Fluctuations in the thermal expansion of disordered systems

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Giant, large-scale fluctuations occur in the thermal expansion of glasses and related systems.

The low-temperature thermal properties of disordered systems (glasses, irradiated crystals, and polymers) all exhibit the same behavior, while being anomalous from the standpoint of the corresponding properties of crystals.[1] The best known of these many properties are the specific heat, which is linear in the temperature ($c \propto T$), and the thermal conductivity, which is quadratic ($\chi \propto T^2$). Anomalies are also observed in the thermal expansion: The thermal expansion coefficient satisfied $\alpha \propto T$; the Grüneisen parameter $\Gamma = \alpha B/c$ (B is the elastic modulus) can reach very large values, $|\Gamma| \gg 1$. For example, we find $\Gamma = -65$ at $T = 1$ K in a-SiO_2. (In crystals we have $\alpha \propto T^3$ and $|\Gamma| \sim 1$, because of phonons.)

The anomalies are explained on the basis of two-level systems,[2] which are identified with tunneling states of atoms in two-well potentials. In particular, thermal expansion results from a deformation interaction which changes the energies E of the two-level systems upon a dilatation u, with the result that an increase in the free energy of the two-level system during heating is partially offset by dilatation.[3,4]

The magnitude of the relative thermal expansion $u(T)$ depends on the strain energies $D = \partial E/\partial u$ of the two-level systems. Absolute values $|D| \sim 1$ eV have been found from experiments on heat conduction and the attenuation of sound. These values are anomalously large.[1] By way of comparison, the thermal expansion of crystals is determined by strain potentials of thermal phonons on the order of kT. An important point is that the signs of the strain potentials of two-level systems are random.[1,3–5] The measured thermal expansion $\langle u \rangle$ is determined by the relatively small asymmetry in the distribution of D with respect to sign. As a result, the thermal expansion, while being anomalously large in comparison with the corresponding effect in crystals, is at the same time small because of a cancellation of the contributions of the various two-level systems.

Generalizing, we describe the situation in the following way. In a material there are dilatation centers with an average concentration n and random thermal expansion coefficients $\alpha(\vec{r})$ of different signs ($\vec{r}$ is the spatial coordinate). The probability distributiuon of α is such that its variance is much greater than its mean value: $\langle \alpha^2 \rangle \gg \langle \alpha \rangle^2$. Our basic assertion in this letter is that giant, large-scale fluctuations occur in the thermal expansion in this situation: $|u| \gg |\langle u \rangle|$. These fluctuations stem from random spatial accumulations of dilatation centers of the same sign. Let us find the probability distribution for such fluctuations.

Our analysis is based on a simple phenomenological expression for the free energy density, $Bu^2/2\text{-}BT\alpha u$, which describes a local thermal expansion $u = \alpha T$. The free energy

$$F = \int d^3r\{A(\nabla u)^2 + Bu^2/2 - B < \alpha > Tu\} - x \tag{1}$$

contains the random quantity $x = \int d^3 rBTu\delta\alpha$, where $\delta\alpha \equiv \alpha - \langle\alpha\rangle$. The constants A and B are of atomic scale, so that $(2A/B)^{1/2} \equiv \alpha$ is on the order of an interatomic distance in the material. Our problem is to find the probability density $P(U)$ of the quantity

$$U = \int_V u(\vec{r})d^3r/V \tag{2}$$

at large values $|U| \gg |\langle u\rangle|$, where V is the volume of a fluctuation.

We are interested in large-scale fluctuations, with $Vn \gg 1$. For them, x is the sum of a large number of random terms, and we can use Gaussian statistics:

$$P(x) = \exp(-x^2/2\sigma^2) \equiv \exp(-S),$$
$$\sigma^2 = < x^2 > = (BT)^2 \int\int d^3r d^3r' G(\vec{r} - \vec{r}')u(\vec{r})u(\vec{r}'). \tag{3}$$

In the absence of a spatial correlation we would have

$$G(\vec{r} - \vec{r}') = < \delta\alpha(\vec{r})\delta\alpha(\vec{r}') > = n^{-1} < \alpha^2 > \delta(\vec{r} - \vec{r}').$$

To find the maximum of P under the condition of a minimum F, we seek the extremum of the functional $\phi = S + \lambda(F - \epsilon \int u d^3 r)$, where λ and ϵ are Lagrange multipliers. A variation of ϕ with respect to $u(\vec{r})$ and x leads to equations for the nonuniform part of the dilatation u (after we subtract the mean value $\langle u\rangle$):

$$-\xi^2 \Delta u + u = 0, \quad x = \lambda\sigma^2,$$

where

$$\xi^2 = a^2(1 - \lambda BT^2 n^{-1} < \alpha^2 >)^{-1},$$

and where we have used the condition that there is no uniform component of $\epsilon = -\langle\alpha\rangle TB$. We are interested in a spherically symmetric solution for u, which vanishes as $r \to \infty$. This solution is of the form $u = u_0(\xi/r)\exp(-r/\xi)$. The singularity at $r = 0$ is unimportant, since the continuum approximation which we are using here becomes meaningless in that limit, and the intergals in (2) and (3) are determined by the region far from $r = 0$. Substituting this solution into (2), we find a relationship among the quantities u_0, ξ, and UV. The quantity we are seeking is $S = \lambda^2\sigma^2/2$, where σ^2 can be calculated by directly substituting $u(r)$ into (3). As a

result, we find that for any given u_0 the value of S is at a minimum (and the probability for fluctuation is at a maximum) if $\xi/r \gg 1$. Considering only this case, we note that for the large-scale fluctuations in which we are interested here the condition $\xi \gg a$ must hold. Hence $\lambda \approx n/BT^2\langle\alpha^2\rangle$. Also using the relationship between the radius and volume of a fluctuation, $V = (4\pi/3)r^3$, we finally find

$$S(U) = \left(\frac{U - \langle u\rangle}{\langle u\rangle}\right)^2 \frac{\langle\alpha\rangle^2}{\langle\alpha^2\rangle}\frac{nV}{3}. \tag{4}$$

The condition $\langle\alpha\rangle^2 \ll \langle\alpha^2\rangle$ guarantees a significant probability for the existence of large-scale ($nV \gg 1$) fluctuations with $|U| \gg |\langle u\rangle|$.

Let us put the result in (4) in a more concrete form for the case discussed above, in which the dilatation centers are two-level systems. Following Ref. 3, we estimate the typical partial Grüneisen parameter of one two-level system to be $\gamma \sim D/T$. Using the typical values $|\Gamma| \sim 30$, $|D| \sim 1$ eV, $T \sim 1$ K and $n \sim 10^{17}$ cm^{-3}, we find $n\langle\alpha\rangle^2/\langle\alpha^2\rangle \sim n\Gamma^2/\gamma^2 \sim 10^{12}$ cm^{-3}. In accordance with (4), the linear dimension of a typical fluctuation is on the order of 1 μm; in a volume with a linear dimension of 0.1 μm, fluctuations $|U| \sim 30|\langle u\rangle|$ occur with a nearly unit probability.

Dilatation factors u_e other than the two-level systems are also influencing the situation: external forces or a phonon thermal expansion. When these other factors are incorporated, we find a shift $\langle u\rangle \to \langle u\rangle + u_e$ in the $S(u)$ distribution in the numerator in (4). The result is an exponential increase in the probability for the occurrence of one sign. In particular, although the average dilatation at high T is determined essentially completely by phonons ($|u_e| \gg |\langle u\rangle|$), fluctuations in the dilatation are still caused by two-level systems. The probabilities for the realization of values $|U| \gg |\langle u\rangle|$ increase exponentially with increasing T, by virtue of the increase in $|u_e|$. This is apparently the first prediction of a manifestation of two-level systems at high T. This effect might be observed in experiments on the absorption and scattering of sound and light in glasses. We might also expect to see manifestations of fluctuations in the pressure dependence of various properties of glasses.

These fluctuations might play an important role in applications, since they correspond to local stresses which are capable of fracturing materials and structures. For example, they might cause cracking and peeling of noncrystalline films.

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