Quantum Breaking of Elastic String

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Breaking of an atomic chain under stress is a collective many-particle tunneling phenomenon. We study classical dynamics in imaginary time by using a conformal mapping technique, and derive an analytic formula for the probability of breaking. The result covers a broad temperature interval and interpolates between two regimes: tunneling and thermal activation. Also, we consider the breaking induced by an ultrasonic wave propagating in the chain, and propose to observe it in a scanning tunneling microscopy experiment.

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Among various examples of quantum decay in condensed matter [1] of special interest are those where the tunneling system is strongly coupled to a macroscopic environment. Several such systems were studied, including metastable current states of Josephson junctions [2,3], transport in tunnel junctions [4], and quantum diffusion and properties of two-level systems coupled to a thermal bath [5]. Our purpose here is to discuss yet another case where decay is a many-particle effect: breaking of elastic string stretched by an external force. The cooperative nature of decay in this problem was emphasized by Dyakonov [6]. In this paper we study the dynamics of this system in imaginary time and show the breaking results from two distinct processes with different time scales: fast "virtual breaking" which initiates the tunneling and slow many-atom motion that actually controls the decay rate. This picture is used to formulate quantitative theory.

Our central example will be a polymer chain torn by an external force applied to its ends. At finite temperature and small force the molecule breaking is thermally assisted, with the breaking rate $w \sim \exp(-E_0/T)$, where E_0 is the energy of one bond. However, at low temperature the breaking will result from quantum tunneling under the barrier of height E_0 and of the effective length set by the stretching force. In this regime the breaking rate is temperature independent and depends mainly on the force. The saturation of the limiting stress at small temperature has been reported [7].

Our model of the polymer will be a 1D chain of atoms with the nearest neighbor interaction $U(x)$. The interaction $U(x)$ is repulsive at $x < a_0$ and attractive at $x > a_0$, like the 6-12 model potential. The Hamiltonian of the system is

$$\mathcal{H} = \sum_{k=1,\ldots,N} \left[\frac{\hat{p}_k^2}{2m} + U(\hat{q}_k - \hat{q}_{k-1}) \right] + f(\hat{q}_1 - \hat{q}_N), \tag{1}$$

where m is atomic mass and q_k are the atoms' coordinates. Mean spacing a is related to the force by $f = U'(a)$. For small f we can use the harmonic approximation $U(a) = -E_0 + m\omega_0^2(a - a_0)^2/2$, where a is close to the spacing a_0 of the nonstretched chain.

We consider the limit of small tension, when the tunneling results from coherent motion of many atoms. A simple argument that allows one to estimate the number of moving atoms and the exponent in the breaking probability was given by Dyakonov [6]. During the time of tunneling t, acoustic waves propagate at the distance ct, where c is the sound velocity. At small tension, the time t is big, and thus the mass involved in the tunneling, $m_* = pct$, is much bigger than the single atom mass. (Here ρ is the density of the chain.) One can then describe dynamics approximately as tunneling of the mass m_* under a triangular barrier $U(x) = E_0 - fx$, where E_0 is the energy of the broken bond and f is the tension. Then it is straightforward to estimate the action $S \simeq f^{-1}m_*^{1/2}E_0^{3/2}$ and the time $t \simeq f^{-1}m_*^{1/2}E_0^{1/2}$. By solving the latter equation together with the self-consistency relation $m_* = \rho ct$, one finds $t \simeq \rho cE_0/f^2$, $m_* \simeq \rho^2 c^2 E_0/f^2$, which gives the probability of breaking $W \approx \exp(-\text{const} \times E_0^2\rho c/\hbar f^2)$. This argument shows that collective effects are essential, as m_* grows at small tension. In this form, however, it only gives a rough estimate of $\ln W$, leaving an unknown constant in the exponent to be determined by a more precise calculation.

In this paper we derive a formula for the probability of breaking

$$W = \Delta \exp(-2E_0^2\rho c/\pi\hbar f^2), \tag{2}$$

where $\Delta \simeq \omega_D e^{-E_0/\omega_D}$ is the probability of a single atom tunneling at one atomic spacing. Let us note an agreement with the qualitative estimate given before. We generalize this result to a finite temperature and derive an exact formula that covers a broad temperature range, including thermal activation at high temperatures. We also consider the breaking due to alternating tension which corresponds to ultrasonic waves. Finally, we shall discuss possible experiments.

Zero-temperature calculation.—We shall use the following picture of tunneling. The energy $U(x)$ of a bond

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falls off as its length x exceeds several angstroms. Therefore, because of zero-point fluctuations, the bond length occasionally makes excursions to a large x state where the restoring force is very small with the frequency of excursions $\simeq \Delta$. We call such an excursion virtual breaking, since it does not lead to breaking at zero tension. The time scale of excursions is ω_D^{-1}. If there were no tension, after every such excursion the bond would return back to its equilibrium length. However, in the presence of the force stretching the chain, after the bond is virtually broken, the ends of the tear can start moving apart in the classically forbidden region, until the distance between them reaches $\simeq E_0/f$, where the barrier ends and the bond is really broken. This second stage takes much longer than ω_D^{-1}, as it involves motion of many atoms at large distance. Thus, we have two subsequent stages of tunneling: (1) fast virtual disappearance of one bond and (2) slow collective motion under applied force while traversing the classically forbidden region. After we use this picture to do the calculation, we check self-consistency of the assumptions, and confirm the validity of the approach for the tension small on the atomic scale.

Because of the large difference of the time scales of the stages (1) and (2) one can formulate the theory by analogy with the Franck-Condon argument for transitions in molecules, which states that the phonons are slow, so that electronic transitions are "vertical." In the chain breaking the fast process is the virtual breaking, and the slow one is the underbarrier motion of the many-atom fragments of the chain on both sides of the tear. Clearly, since the fast stage is essentially one particle, it does not depend on the tension and it only contributes a constant prefactor $\simeq \Delta^{1/2}$ of the exponentially small amplitude due to the slow stage. Therefore, we can write the rate of transition to the broken state as

$$W = \Delta\omega_D \int_{-\infty}^{\infty} \langle\psi(0)|\psi(t)\rangle\, dt, \tag{3}$$

where $\psi(0)$ is the ground state of the nonbroken chain and the evolution $\psi(t)$ is according to the Hamiltonian (1) with one bond removed: $\psi(t) = \exp(-i\hat{\mathcal{H}}'t/\hbar)\psi(0)$, $\hat{\mathcal{H}}' = \hat{\mathcal{H}} - U(\hat{x}_j - \hat{x}_{j-1}) + E_0$. (We add E_0 to assure energy conservation.) The reader may note the analogy with the method of sudden switching [8].

Following the usual treatment [9], we consider the tunneling as a motion in imaginary time: First, we evaluate the overlap in (3) at imaginary values of t, then continue it from the upper half plane down to the real axis and compute the integral over t by the saddle point method. To compute the overlap $\langle\psi(0)|\psi(it)\rangle$, we write it as the path integral

$$\langle\psi(0)|\psi(it)\rangle = e^{-E_0 t/\hbar} \int \mathcal{D}[q] \exp\left(-\frac{1}{\hbar} S_{t/2}[q]\right). \tag{4}$$

Here S_τ is the classical action of the chain with one bond broken during the time interval $[-i\tau, i\tau]$:

$$S_\tau[q] = \int [\mathcal{H} - \theta(\tau^2 - t^2)U(q_j - q_{j-1})]\, dt, \tag{5}$$

where j is the number of the broken bond. The integral (4) is taken over paths going from $t = -\infty$ to $t = \infty$, i.e., over all states $\{q_k(t)\}$ of the chain. Since at small tension the tunneling involves only long wavelength distortions, we go to the continual limit

$$S = \int\int \left[\frac{\rho}{2} u^2 + \frac{\rho c^2}{2} u_x^2 - f u_x\right] dx\, dt, \tag{6}$$

where $x(k) = a_0 k$, and the atoms' coordinates q_k are written through the displacements relative to the equilibrium positions $q_k(t) = u(x,t) + a_0 k$. [The action (6) is accurate outside the two space-time regions marked in Fig. 1. After evaluating the saddle-point action we will see that the contribution of these regions is insignificant.] Together with the boundary condition corresponding to the broken bond at $x = 0$, this defines a linear problem. We solve it and evaluate the functional integral by the saddle-point method.

Beginning from here we use the units $\hbar = \rho = c = 1$, and recover the usual units only when necessary. The classical equation of motion obtained from Eq. (6) is

$$\partial^2 u/\partial x^2 + \partial^2 u/\partial t^2 = 0. \tag{7}$$

We assume that the breaking occurs far from the ends and treat the chain as infinite. Then Laplace's equation is supplied with the following boundary conditions: (i) $u(x,t) \to u_0(x,t) = f_x$ at $|x|, |t| \gg \tau$, i.e., the chain is uniformly stretched away from the tear; (ii) $\partial u/\partial x = 0$ at $x = \pm 0$, $-\tau < t < \tau$, i.e., the ends of the tear at $x = 0$ are free during the tunneling. By analogy with 2D electrostatics, the boundary value problem can be solved by a proper conformal mapping. For that, let us introduce the complex variable $z = x + it$ and consider the analytic function

$$w(z) = (z + \sqrt{z^2 + \tau^2})/\tau. \tag{8}$$

The cut $[-i\tau, i\tau]$ in the z plane is mapped on the unit circle $|w| = 1$, and thus we come to Laplace's equation

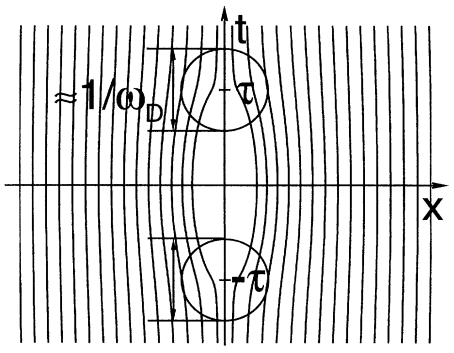

FIG. 1. Atoms world lines in the instanton. Continuum theory holds outside the two marked regions.

in the domain $|w| > 1$ with the boundary conditions

$$\text{(i) } u|_{|w|\gg 1} = u_0(w), \qquad \text{(ii) } \frac{\partial u}{\partial |w|}\bigg|_{|w|=1} = 0. \tag{9}$$

It has a solution

$$u(z) = \tfrac{1}{2} f\tau \,\mathrm{Re}(w + 1/w) = f\,\mathrm{Re}\sqrt{z^2 + \tau^2} \tag{10}$$

(see Fig. 1). Because of conformal invariance, the action can be evaluated in the w plane: $S_\tau[u - u_0] = -\pi f^2\tau^2/2$. Then we continue S_τ to the real axis, substitute it into Eq. (3), compute the integral

$$W \simeq \int d\tau \,\exp(-\pi f^2\tau^2/2 - 2iE_0\tau), \tag{11}$$

and get Eq. (2) for the probability.

With the result (10), we can check the self-consistency of the method. During the tunneling, the width of the tear $u(x = +0, t) - u(x = -0, t) = (2f/\rho c)\sqrt{\tau^2 - t^2}$ is estimated as E_0/f, as the saddle-point evaluation of the integral (11) sets $\tau \approx 2\rho c E_0/\pi f^2$. If the tension f is small in atomic units, the tear is much wider than the interatomic spacing, except for t very close to $\pm\tau$, and thus indeed it can be described by the free end boundary condition at the cut. Finally, we note that the optimal tunneling time τ is much longer than the virtual breaking time ω_D^{-1}, which justifies the assumption of a large difference of the time scales of the two stages of breaking.

Finite temperature.—The temperature dependence of the breaking begins very early, at the temperature set by the inverse tunneling time, $T_c \simeq \hbar/\tau = \hbar f^2/\rho c E_0$. If the tension is weak, T_c can be much smaller than the usual temperature $\hbar\omega_D$ of transition to the thermally assisted tunneling. For such temperatures the breaking can be studied by a generalization of the zero temperature calculation.

The functional integral treatment of tunneling at finite temperature amounts to integrating over periodic trajectories with the imaginary period $i\beta = i/T$ [9]. For the chain, we have to evaluate the path integral Eq. (4) taken over all functions $u(z)$ periodic in the z plane with the period $i\beta$: $u(z + i\beta) = u(z)$. Repeating the steps that lead to Laplace's equation, we get a boundary value problem for the function $u(z)$ whose normal derivative vanishes near a periodic system of cuts, $z \in [-i\tau + i\beta n, i\tau + i\beta n]$. (The condition at $z = \infty$ remains unchanged.)

Corresponding conformal mapping can be constructed in two successive steps. First, let us consider the function $\eta(z) = \exp(2\pi T z)$ that transforms the strip $0 < \mathrm{Im} z < \beta$ to the whole complex plane, and maps $z = \infty$ to two points: $\eta = 0$, $\eta = \infty$. The cut is mapped to the arc of the unit circle that goes from $\alpha = \exp(2\pi i T\tau)$ to $\bar{\alpha}$ counterclockwise. The second function we take is $w(\eta) = (\eta - \alpha)/(\alpha\eta - 1)$. In the w plane the two images of $z = \infty$ are $w_1 = \alpha$, $w_2 = \bar{\alpha}$, and the cut goes along the negative real half axis $w < 0$. Then the boundary value problem is solved by

$$u(w) = \frac{if}{2\pi T} \ln\left(\frac{(\sqrt{w} - \sqrt{w_1})(\sqrt{w} + \sqrt{w_2})}{(\sqrt{w} - \sqrt{w_2})(\sqrt{w} + \sqrt{w_1})}\right), \tag{12}$$

with the standard branch of the square root. Computation of the action $S_\tau[u - u_0]$ is facilitated by comparing with the analogous problem of 2D magnetostatics: two opposite charge magnetic monopoles situated at the points $w_{1,2}$ near a superconducting slit going along the real axis, from 0 to the left. In this formulation, the action corresponds to the interaction energy of the monopoles and their images. Straightforward calculation gives

$$S_\tau[u - u_0] = \lambda \ln\cos^2(\pi T\tau), \quad \lambda = f^2/2\pi T^2. \tag{13}$$

To obtain the probability W, we take $i\tau$ back to the real axis, substitute S_τ into Eq. (3), and compute the integral

$$W \simeq \int \frac{e^{2iE_0\tau} d\tau}{\cosh^{2\lambda}(\pi T\tau)} = \frac{2^{2\lambda}}{2\pi T} \frac{\Gamma(\lambda_+)\Gamma(\lambda_-)}{\Gamma(2\lambda)}, \tag{14}$$

with $\lambda_\pm = \lambda \pm iE_0/\pi T$. This expression covers a large temperature range, up to $T \simeq \omega_D$. Asymptotically, by using the Stirling formula, at high temperature we get an Arrhenius law $W \simeq \lambda e^{-E_0/T}$, and in the opposite limit Eq. (14) matches Eq. (2).

Breaking due to alternating tension.—Now, let us discuss how the breaking can be stimulated by a sound wave. Local tension in the wave varies along the string, and so does the breaking probability. To study the spatial dependence, let us put a phase ϕ in the wave

$$u_0(x, t) = (f_0/\rho c\Omega)\cos[\Omega(x/c - t) + \phi], \tag{15}$$

where f_0 is the tension amplitude, and then study breaking at $x = 0$ at different values of ϕ. In the z plane

$$u_0(z) = (f_0/\rho c\Omega)\mathrm{Re}\, e^{i(\kappa z - \phi)}, \tag{16}$$

where $\kappa = \Omega/c$. Let us assume zero temperature, then we have Laplace's equation for the displacement field $u(z)$ with the boundary conditions identical to that we had in the $T = 0$ constant force problem. By the conformal transformation Eq. (8) we go to the domain $|w| > 1$ in the w plane, $z = \tau(w - 1/w)/2$, where we get the boundary value problem (9) with $u_0(w)$ corresponding to Eq. (16). A solution is readily obtained by writing the Laurent series for $u(w)$ and $u_0(w)$, solving separately for each term, and then collecting the series

$$u(w) = u_0(w) + \frac{2f_0}{\Omega} \sin\phi\, \mathrm{Re} \sum_{m=1}^{\infty} \frac{i^{m+1}}{w^m} J_m(i\Omega\tau), \tag{17}$$

where $J_m(x)$ are Bessel functions. The action is

$$S_\tau[u - u_0] = -2\pi \frac{f_0^2}{\Omega^2} \sin^2\phi \sum_{m=1}^{\infty} m|J_m(i\Omega\tau)|^2. \tag{18}$$

This general form simplifies in the two limits:

$$S_\tau = \begin{cases} -\frac{\pi f_0^2 \tau^2}{2\rho c} \sin^2\phi, & \Omega\tau \ll 1, \\ -\frac{f_0^2 \sin^2\phi}{\rho c \Omega} \tau e^{2\Omega\tau}, & \Omega\tau \gg 1. \end{cases} \quad (19)$$

The first expression is what one gets for constant tension with the local value $f = f_0 \sin\phi$. In the second case (high frequency) the probability of breaking is

$$W \sim \exp[-(E_0/\hbar\Omega)\ln(E_0\rho c\Omega/f_0^2 \sin^2\phi)]. \quad (20)$$

Let us note a similarity between Eq. (20) and the ionization rate of an atom in a low frequency electric field $f\cos\Omega t$: $W \sim f^{2n}$, where $n = \mathrm{Ry}/\hbar\Omega$ is interpreted as the number of absorbed quanta and f^2 as the single quantum absorption rate. This interpretation stands meaningfully for the string as well.

To summarize, at $\Omega \ll \Omega_c = f_0^2/\rho c E_0$ the breaking occurs at the nodes, and the breaking rate is staticlike. At $\Omega \geq \Omega_0$ the frequency dependence begins and the probability sharply increases following Eq. (20). The spatial dependence practically vanishes in this limit, since many cycles are repeated during the tunneling.

Discussion of experiment.—Beyond a theoretical interest, the quantum problem of string breaking is relevant for the physics of polymers, since at low temperature this process determines maximal stress $\sigma_{\max}$ that a polymer material can sustain. At high temperature, the breaking is thermally assisted: $\sigma_{\max}(T) \sim \exp E_0/T$. At low temperature, a saturation of the raise of $\sigma_{\max}(T)$ was reported [7], however, the relation with tunneling has not been clarified. It would be of interest to check whether the saturation indicates tunneling by using, e.g., the conventional technique of isotopic substitution. Since $\ln W$ scales as $1/\rho c$, there is an isotope effect in the quantum regime: $\ln W \sim \sqrt{M}$, which disappears in the thermally assisted regime. Also, one could look at breaking enhancement in the presence of an alternating stress caused, e.g., by a microwave radiation. In this case, the characteristic feature to observe is the threshold frequency Ω_0 where the breaking enhancement described by our Eq. (20) begins. The threshold is set by inverse tunneling time $t^{-1} \simeq f^2/\rho c E_0$, and thus it is a function of the tension f and can be much lower than Debye's frequency ω_D, the characteristic threshold for the frequency effect in the thermally assisted regime.

Also, in light of recent progress in manipulating single atoms by a scanning tunneling microscope (STM) [10], it is of interest to think of an STM experiment with a single polymer molecule suspended between the surface and the STM tip acting as a probe. In this setup one can study the molecule breaking at small and at large temperature, where our calculation predicts different regimes. In addition, there is a possibility of combining constant force with an ac tension field caused, e.g., by an ac signal on the tip, and of looking at the resonance effects related with exciting a standing ultrasonic wave in the molecule.

To conclude, we have studied breaking of a polymer chain, and derived an analytic expression for the breaking probability that describes transition from quantum tunneling to an Arrhenius law. Also, we have studied breaking induced by an ultrasonic wave, and discussed opportunities for experiment.

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