Quantum Breaking of Elastic String

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Abstract

Breaking of an atomic chain under stress is a collective many-particle tunneling phenomenon. We study classical dynamics in imaginary time by using 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 an STM experiment.

PACS numbers: 05.30.-d, 61.16.Di, 11.17.+y
Introduction. Among various examples of quantum decay in condensed matter of special interest are those where the tunneling system is strongly coupled to a macroscopic system. Several such systems were studied, including metastable current states of Josephson junctions, transport in tunnel junctions, quantum diffusion and properties of two-level systems coupled to thermal bath. Our purpose here is to discuss yet another system where decay is a many-particle effect: breaking of elastic string stretched by an external force. Our central example will be a polymer chain teared under stress, however the formalism we present is more general. For instance, it describes critical velocity of a superfluid flow in a long channel and breakdown of a supercurrent carried by a thin wire or by many small capacitance Josephson junctions connected in series.

For the string, the leading contribution to the tunneling exponent is due to a collective motion during breaking. According to the Caldeira-Leggett theory, since the string corresponds to their “ohmic” case and is described by a harmonic Hamiltonian, the internal degrees of freedom can be integrated out to produce an effective action for which a classical trajectory in imaginary time has to be determined. Although in principle there is no difficulty in carrying out this program, we chose a different method. The “collective motion” is just a propagation of acoustic waves, and it can be treated exactly: in imaginary time the wave equation becomes two dimensional Laplace’s equation that can be solved by conformal transformations. The conformal mapping method gives a clear intuitive picture of the entire system motion in imaginary time and allows to treat in parallel several related problems: tunneling at zero temperature and at finite temperature, and also tunneling caused by an alternating tension. The latter problem is of a particular practical interest because it corresponds to the breaking induced by an ultrasonic wave propagating in a polymer.

We consider the limit of small tension, when the tunneling results from coherent motion of many atoms. A simple argument that allows to estimate the number of moving atoms and the exponent in the breaking probability was given by Dyakonov. 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, \( m_* = \rho ct \), is much bigger than the single atom mass. (Here \( \rho \) 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 \( S \approx f^{-1}m_*^{1/2}E_0^{3/2} \) and the time \( t \approx f^{-1}m_*^{1/2}E_0^{1/2} \). By solving the latter equation together with the selfconsistency relation \( m_* = \rho ct \), one finds \( t \approx \rho cE_0/f^2 \), \( m_* \approx \rho^2c^2E_0/f^2 \), which gives the probability of breaking \( W \approx \exp(-\text{const}E_0^2\rho c/hf^2) \). The argument of Dyakonov 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.

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, 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 presence of an alternating stress caused, e.g., by a microwave radiation. In this case, the characteristic feature to observe is the threshold frequency \( \Omega_0 \) where the breaking enhancement described by our Eq.(19) begins. The threshold is set by inverse tunneling time \( t^{-1} \approx f^2/\rho c E_0 \), and thus it is a function of the tension \( f \) and can be much lower than Debye’s frequency \( \omega_D \), the characteristic threshold for the frequency effect in the thermally assisted regime.

Also, in the light of recent progress in manipulating single atoms by a scanning tunneling microscope [8], it is of interest to discuss 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 to combine constant force with an AC tension field caused, e.g., by an AC signal on the tip, and to look at resonance effects related with exciting a standing ultrasonic wave in the molecule. Due to a large acoustic mismatch with the surface, reflection of the ultrasonic wave at the ends of the molecule is almost perfect. Thus the molecule of length \( L \) works like a high quality phonon resonator with resonance frequencies \( \omega_n = \pi nc/L \) corresponding to sinusoidal standing waves. For example, in a chain of 1000 atoms one estimates \( \omega_1 \approx 10^{-3} \omega_D \approx 5 – 10 \text{ GHz} \). A signal in this frequency range presumably can be supplied by coupling the STM tip to a microwave source.

Breaking then will occur at the nodes of the wave, where local tension is maximal, and this will result in simple ratios of broken halves: 1:1, 2:1, 3:2, etc. On the other hand, at high frequency there is no particular spatial structure of the breaking. Like in the bulk polymer, the experiment is facilitated by anomalously low frequency threshold \( \Omega_0 \sim t^{-1} \) above which the breaking is exponentially enhanced.

*Result and method.* The string is described by the wave equation that in imaginary time turns into Laplace’s equation. We solve the latter by a conformal mapping and derive a formula for the probability of breaking

\[
W = \Delta \exp \left(-\frac{2E_0^2\rho c}{\pi\hbar f^2}\right),
\]

where \( \Delta \sim \omega_D e^{-E_0/\omega_D} \) 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 shall use the following picture of tunneling. The energy \( U(x) \) of a bond falls off as its length \( x \) exceeds several angstroms. Therefore, due to zero-point fluctuations, the bond occasionally makes excursions in the state where it is virtually broken, with the frequency \( \Delta \). 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 \( \approx E_0/f \), where the barrier ends and the bond is really broken. This second stage takes much longer than \( \Delta^{-1} \) as it involves motion of many atoms at large distance. Thus, we have two stages of tunneling: (1) fast virtual disappearance of one bond; (2) slow collective motion under applied force traversing classically forbidden
region. After we use this picture to do the calculation, we check self-consistency of the assumptions, and confirm validity of the approach for the tension small on the atomic scale.

Clearly, since the first stage is essentially one-particle and does not depend on the tension, it only contributes a prefactor \( \Delta^{1/2} \) of the exponentially small amplitude due to the second stage. The latter can therefore be analyzed using the method of sudden switching \([4]\). Let us consider a Hamiltonian

\[
\mathcal{H} = \sum_{k=1}^{N} \left[ \frac{\hat{p}_k^2}{2M} + U(\hat{q}_k - \hat{q}_{k-1}) \right] + U(\hat{q}_1) + U(L - \hat{q}_N)
\]

where \( M \) is atomic mass, \( U(x) \) is the interaction of neighbors, \( q_k \) are atoms’ coordinates. The ends of the chain are fixed at \( x = 0, L \), which determines interatomic spacing \( a = L/(N+1) \) and the tension \( f = U'(a) \). Our \( f \) is small, so \( a \) is close to the equilibrium spacing \( a_0 \) for which \( U'(a_0) = 0 \), and we can use harmonic approximation

\[
U(x) = -E_0 + \frac{1}{2} m\omega_0^2(x - a_0)^2
\]

for all bonds except the one that breaks. For the breaking bond, we practically do not need exact profile of the potential \( U(x) \), as it is important only during a very short time interval \( \Delta^{-1} \) at the beginning of the tunneling. Therefore, as we discussed, it contributes only to the prefactor of Eq.(1). According to \([4]\), we write the rate of transition to the broken state as

\[
W = \Delta \int_{-\infty}^{\infty} \langle \exp(-\frac{i}{\hbar} \hat{\mathcal{H}}') \rangle dt,
\]

where the Hamiltonian \( \hat{\mathcal{H}}' \) describes the chain with one bond removed: \( \hat{\mathcal{H}}' = \hat{\mathcal{H}} - U(\hat{x}_j - \hat{x}_{j-1}) - E_0 \). (We subtract \( E_0 \) to assure energy conservation.) The average in Eq.(3) is taken over the initial state, i.e., the ground state of \( \hat{\mathcal{H}} \).

Following the usual treatment \([10]\), we consider the tunneling as a motion in imaginary time: first, we evaluate the average in (3) at imaginary values of \( t \), then continue it from the upper half-plane down to the real axis and do the integral over \( t \) by the saddle point method. To compute the average, we write \( \exp(-t\hat{\mathcal{H}}'/\hbar) \) averaged over the initial wave function as the path integral

\[
\langle \exp(-\frac{t}{\hbar} \hat{\mathcal{H}}') \rangle = e^{-E_0t/\hbar} \int \mathcal{D}[q] \exp \left( -\frac{1}{\hbar} S_{i\tau/2}[q] \right)
\]

Here \( S_{i\tau} \) is the classical action of the chain with one bond broken during the time interval \([-i\tau, i\tau] \):

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

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: \( q_k(t) = u(x, t) + a_0 k \). 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. Classical equation of motion obtained from Eq.(6) is
\[ \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial t^2} = 0 . \]  
\tag{7} 

We assume that the breaking occurs far from the ends and treat the chain as infinite. Then the Laplace’s equation is supplied with the boundary conditions:
(i) \( u(x, t) \rightarrow u_0(x, t) = f x \) at \( |x|, |t| \gg \tau \), i.e., the chain is uniformly stretched away from the tear;
(ii) \( \partial u / \partial x = 0 \) at \( x = \pm \tau, -\tau < t < \tau \), 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 complex variable \( z = x + i t \) and consider 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 in the domain \(|w| > 1\) with the boundary conditions
\[ (i) \ u = u_0(w) \text{ at } |w| \gg 1; \quad (ii) \ \frac{\partial u}{\partial |w|} = 0 \text{ at } |w| = 1 \]  
\tag{9} 

It has a solution
\[ u(z) = \frac{1}{2} f \tau \text{ Re} \left( w + \frac{1}{w} \right) = f \text{ Re} \sqrt{z^2 + \tau^2} . \]  
\tag{10} 

Due to conformal invariance, the action can be evaluated in the \( w \)-plane: \( S_{i\tau}[u - u_0] = -\pi f^2 \tau^2 /2 \). Then we continue \( S_{i\tau} \) to the real axis, substitute it in Eq.(1), do the integral
\[ W \simeq \int d\tau \exp \left( -\frac{\pi}{2} f^2 \tau^2 - 2 i E_0 \tau \right) \]  
\tag{11} 

and get Eq.(1) for the probability.

With the result (11), we can check the selfconsistency of the method. During the tunneling, the width of the tear \( u(x = +0, t) - u(x = -0, t) = \frac{2L}{\rho c} \sqrt{\tau^2 - t^2} \) is estimated as \( E_0/f \), as the saddle point evaluation of the integral (11) sets \( \tau = 2i \rho c E_0/\pi f^2 \). 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.
**Finite temperature.** Temperature dependence of the breaking begins very early, at the temperature set by the inverse tunneling time, $T_c \approx \hbar / \tau = \hbar f^2 / \rho c E_0$. 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 temperature 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 $i\beta = i/T$. For the chain, we have to evaluate the path integral Eq. (11) 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, $z \in [-i\tau + i\beta n, i\tau + i\beta n]$. (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 $0 < \text{Im} z < \beta$ 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 $w(\eta) = \eta - \alpha \alpha^{-1}$. 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

$$u(w) = \frac{i f}{2\pi T} \ln \left( \frac{\sqrt{w} - \sqrt{w_1}}{\sqrt{w} - \sqrt{w_2}} \frac{\sqrt{w} + \sqrt{w_2}}{\sqrt{w} + \sqrt{w_1}} \right)$$

with the standard branch of the square root. Computation of the action $S_{i\tau}[u - u_0] = \lambda \ln \cos^2(\pi T \tau)$ is facilitated by comparing with 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

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

To obtain the probability $W$, we take $i\tau$ back to the real axis, substitute $S_{i\tau}$ in Eq. (11), and do the integral:

$$W \simeq \int \frac{e^{2iE_0\tau}}{\cosh^2(\pi T \tau)} d\tau = \frac{2^{2\lambda}}{2\pi T} \frac{\Gamma(\lambda_+) \Gamma(\lambda_-)}{\Gamma(2\lambda)}, \quad (12)$$

$\lambda_{\pm} = \lambda \pm iE_0 / \pi T$. This expression covers a large temperature range, up to $T \simeq \omega_D$. By using Stirling formula we rewrite the result:

$$\ln W(f, T) = -\frac{E_0}{\pi T} \left(2 \tan^{-1} \xi - \frac{1}{\xi} \ln(\xi^2 + 1)\right),$$

where $\xi = 2TE_0 \rho c / h f^2$. Asymptotically, at high temperature, $\xi \gg 1$, we get Arrhenius law $W \simeq \lambda e^{-E_0 / T}$, and in the opposite limit, $\xi \ll 1$, Eq. (12) matches Eq. (1).
Breaking due to alternating tension. Now, let us discuss how the breaking can be stimulated by a sound wave. Local tension in the wave is varying along the string, and so is the breaking probability. To study the spatial dependence, let us put a phase $\phi$ in the wave,

$$u_0(x, t) = \frac{f_0}{\rho c \Omega} \cos(\Omega(x/c - t) + \phi),$$  \hspace{1cm} (13)

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

$$u_0(z) = \frac{f_0}{\rho c \Omega} \Re e^{i(\kappa z - \phi)},$$  \hspace{1cm} (14)

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.(14). Solution is readily obtained by writing Laurent series for $u(w)$ and $u_0(w)$, solving separately for each term, and then collecting the series:

$$u(w) = u_0(w) + \frac{2f_0}{\Omega} \sin \phi \Re \sum_{m=1}^{\infty} \frac{i^{m+1}}{w^m} J_m(i \Omega \tau),$$  \hspace{1cm} (15)

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

$$S_{ir}[u - u_0] = -2\pi \frac{f_0^2}{\Omega^2} \sin^2 \phi \sum_{m=1}^{\infty} m |J_m(i \Omega \tau)|^2$$  \hspace{1cm} (16)

This sum can be done in the following two cases.

I. (low frequency: $\Omega \tau \ll 1$) Here $J_n(x) = O(x^n)$, and only the $m = 1$ term survives:

$$S_{ir} = -\frac{\pi f_0^2 \tau^2}{2\rho c} \sin^2 \phi$$  \hspace{1cm} (17)

This expression is just what one has for constant tension with the local value $f = f_0 \sin \phi$. So, in this limit the breaking occurs predominantly at the nodes of the displacement, where the tension is maximal.

II. (high frequency: $\Omega \tau \gg 1$) Here we use the $x \gg m$ asymptotics, $J_m(ix) \approx i^m e^x/\sqrt{2\pi x}$, and get

$$S_{ir} = -\frac{f_0^2 \sin^2 \phi}{\rho c \Omega} \tau e^{2\Omega \tau}$$  \hspace{1cm} (18)

So, the probability of breaking in this limit is

$$W \sim \exp \left[ -\frac{E_0}{\hbar \Omega} \ln \left( \frac{E_0 \rho c \Omega}{f_0^2 \sin^2 \phi} \right) \right]$$  \hspace{1cm} (19)

Let us note a similarity between Eq.(19) and the ionization rate of an atom in a low frequency electric field $f \cos \Omega t$: $W \sim f^{2n}$, where $n = \text{Ry}/\hbar \Omega$ is interpreted as the number of absorbed
quanta and \( f^2 \) as the single quantum absorption rate. This interpretation stands meaningful for the string as well.

To summarize, the frequency dependence of the breaking probability is as follows: at \( \Omega \ll \Omega_0 = \tau^{-1} = f_0^2/\rho cE_0 \) it is given by (1), and the breaking occurs at the nodes of the wave. At \( \Omega \geq \Omega_0 \) the frequency dependence begins and the probability sharply increases following Eq.(19). The spatial dependence practically vanishes in this limit, since many cycles are repeated during the tunneling.

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

ACKNOWLEDGMENTS

We are grateful to M.I.Dyakonov and S.E.Korshunov for valuable and illuminating discussions. Research at the Landau Institute is supported by ISF grant #M9M000. Research of L.L. is supported by Alfred Sloan fellowship.
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