ON THE TEMPERATURE DEPENDENCE OF THE LIFETIME OF SOLIDS

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Abstract

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ON THE TEMPERATURE DEPENDENCE OF THE LIFETIME OF SOLIDS

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On the basis of experiments, S. N. Zhurkov advanced the idea that the fracture of a solid specimen stressed in tension occurs as the result of an activation process of gradual rupture of stretched chemical bonds by thermal fluctuations ([1-3]). In this case the activation energy is a linearly decreasing function of the stress, while the average energy of thermal fluctuations has a purely classical character, i.e., is equal to kT.

Meanwhile, the latter may fail to hold because of quantum effects, which begin to play a role at temperatures of the order of the Debye temperature $T \sim T_* = h(kt_0)^{-1}$, where t_0 is the characteristic period of fluctuations. Measurements of the lifetimes of loaded specimens give the usual order $t_0 \sim 10^{-12}$—10^{-13} sec, whence it follows that T_* lies in the range 50-500°K, i.e., it falls within the working range. For $T < T_*$, the most energy-intensive (high-frequency) degrees of freedom are not excited, and the average fluctuation energy must be calculated with quantum effects taken into account. Evidently the same must be done for any phenomena determined by fluctuations, such as diffusion, evaporation, etc.

We shall demonstrate a possible approach to the problem on the simplest model of a polymer, considered as an aggregate of long molecules, the bonds between which are considerably less strong than the molecules themselves. Nevertheless, owing to the great length of the molecules and their entanglement, fracture of the macrospecimen ultimately occurs as a result of rupture of these molecules themselves (chemical bonds), and not of their splitting apart; moreover, decisive for strength are those segments of these molecules (the usual definition of a segment, associated with the bending rigidity of the molecule, is meant ([4])) that are oriented in the direction of the applied stress. Intermolecular bonds substantially affect only the redistribution of stress among the segments, i.e., the value of the mean tensile stress g stretching a given segment, but in the first approximation they do not affect the random stresses g_s excited by fluctuations in the segment and associated with longitudinal vibrations, which, as in ([5, 6]), we shall regard as the principal cause of ruptures. The mean amplitude g_s is small compared with the strength of the segment g_0; however, together with g, when

the latter is sufficiently large, it may exceed g_0 with appreciable probability. In this case the probability of restoration of bonds already ruptured may be neglected. To single out the principal effect, we shall consider the segment as a continuous linearly elastic rod. As a result we arrive at a scheme analogous to the simplified consideration of fluctuation displacements in a single crystal ([7]).

The stress g_s in such a rod is represented as a superposition of standing waves with amplitudes satisfying the equations of harmonic oscillators with frequencies $\omega_j = j\omega = j\pi c l^{-1}$, where c is the speed of sound and l is the length of the rod, $j = 1, 2, \ldots, N$. The value N, by analogy with the interpolation theory of Debye, is chosen equal to the number of elements of the rod, whose role may be played by individual atoms or groups of atoms participating in the pro-

longitudinal vibrations as a whole. Passing to the quantum description of the oscillators and calculating the correlation function $K(x,\tau) = \frac{1}{2}\overline{[g_s(x,t)g_s(x,t+\tau) + g_s(x,t+\tau)g_s(x,t)]}$, where the bar denotes statistical averaging at temperature T ([8], Ch. XII), after elementary calculations we find

$$K(x,\tau) = \frac{Gk\theta}{2NV}\sum_{j=1}^{N} j \operatorname{cth}\frac{\hbar\omega_j}{2kT}\cos\omega_j\tau\cos^2\omega_j\frac{x}{c}; \qquad \theta = \frac{\hbar\omega_N}{k}. \tag{1}$$

This expression has been obtained under the assumption that the ends of the rod are rigidly fixed. Here G is the modulus of elasticity; $V = NV_0$ is the volume of the rod; G is of the order of the binding energy in the chain (60 kcal/mole), divided by the volume V_0 of one element (10^{-23} cm^3), i.e. it is $4 \cdot 10^{11}$ dyn/cm^2, respectively; $c \sim 4 \cdot 10^5$ cm/sec. The probability density $\varphi(g_s)$, owing to the stationarity of the process, does not depend on time and is Gaussian with variance $D(x) = K(x,0)$, since g_s is a linear combination of independent random variables, each of which is distributed according to the normal law ([8], p. 111).

From an analysis of (1) it is established that for $N \gg 1$ there is a sharp peak at $\tau = 0$, as well as peaks associated with reflections from the ends (the latter arise because of the absence of damping in the model, and they can evidently be neglected); between the peaks K is negligibly small. Owing to the increase of the stress at the ends when waves are reflected, the variance $D = D_0$ here is appreciably larger than in the internal cross sections. For what follows, the main interest is the large value of the exponent in the expression for $\varphi(g_s)$— several tens. In this case the appreciable increase of the variance leads to such a tremendous increase in the probability that, despite the approximately N-fold smaller weight in the total probability of rupture of the end sections in comparison with the others, the contribution of the latter can be neglected for all reasonable values of N, i.e. it may be assumed that ruptures occur only at the ends. If, conversely, the ends are assumed to be completely free, then in the same way we are convinced that only ruptures in the middle should be taken

into account, and the final result will be the same.

The mean value of $(dg_s/dt)^2$ is equal to $(\partial^2 K/\partial\tau^2)_{\tau=0} \equiv D\tau_0^{-2}$, i.e. over the time τ_0 it changes on the average by a negligibly small amount $D^{1/2}$. At times separated by an interval greater than τ_0, however, the values of g_s may be regarded as statistically independent, since, on the other hand, $\tau_0 \sim l(Nc)^{-1} \sim 10^{-13}$ sec characterizes the width of the peak of K. Thus we arrive at a Poisson process, with the rupture probability $P\{g + g_s > g_0\}$ at each step being the same and being found from $\varphi(g_s)$. As a result, calculating the mean lifetime of the rod from the moment of application of the stress g (the durability), we find that for $(g_0 - g)^2 \gg D$

$$t = \tau_0 \left[\frac{2\pi V_0 (g_0 - g)^2}{GkTf(\theta/T)}\right]^{1/2} \exp\left[\frac{(g_0 - g)^2 V_0}{2GkTf(\theta/T)}\right]; \qquad f(\xi) = \frac{\xi}{2N^2}\sum_{j=1}^{N} j \operatorname{cth}\frac{j\xi}{2N}. \tag{2}$$

In the classical case $\xi \ll 1$, $f(\xi) = 1$, and formula (2) is completely analogous to result (7). In the quantum case it retains its meaning only so long as one can speak of an unambiguous relation between fluctuations of energy and mechanical stress (quasiclassicality). At lower temperatures the latter, while still retaining the meaning of a measure of the mutual remoteness of particles, loses it as a measure of strength.

From the point of view of heat capacity, the present model essentially coincides with one of those considered in ([9]). If the highest frequency of the flexural vibrations of a segment is at least several times smaller than that for the longitudinal ones (in the terminology of ([9]), $\nu < 1$), a temperature interval is possible in which quantum effects are substantial only for the most energy-intensive longitudinal vibrations, while all the other degrees of freedom are excited classically. The energy of the longitudinal vibrations is equal to twice the potential ···

energy, i.e., it can be calculated by integrating $D(x)G^{-1}$ over the volume of the rod. Proceeding from this, we obtain the following relation between the function f, which enters expression (2) for the lifetime, and the heat capacity $c(T)$

$$f = 1 + \frac{\mu}{RT\rho}\int_T^\infty [c(\infty) - c(T)]\, dT, \tag{3}$$

where μ is the molecular weight of an element of the rod; ρ is the density; R is the gas constant; $c(\infty)$ is the constant heat capacity corresponding to classical behavior, found by extrapolation to high temperatures, if this is not hindered by other processes not taken into account by the present model.

For $g \ll g_0$, it follows from (2) that the activation energy decreases linearly with g; in this case the role of the energy U of the chemical bond is played by the maximum elastic energy that can be stored in the volume of one element

of the rod: $V_0 g_0^2 (2G)^{-1}$. Hence, for $T \gg \theta$, a result analogous to Zhurkov' s formula, mentioned at the beginning, is obtained. However, the latter describes experiments in a much wider range of stress variation, in which a quadratic dependence can be confidently distinguished from a linear one, so that the analogy is incomplete. In [6] the explanation of the linearity of the activation energy with respect to stress is based on the fact that a breaking fluctuation within one link of a sufficiently long chain in fact does not affect its tension. The present model differs from that used in [6] only in a simplified interpretation of the interaction of the chain elements, and the argument indicated there is applicable to it. The contradiction that arises is connected with the fact that the argument in [6] is static and does not pertain to fluctuations with a period comparable with the travel time of an elastic wave over the length of one link, which is what they always are.

Lifetime data are usually processed by constructing the dependence of $\lg t$ on T^{-1}. In the classical case, at different stresses, a fan of rays is obtained, issuing from a single point on the ordinate axis (the pole). However, even in those cases when this is not so, one tries to fit all the data nevertheless to a fan of straight lines, reducing them to a pole that turns out to be displaced from the ordinate axis [10]. Such a situation, as is easy to see, may be the result of an actual linearization of a dependence differing from the classical one by the replacement of T by $F(T)$ (if the linearization is carried out in the middle $T = T_0$ of some temperature interval). Formula (2) is precisely an example of this kind and leads to a displacement of the pole into the region of negative temperatures, which tends to zero as $T_0 \to \infty$ as T_0^{-3}.

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Note: Figure translations are in progress. See original paper for figures.