].

A process occurring in the absence of an imposed stress is usually taken to follow the steepest-descent pathway (SDP) from a transition state to a reactant [20, 21]. However, an advantage of transition-state theory is that the rates do not depend on the reaction pathway, just the energy difference between the initial and transition states and their partition functions [22]. Efficient methods have been developed to calculate the structure and properties of the metastable activated complex of a transition state [23–25].

An approach to calculating the effect of an external perturbation such as a pressure on a reaction rate constant has been proposed by Evans and Polanyi [26, 27] based on the concepts of transition-state theory. Note that this theory is

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different from the linear-free-energy relation, also named for Evans and Polanyi, that has been used to model catalytic reaction kinetics [28–30].

As conventionally analyzed, transition-state theory assumes that the reactant and the transition-state (activated complex) structures are in thermodynamic equilibrium and uses statistical thermodynamics to calculate an equilibrium constant between them to obtain a reaction rate constant [22]. Instead, Evans and Polanyi used a thermodynamic analysis to calculate the effect of a perturbation such as hydrostatic pressure P on the rate constant [31, 32]. In the following, we review the analysis used by Evans and Polanyi to describe the effect of hydrostatic pressure on the rate of a chemical reaction. In the section following that, we extend the analysis to investigating the influence of a general applied stress on a reaction rate, and finally we apply the model to sliding friction to illustrate how it can provide deeper insights into the molecular origins of friction than more conventional Prandtl–Tomlinson-type models.

2 Summary of Evans–Polanyi Analysis of Pressure-Dependent Reaction Rates

The Evans–Polanyi analysis is based on the idea that the equilibrium constant of chemical reaction, K, can be obtained from the standard Gibbs free energy change per mole for the process, $\Delta G^{\ominus}$, as:

$$\Delta G^{\ominus} = -RTlnK, \tag{1}$$

where R is the gas constant and T is the absolute temperature [33]. Note that, because the number of moles of reactant and product are equal, K is unitless. Since $\Delta G = \Delta U + P\Delta V - T\Delta S$, the variation in equilibrium constant with (hydrostatic) pressure is given by $\left.\frac{\partial lnK}{\partial P}\right|_T = -\frac{\Delta V}{RT}$, where here ΔV has the units of volume per mole; it corresponds to some molar volume change between the reactant and the product. Evans and Polanyi argued that, rather than using statistical thermodynamics to calculate the equilibrium constant between the transition state and the reactant [22], classical thermodynamic concepts could be used instead. As a result, a similar equation could be written for a rate constant k as: $\left.\frac{\partial lnk}{\partial P}\right|_T = -\frac{\Delta V^{\ddagger}}{RT}$, where $\Delta V^{\ddagger}$ is known as an activation volume, measured for one mole under standard conditions. It has the units of volume per mole (or per molecule) and is formally a volume difference between the activated complex and the reactant. The physical interpretation of this volume change will be clarified below. Evans and Polanyi also pointed out that this idea could be extended to analyzing the effect of any external potential, f, on the rate constant k of a chemical reaction [26, 27], and showed that $\frac{dlnk}{df} = -\frac{(\alpha-\alpha\prime)}{RT}$, where α and $\alpha\prime$ are factors such that $(\alpha - \alpha\prime)f$ is the energy change of the system in passing from the initial to the transition state. That is, α is the intensive variable conjugate to f. For example, if $f = P$, the hydrostatic pressure, the conjugate variable is $-V$. Thus, the variable conjugate to an imposed stress has the units of volume.

If the rate constant under a standard pressure is k_0, then $k(P) = k_0 exp\left(-\frac{P\Delta V^{\ddagger}}{RT}\right)$. This has been called the Bell equation [34] and was originally applied to analyzing cell adhesion. Using the Arrhenius form of the rate constants shows that $E_{act}(P) = E^0_{act} + P\Delta V^{\ddagger}$, where E^0_{act} is the activation barrier in the absence of an applied pressure and $E_{act}(P)$ is the pressure-dependent barrier. Thus, a decrease in volume of the activated complex compared to the reactant causes $\Delta V^{\ddagger}$ to be negative, so that increasing the pressure reduces the activation barrier and increases the reaction rate. Conversely, a positive activation volume results in a decrease in rate with increasing pressure.

There are several advantages to using such an approach compared to those that use a force-modified potential energy surface [15, 35] or a one-dimensional periodic function. First, as a consequence of Hess' law [33], such a thermodynamic analysis does not depend on the pathway between the activated complex and the reactant [17]. This provides a significant advantage for applications to real systems, because calculating the potential-energy surface is tedious, while obtaining just the reactant and transition-state energies and structures and their properties is much simpler [23–25, 36].

Second, analyses such as those used to describe the molecular origins of friction and viscosity invariably only use a single force, while both normal and shear stresses are invariably applied at the same time in real experiments. The Evans–Polanyi perturbation model can easily be extended to describe the effect of a combination of stresses as well as including the effects of other perturbations. This approach facilitate linking macroscale sliding phenomena to the molecular origins that underpin them.

Thus, the central concept that underpins Evans–Polanyi (E–P) perturbation theory is that the Gibbs Free Energy G of a system can include the effect of some perturbation of the system described by an intensive variable, I, by using an associated extensive conjugate variable, C, where IdC equals the reversible work, so that $G = U - TS + IC$ [37]. In the case of a chemical process in which there are two states, we can define two values of the Gibbs free energies for each state under standard conditions of pressure and temperature so that $\Delta G^{\ominus} = G_2^{\ominus} - G_1^{\ominus}$. For constant values of temperature T and I, $\Delta G^{\ominus} = \Delta U^{\ominus} - T\Delta S^{\ominus} + I\Delta C^{\ominus}$. This equation can be used to calculate the way in which the equilibrium constant (K) or the rate constant (k) of a chemical process depends on the perturbation I. Note that, in many

cases, the value of the conjugate variable, C, can itself depend on I, as was alluded to by Evans and Polanyi [26, 27], so that the equation for the standard Gibbs free energy change becomes:

$$\Delta G^{\ominus} = \Delta U^{\ominus} - T\Delta S^{\ominus} + I\Delta C^{\ominus}(I). \tag{2}$$

$\Delta C^{\ominus}(I)$ can most conveniently be evaluated by carrying out a Taylor series expansion. The rate constant k is given by:

$$lnk(I) = lnk_0 - \frac{\Delta C^{\ddagger}}{RT} I, \tag{3}$$

where again k_0 is the rate constant for the process in the absence of the perturbation. In the following analysis, we will apply this general method to examining stress-modified surface processes but will neglect the variation of the variable C, and this will be discussed in more detail elsewhere. The method will be used to analyze the molecular origins of pressure-dependent shear stresses within the general framework of the Prandtl–Tomlinson friction model [3, 4, 11, 38].

3 Application of Evans–Polanyi Perturbation Theory to Stress-Modified Processes

In a reactive process, whether a chemical reaction or a sliding contact, the atoms located at some initial, stable configuration, $\boldsymbol{r}_i(Reactant)$, $i = 1\,to\,N$, where N is the number of atoms in the molecular assembly, undergo a transformation by transiting an energy barrier which has a transition-state structure (an activated complex) with atomic positions, $\boldsymbol{r}_i(TS)$, to yield a product with different atomic position vectors, $\boldsymbol{r}_i(Product)$ [22]. The reactants and products have local minima with positive normal mode eigenvalues, while the transition-state is metastable with one negative eigenvalue [25]. In this analysis, we are interested in calculating the Gibbs free energy change between the transition state and the reactant with a view to evaluating the stress dependence of the reaction rate constant using the E–P perturbation method described above. The reaction involves motion of the ith atom given by $\boldsymbol{r}_i(TS) - \boldsymbol{r}_i(Reactant)$. These structures and their position vectors can be calculated using quantum mechanics [23–25, 36, 39].

Thermomechanical properties are analyzed using continuum mechanics by distorting some reference configuration (typically the reactant state) so that it undergoes a transformation $\boldsymbol{x} = \boldsymbol{x}(\boldsymbol{X})$, to give the position $\boldsymbol{x}$ of the particle with original position $\boldsymbol{X}$. This mapping is assumed to be continuous, differentiable and invertible. The transformation is described by the deformation gradient tensor $\boldsymbol{F}$, where $F_{ij} = \frac{\partial x_i}{\partial X_j}$, and is represented by a 3×3 matrix. The deformation of a reference configuration with volume V_0 into a new configuration with volume V is given by $V = V_0 \det(\boldsymbol{F}) = V_0 J$, where $J = \det(\boldsymbol{F})$ is the determinant of the deformation gradient tensor [40].

In order to implement the Evans–Polanyi perturbation method for mechanically induced processes, it is necessary to define the relevant conjugate variables C (strain) and I (stress). Using the convention used in the analysis of the mechanical properties of materials of using a reference density ρ_0, the internal work per unit mass is given by: $\overline{\omega}_0^{int} dt = \rho_0 dW_0 = IdC = J\boldsymbol{T} : d\boldsymbol{F}\boldsymbol{F}^{-1} = \boldsymbol{\Pi} : d\boldsymbol{F} = \boldsymbol{S} : d\boldsymbol{E}$, where $\overline{\omega}_0^{int}$ is the stress power per unit reference volume [37] and $\boldsymbol{T}$, $\boldsymbol{\Pi}$ and $\mathbf{S}$ are the Cauchy and first and second Piola–Kirchhoff stress tensors, while $\boldsymbol{E}$ is the Green–Lagrange deformation tensor [40]. Here the double dot: denotes the standard scalar product of two tensors; $\boldsymbol{A} : \boldsymbol{B} = tr(\boldsymbol{A}\boldsymbol{B}^T) = A_{ij}B_{ij}$.

In the case of a hydrostatic pressure, P, the Cauchy stress $\boldsymbol{T} = -P\boldsymbol{I}$, where $\boldsymbol{I}$ is the unit tensor, and the internal work reduces to $\rho_0 dW_0 = J\boldsymbol{T} : d\boldsymbol{F}\,\boldsymbol{F}^{-1} = -PJtr\left(d\boldsymbol{F}\,\boldsymbol{F}^{-1}\right) = -PdJ = -PdV$, which is used in the original E–P paper [26]. Here, the conjugate pair, $(C, I) = (-V, P)$. Unfortunately, this is the only case in which the Cauchy stress tensor can be used to model stress-induced processes.

From the above equation, two candidates for the combinations of strain and stress are $(\boldsymbol{F}, \boldsymbol{\Pi})$ and $(\boldsymbol{S}, \boldsymbol{E})$. The first conjugate pair is generally not appropriate because the elastic constitutive equation, $\boldsymbol{\Pi}(\boldsymbol{F})$ cannot be inverted to yield $\boldsymbol{F}(\boldsymbol{\Pi})$, thus making it impossible to define a Gibbs free energy $G(\boldsymbol{\Pi})$. In contrast, $(C, I) = (\boldsymbol{E}, \boldsymbol{S})$ can be inverted and can thus provide an appropriate conjugate pair to define a Gibbs free energy change occurring during a chemical transformation. The disadvantage to this choice is that, while the Green–Lagrange strain tensor, $\boldsymbol{E}$, has a clear physical meaning, the second Piola–Kirchhoff stress tensor, $\mathbf{S}$, does not.

For the sake of simplicity in the following, it will be assumed that the deformation is constrained to have an invariant plane coincident with the sliding plane. Other deformations can be included quite easily, if necessary. However, this is the most common occurrence in tribological problems, where a normal stress is exerted along the perpendicular $x_3\,(z)$ direction combined with shear within the x_1x_2 (xy) plane so that the transformation is: $x_1 = X_1, x_2 = X_2, x_3 = \gamma_1 X_1 + \gamma_2 X_2 + f_3 X_3$ (Fig. 1) and the gradient tensor is given by $\boldsymbol{F} = \begin{pmatrix} 1 & 0 & \gamma_1 \\ 0 & 1 & \gamma_2 \\ 0 & 0 & f_3 \end{pmatrix}$ with

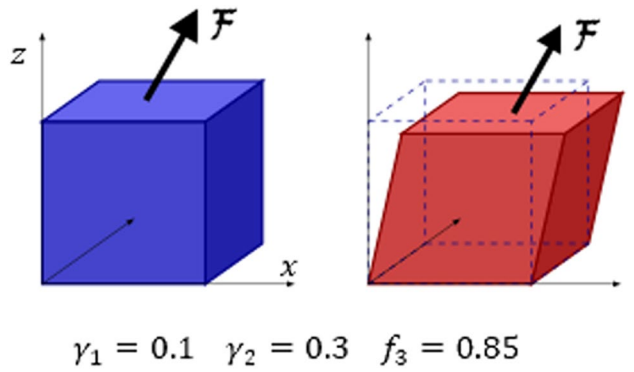

Fig. 1 Depiction of the deformation of a unit cube with an invariant *xy* plane

$detF = J = f_3$. Its inverse is $\boldsymbol{F}^{-1} = \begin{pmatrix} 1 & 0 & -\gamma_1/f_3 \\ 0 & 1 & -\gamma_2/f_3 \\ 0 & 0 & 1/f_3 \end{pmatrix}$, so that $\boldsymbol{dFF}^{-1} = \begin{pmatrix} 0 & 0 & d\gamma_1 \\ 0 & 0 & d\gamma_2 \\ 0 & 0 & df_3 \end{pmatrix}\begin{pmatrix} 1 & 0 & -\gamma_1/f_3 \\ 0 & 1 & -\gamma_2/f_3 \\ 0 & 0 & 1/f_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & d\gamma_1/f_3 \\ 0 & 0 & d\gamma_2/f_3 \\ 0 & 0 & df_3/f_3 \end{pmatrix}$. In the case of a general Cauchy stress $\boldsymbol{\sigma} = \boldsymbol{T} = \begin{pmatrix} \sigma_1 & \tau_{12} & \tau_{13} \\ \tau_{12} & \sigma_2 & \tau_{23} \\ \tau_{13} & \tau_{23} & \sigma_3 \end{pmatrix}$. It is appropriate to use molar quantities in the case of a molecular transformation so that the work is given by $\frac{dW_0}{V_0} = \boldsymbol{JT} : \boldsymbol{dFF}^{-1} = \tau_{13}d\gamma_1 + \tau_{23}d\gamma_2 + \sigma_3 df_3$, where V_0 is the molar volume in the reactant state which, in the following, is taken to be the reference configuration. This leads to the conjugate pair $I = (\sigma_3, \tau_{13}, \tau_{23})$ and $C = V_0(f_3, \gamma_1, \gamma_2)$, and the resulting Gibbs free energy change between the transition state and the reactant under standard conditions is:

$$\Delta G^{\ominus} = \Delta U^{\ominus} - T\Delta S^{\ominus} + V_0(\tau_{13}d\gamma_1 + \tau_{23}d\gamma_2 + \sigma_3 df_3). \tag{4}$$

We note that the same result could have been obtained more directly by calculating the work done by a force $\mathcal{F} = (\mathcal{F}_1, \mathcal{F}_2, \mathcal{F}_3)$ exerted on an invariant surface, x_3 = Constant. This, in fact, also corresponds to the alternative form $\boldsymbol{\Pi} : d\boldsymbol{F}$ since in this case $\boldsymbol{\Pi}_{i3} = \boldsymbol{T}_{i3}, i = 1 \ldots 3$. More generally, it can also be shown that, after some computation using the particular structure of the deformation gradient, the $C - I$ term in the Gibbs free energy can equally well be written as $IC = \tau_{13}\gamma_1 + \tau_{23}\gamma_2 + \sigma_3 f_3 = \boldsymbol{F} : \boldsymbol{\Pi} = \boldsymbol{S} : \boldsymbol{E}$.

4 Molecular Origins of Sliding Friction; Evans–Polanyi Analysis of the Prandtl–Tomlinson Friction

The above concept will be used to calculate the friction force within the framework of the Prandtl–Tomlinson model for constant-force sliding, but could readily be extended to analyzing compliant sliding in atomic-force microscopy (AFM) and nanoscale [41] friction measurements. Furthermore, we will initially ignore the effect of an applied stress on the activation volume; this is formally equivalent to the Bell model in mechanochemistry [34].

Experimentally, the shear stress τ has been found to have a contribution that depends on the normal stress (the contact pressure P) and a term that is independent of the normal stress [42–45]:

$$\tau = \tau_0 + \mu_L P, \tag{5}$$

where τ_0 is a pressure-independent stress. The associated friction coefficient $\mu = \frac{\tau}{P} = \frac{\tau_0}{P} + \mu_L$, and if τ_0 is small, the friction coefficient obeys Amontons' law [46]. Both macroscopic and microscopic explanations have been proposed for this behavior. For example, Barquins proposed that the friction stress is the sum of adhesive and ploughing contributions [47], while an alternative postulate suggests that, according to Greenwood and Williamson theory [48], when randomly rough surfaces contact only at the tips of the highest asperities, the real contact area increases in direct proportion to the normal applied load to give a load-dependent shear stress [48]. The effect of roughness on the pressure-dependent contribution to friction stress was also highlighted and discussed in Ref. [44] where the coupling with the molecular architecture of the adsorbed nanometric layers was investigated. Derjaguin ascribed τ_0 to adhesion between the contacting surfaces [49, 50] and Briscoe and Evans [51] proposed a formula for the velocity and temperature dependences of self-assembled monolayers (SAMs) that agreed well with experiment [52, 53]. It has also recently been suggested that the relative values of τ_0 and μ_L, and thus how well a system obeys Amontons' law, depends on the scale of the contact [54].

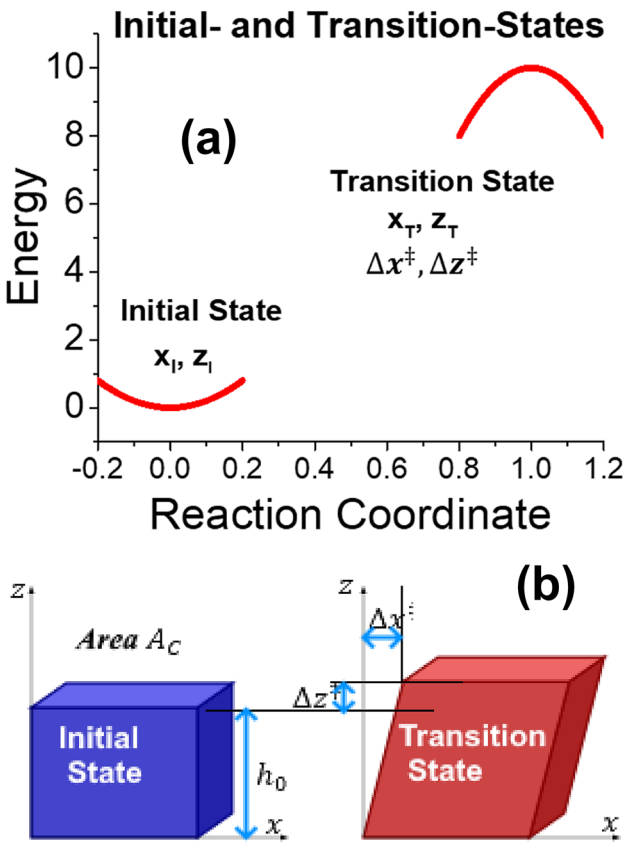

Fig. 2 **a** Plot of the potential energy profile for analyzing a pressure-dependent shear strength from an initial state to a transition state. **b** An illustration of the deformations from the initial-state structure to the transition state used in the analytical model

5 Results and Discussion

5.1 Velocity Dependence of Shear-Modified Processes

As explained by Prandtl [1] and by Eyring [7, 14], the velocity dependence of sliding friction is established by equating the stress-dependent rate constant for the transit over an activation barrier, $k(\boldsymbol{\sigma})$, to the velocity-dependent transit time, $t = \frac{\Delta x^\ddagger}{v}$, where the distance from the reactant to the activated complex along the sliding direction is an activation length, $\Delta x^\ddagger$, and v is the sliding velocity. This yields the equation $k(\boldsymbol{\sigma}) = v/\Delta x^\ddagger$ where $k(\boldsymbol{\sigma})$ is calculated using Evans–Polanyi perturbation theory.

5.2 Normal-Stress-Dependent Shear Stresses

The following illustrates the ability of Evans–Polanyi perturbation theory to simultaneously analyze the effects of normal and shear stresses on Prantl–Tomlinson friction. We analyze the effect of a combined normal stress, $\sigma_z \equiv P$ for sliding along the x direction with a shear stress $\tau_{xz} \equiv \tau$. Note here that σ_z and the z axis of τ_{xz} are directed along $+z$. This yields a Cauchy stress tensor:

$$\boldsymbol{\sigma} = \begin{pmatrix} 0 & \tau_{xz} \\ \tau_{zx} & \sigma_z \end{pmatrix}. \tag{6}$$

The energy profile depicted in Fig. 2a shows that the initial (reactant) state is located at (x_I, z_I) and the transition state is at (x_T, z_T). That is, going from the initial- to the transition-state involves motion both along the x and z directions. Note that the value of the energy barrier is not required for the analysis, just the rate in the absence of a stress, k_0. Considering a volume element of initial thickness h_0 and an area A_C over which the stresses act, the components of the (2×2) deformation gradient tensor, $\boldsymbol{F}$, as illustrated in Fig. 2b, are given by $\boldsymbol{F} = \begin{pmatrix} 1 & \Delta x^\ddagger/h_0 \\ 0 & 1 + \Delta z^\ddagger/h_0 \end{pmatrix}$. Applying the results obtained above where $I = (\sigma_z, \tau_{xz})$ and $C = V_0(1 + \Delta z/h_0, \Delta x^\ddagger/h_0)$ finally yields: $G = \Delta U - T\Delta S + V_0(\tau_{xz}\left(\frac{\Delta x^\ddagger}{h_0}\right) + \sigma_z\left(\frac{\Delta z^\ddagger}{h_0}\right))$. This emphasizes the idea that the activation volume depends on the direction of the stress relative to the surface. If we take the V_0 to be the initial volume of the system so that $\frac{V_0}{h_0} = A_C$, the activation volumes in the x and z directions can be written as $\Delta V_x^\ddagger = A_C \Delta x^\ddagger$ and $\Delta V_z^\ddagger = A_C \Delta z^\ddagger$, in accord with a proposal made by Stearn and Eyring [14]. These have the units of volume and are the product of an area (A_C) and a displacement along x and z given by $\Delta x^\ddagger = x_T - x_I$ and $\Delta z^\ddagger = z_T - z_I$. This formula for the stress-dependent Gibbs free energy change between the reactant and transition state can be used to calculate a stress-dependent rate constant. The change in the rate constant due to pressure and shear is given by: $\delta lnk(\tau, P) = \left.\frac{\partial lnk(\tau,P)}{\partial \sigma_z}\right|_{\tau_{xz}} \delta\sigma_z + \left.\frac{\partial lnk(\tau,P)}{\partial \tau_{xz}}\right|_{\sigma_z} \delta\tau_{xz}$. Using Evans and Polanyi perturbation theory gives $\left.\frac{\partial \ln(k(\tau,P))}{\partial \tau_{xz}}\right|_{T,\sigma_z} = -\frac{A_C \Delta x^\ddagger}{k_B T}$ and $\left.\frac{\partial \ln(k(\boldsymbol{\tau},\boldsymbol{P}))}{\partial \sigma_z}\right|_{T,\tau_{xz}} = -\frac{A_C \Delta z^\ddagger}{k_B T}$ so that $\delta lnk(\tau, P) = -\frac{A_C \Delta z^\ddagger}{k_B T}\delta\sigma_z - \frac{A_C \Delta x^\ddagger}{k_B T}\delta\tau_{xz}$. Putting $\sigma_z = -P$ and $\tau_{xz} = -\tau$ and integrating gives: $lnk(\tau, P) = lnk_0 + \frac{A_C \Delta z^\ddagger}{k_B T}P + \frac{A_C \Delta x^\ddagger}{k_B T}\tau$. This enables a value of the rate constant as a function of shear stress and pressure, $k(\tau, P)$ to be calculated and equated to the sliding velocity v as:

$$k(\tau, P) = k_0 \exp\left(+\frac{A_c\left(\tau \Delta x^\ddagger + P \Delta z^\ddagger\right)}{k_B T}\right) = v/\Delta x^\ddagger, \tag{7}$$

for sliding along the x direction, where the transition rate is dictated by the time for the system to move from the initial

state to the transition state. Straightforward manipulation of this equation gives:

$$\tau = -\left(\frac{\Delta V_z^{\ddagger}}{\Delta V_x^{\ddagger}}\right)P - \frac{k_B T}{\Delta V_x^{\ddagger}} ln\left(\frac{v}{v_0}\right), \tag{8}$$

where $v_0 = k_0 \Delta x^{\ddagger}$. Comparison with Eq. (5) reveals that:

$$\tau_0 = -\frac{k_B T}{\Delta V_x^{\ddagger}} ln\left(\frac{v}{v_0}\right) \text{and } \mu_L = -\left(\frac{\Delta V_z^{\ddagger}}{\Delta V_x^{\ddagger}}\right), \tag{9}$$

so that τ_0 depends on temperature and the sliding velocity, while μ_L depends only on the nanoscale topography of the sliding interface through the ratio of the activation volumes for motion in the z direction relative to the motion along the x direction. The activation volume along the x direction, $\Delta V_x^{\ddagger}$ should be negative for the shear stress to reduce the energy barrier to yield the same temperature dependences as found for an analysis of the Prandtl–Tomlinson model for constant-force sliding using a sinusoidal potential [9]. It should be mentioned that other temperature dependences have been found experimentally but have been ascribed to additional effects such as an activated attachment of the tip to the surface [55], by unusual properties of a compliant atomic force microscope tip Manzi [11], or to the formation thermally activated capillary bridges between the tip and substrate [56]. Note that here k_0 is a rate constant and thus depends on theactivation energy, E_{act}, of the process, however, the Evans–Polanyi perturbation method directly calculates a rate constant. This depends on the activation energy and the temperature, T, through the Arrhenius equation: $k_0 = Aexp\left(-E_{act}/k_B T\right)$, where A is a pre-exponential factor and k_B is the Boltzmann constant. Substituting for k_0 in the formula for v_0 yields the following form of Eq. 8:

$$\tau = -\frac{k_B T}{\Delta V_x^{\ddagger}} ln\left(\frac{v}{v_C}\right) - \frac{E_{act}}{\Delta V_x^{\ddagger}} - \left(\frac{\Delta V_z^{\ddagger}}{\Delta V_x^{\ddagger}}\right)P, \tag{10}$$

where now $v_C = A\Delta x^{\ddagger}$. It is instructive to compare this equation with that derived and compared with experiment by Briscoe and Evans for SAM friction [51], where we maintain their nomenclature as:

$$\tau = \frac{k_B T}{\phi} ln\left(\frac{v}{V_0}\right) + \frac{1}{\phi}\left(Q' + P\Omega\right), \tag{11}$$

where ϕ is known as the stress activation volume and Ω is the pressure activation volume. $Q\prime$ is the barrier height and V_0 is a velocity factor. It is clear that the equation derived from Evans–Polanyi theory and that obtained semi-empirically and confirmed experimentally by Briscoe and Evans are identical; $\phi \equiv \Delta V_x^{\ddagger} = A_C \Delta x^{\ddagger}$, $\Omega = -\Delta V_z^{\ddagger} = A_C \Delta z^{\ddagger}$ so that ratio Ω/ϕ is expected to be a constant and quite small. Briscoe and Evans found it to be 0.038 for stearic acid ($C_{18}H_{37}COOH$) and 0.036 for behenic acid ($C_{21}H_{43}COOH$). The velocity factor $V_0 = v_C = A\Delta x^{\ddagger}$.

The stress activation volume ϕ has been interpreted as the volume of molecules that are moved during shear [57–61] but the above analysis indicates that it is due to the lateral motion of the system during sliding. This comparison shows how an Evans–Polanyi analysis in this case of Prandtl–Tomlinson sliding can reveal the nature of the molecular-scale processes that lead to the appearance of macroscale tribological phenomena.

Similar pressure-dependent shear stresses have been found for solid sliding [43] and in particular for thin potassium chloride films on various metal substrates [62, 63], where the properties of the film were analyzed using density functional theory (DFT) [64]. This revealed that the friction coefficient did depend on the contact pressure and correlated with the corrugation of the surface topology, i.e., $\Delta z^{\ddagger}$, calculated by DFT in accord with the model outlined here [65, 66].

The scale of the contact has been suggested to influence the relative sizes of τ_0 and μ_L [54] with nanoscale contacts suggested to have $\tau_0 > \mu_L P$ and macroscale contacts are proposed to have the opposite behavior, of $\tau_0 < \mu_L P$. Equation 10 predicts that μ_L depends only on materials properties while τ_0 also depends on the experimental conditions (sliding velocity and temperature). Thus, Eq. 10 predicts that the lower sliding velocities used for nanoscale experiments would lead to relatively lower the value of τ_0, while experiments at the macroscale should have larger τ_0 values. This may suggest that an alternative explanation may be due to disparities in the sliding velocity between the regimes. Other interpretations based on the location of the shear plane in the contact might also explain this contradiction [45].

6 Conclusion

This work illustrates the use of a perturbation method developed by Evans and Polanyi to analyze the rates of stress-accelerated processes using the Prandtl–Tomlinson model, initially focusing on analyzing the molecular origins of friction. The approach consists of a thermodynamic analysis of the way in which the equilibrium constant between the initial state and the transition state (activated complex) in transition-state theory is influenced by an external perturbation, here an applied stress. An important property of such a thermodynamic analysis is that it is independent of the path between the two states and only depends on the locations of the transition state relative to the reactant. This makes the approach straightforward to apply to real systems because the energies, positions and properties of the initial state and

the transition state are relatively straightforward to calculate [23–25].

We note that there have been previous attempts to carry out thermodynamic analyses of friction and wear [67, 68] using the concepts of non-equilibrium thermodynamics [69]. Since tribo- and mechanochemical processes occur by an applied stress modifying the activation energy [9], we contend that the Evans–Polanyi perturbation method is a more appropriate method for analyzing these processes,

The method is illustrated for sliding friction that allows the molecular-scale energy dissipation processes that control friction to be identified. We analyze the effect of combined normal and shear stresses to identify the molecular origins of the pressure-dependent shear stress using just the linear stress-dependent change in Gibbs free energy, which depends on the volume difference between the reactant and transition state structures. We show that the calculated activation volume is consistent with a proposal made by Stearn and Eyring [14] and equals the distance from the initial to the transition state along the sliding direction (an activation length), multiplied by the area over which the stress acts, and thus has the requisite units of volume. The analysis leads to a value of τ_0 that depends on the temperature and sliding velocity, while a τ_0 that is due to adhesion should be independent of both parameters. Such analyses can be straightforwardly extended to more complex sliding interfaces; to those in which the initial- and transition-states are compliant, and to other dissipation processes such as fluid shear or tribochemistry.

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Declarations

Competing interest The authors declare no competing financial interest.

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