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A chain of interacting particles under strain

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Abstract

We investigate the behaviour of a chain of interacting Brownian particles with one end fixed and the other end moving away at slow speed $\varepsilon > 0$, in the limit of small noise. The interaction between particles is through a pairwise potential U with finite range $b > 0$. We consider both overdamped and underdamped dynamics.

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1. Introduction

The behaviour of a Brownian particle moving in a potential well and acted upon by a linearly increasing force is widely used to model the mechanical failure of molecular bonds arising in dynamic force spectroscopy experiments [19,9,20,13]. This began with the work of Bell [4] and was developed further by Evans and Ritchie [10].

Let q_s denote the length at time s of a bond that is fixed at one end and has a harmonic spring attached to the other. If the spring moves linearly at speed $\varepsilon > 0$, the motion of q_s is typically modelled according to an SDE of the form

$$\mathrm{d}q_s = (-U'(q_s) + \varepsilon s)\,\mathrm{d}s + \sigma\,\mathrm{d}W_s,$$

where $U(q)$ denotes the bond energy (e.g. Lennard-Jones potential), W_s is a standard Brownian motion and $\sigma > 0$ is the (small) noise intensity. Note that this model assumes the motion is

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overdamped. Rupture of the bond corresponds to the first time q_s escapes from the stable well of the effective, time-dependent potential, $H(q, \varepsilon s) = U(q) - \varepsilon s\, q$. The effect of the external force is to lower the barrier height of H, thus making escape more likely. The main objective is to study the distribution of first-breaking times and how the mean first-breaking time scales with the pulling speed ε. Typically, two pulling speed regimes are considered.

For very slow pulling, the particle is able to escape the well through a large deviation event before the potential has changed significantly and the energy barrier is still large. In order to apply the standard theory valid for time-independent potentials [16,11,7,12], the adiabatic approximation is used: at any given time s, the bond has an instantaneous rate of rupture, $k(s)$, and the probability of survival until time s, denoted $P(s)$, decays according to $\dot{P}(s) = -k(s)P(s)$. Note that $1/k(s)$ is given by the usual Eyring–Kramers formula [16,11,7] applied to H at time s.

As the speed of pulling increases, the energy barrier at the time of rupture becomes smaller. If pulling is sufficiently fast, the barrier may be close to vanishing completely when rupture occurs. This means that the external force, given by εs, is almost equal to the maximum slope of U, which occurs at the point of inflection between its minimum and maximum, i.e. maximum slope is $U'(c_0)$, where $U''(c_0) = 0$. For times s at which εs is close to this critical force, the effective potential H is almost cubic near its minimum. This leads to a different rupture rate than that given above, although still calculated within the Kramers framework.

It is interesting to consider what happens as the pulling speed increases yet further and the Eyring–Kramers formula is no longer applicable, nor the adiabatic approximation underpinning the above approach. In this paper, we consider this situation in a model related to that above. More precisely, we consider a chain of two identical bonds in series with one end fixed and the other being pulled at a constant rate ε. Both overdamped and underdamped dynamics are treated. We are interested in which of the two bonds breaks first and how this depends on ε and the noise intensity σ. As above, the dynamics near the inflection point of the bond energy U play an important role and will be the focus of our analysis. Roughly, we find that for $\varepsilon > \sigma^{4/3}$, the right-hand bond breaks first, while for $\varepsilon < \sigma^{4/3}$, both have an equal probability of breaking in the limit of small noise. Thus $\varepsilon = \sigma^{4/3}$ represents the threshold at which the adiabatic approximation becomes valid.

To our best knowledge, the first work to tackle rigorously such models of bonds under an external, time-dependent force was [2]. There the authors consider a similar model of two bonds in series as above, but with an additional assumption that U is cut-off strictly convex. The breaking event corresponds to the first time one of the two bonds exceeds the range of U. Roughly speaking, it is shown that for $\varepsilon > \sigma$, the chain always breaks on the right-hand side, whereas for $\varepsilon < \sigma$, each bond has an equal chance to break in the small noise limit. Thus the threshold between the different types of behaviour is different from that found in the present work, where the bond energy U is taken to be smooth (but also with finite range). In principle, the results of [2] can be extended to arbitrarily many bonds in series [1].

The behaviour of several bonds in series has also been considered by many authors, for both time-dependent and time-independent external forces. The situation when the external force is constant, i.e. one initially stretches the chain by some amount and then fixes both endpoints, has been considered for harmonic potentials [18] and Lennard-Jones potentials [21]. In the harmonic case, it is shown analytically and numerically that the probability to break at either endpoint is half that of breaking at any non-extremal point, which all have the same probability. In the Lennard-Jones case, the motion is not assumed to be overdamped, i.e. the authors consider the equation