

Theory of the low-temperature anomalies in the thermal properties of amorphous structures

V. G. Karpov, M. I. Klinger, F. N. Ignat'ev

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad; M. I. Kalinin Polytechnic Institute, Leningrad

(Submitted 2 August 1982)

Zh. Eksp. Teor. Fiz. **84**, 760–775 (February 1983)

A general approach is taken to the description of local many-well atomic potentials in amorphous systems. It is shown that typical of this kind of system are double-well and critical potentials, the latter characterized by anomalously small quasielastic constants for the atomic motion. Expressions are found that describe the shapes of typical double-well potentials and the energies of the two-level tunneling states in them. The contribution of these states to the low-temperature specific heat and thermal conductivity is examined, and questions regarding the coupling constants between the tunneling states and phonons and regarding the corresponding changes in the spectral structure are briefly discussed. The dependence of the measured low-temperature specific heat on the measurement time is briefly considered.

PACS numbers: 61.40. — a, 65.40.Em, 66.70. + f

1. INTRODUCTION

Experimental studies undertaken in recent decades have revealed significant anomalies in the thermal and ultrasonic properties of a wide class of glasses at low temperature $T \lesssim 1$ K. It has been established that in this temperature region the specific heat c is proportional to T , the thermal conductivity χ to T^2 , and the ultrasound absorption at frequency ω to ω^2/T (see, for example, the reviews in Refs. 1 and 2). These features have not found explanation in terms of the usual concepts. To interpret these effects, W. A. Phillips and Anderson, Halperin, and Varma postulated in their known papers³ the existence of two-level systems identified with the tunneling states in atomic-double-well potentials of the type shown in Fig. 1. To explain the observed behavior it was necessary to assume that the basic properties of the double-well potentials—the strength λ of the interatomic barrier and the energy difference Δ_0 of the minima—are random quantities with an essentially uniform distribution over their respective intervals. The physical nature of the double-well potentials in glasses and the distribution of their parameters have remained for the most part unclear. Recent papers^{4–6} have proposed different, though to a certain extent complementary, approaches to this problem. In contrast to the thermodynamic⁵ and qualitative structural⁶ models, the model developed in Ref. 4 by two of the present authors represents a concrete microscopic approach capable of revealing a number of important features of the tunneling states, at least in amorphous structures having a network of bonds with the

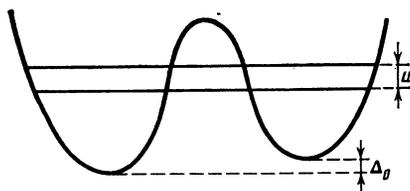


FIG. 1. The two-level system in an atomic double-well potential.

lowest possible coordination number $z = 2$ (chalcogenide glasses, for example). In that paper we also predicted the existence of special “critical” atomic potentials having anomalously small quasielastic constants. The main idea is that ordinary single-well atomic potentials are unstable to transformation to double-well potentials in certain local structures. In the present paper we develop in regard to this idea a more general approach to the problem of double wells and tunneling states, combining certain microscopic and model-independent features of the systems under study. This general approach is consistent not only with Ref. 4 but also with the models of Refs. 5 and 6, and it gives a unified description of double wells in amorphous materials without regard to their specific microscopic structure (Sec. 2). As a result, we are able to study the important dynamical features of atomic particles in double-well potentials (Sec. 3) and to calculate the aforementioned anomalous thermal properties of glasses (Secs. 4–6).

2. GENERAL DESCRIPTION OF LOCAL ATOMIC POTENTIALS

Irrespective of the specific structure of an amorphous system, one can state some general arguments concerning the microscopic nature of the local (and, in particular, double-well) atomic potentials in it. Let us consider an ensemble of several local subsystems of the atomic system of a glass that are identical from the standpoint of composition and topological connections. The potential energy $V(x)$ of each subsystem of the ensemble can be regarded as a function of the set of its internal variables $x \equiv \{x_i\}$ for fixed values of the remaining, “external” variables $x \equiv \{X_i\}$, which play the role of parameters. The variables X describe the state of the set of atoms of the glass which do not belong to a subsystem of the given type. In fact, we take the variables X to mean the set of coordinates describing the equilibrium positions of the atoms which do not belong to the subsystem under consideration. Thus $V(x)$ is a local potential which is to be minimized

on the set of internal variables and depends parametrically on all the remaining, external variables:

$$V(x) = V\{x|X\} = V(x, X)|_{x=\text{const.}}$$

In a disordered system the parameters X fluctuate from one realization to another. Since the form of the function $V(x)$ is, generally speaking, determined by the values of these parameters, it can be assumed that some of their fluctuations correspond precisely to double-well potentials $V(x)$. Naturally, the parameters of the double-well potentials themselves are fluctuating quantities characterized by their respective probability distributions.

To illustrate the foregoing, consider the case⁴ of an ensemble of one-dimensional triatomic fragments. In this case $V(x)$ is the potential relief of the central atom (x is its displacement), and the role of X is played by the fragment length R which fluctuates within the ensemble; there exists a critical value $R = R_c$ such that the potential $V(x)$ is a single well for $R < R_c$ and a double well for $R > R_c$.

The foregoing considerations permit one to describe quite generally the most prevalent and in this sense typical many-well local atomic potentials in amorphous structures by means of a function of a single effective coordinate x of the atom or group of atoms in question:

$$V(x) \approx A\eta x^2 + Btx^3 + Cx^4, \quad |\eta| \ll 1, \quad |t| \ll 1. \quad (2.1)$$

Here A , B , and C are constants of the material, while $\eta \geq 0$ and $t \geq 0$ are parameters which fluctuate in space. The physical meaning of these parameters and of the coordinate x depends on the specific type of local structure. What we have said is equivalent to the assertion that the typical many-well potentials in the amorphous structure are precisely the double-well potentials.

Expressions of the form (2.1) are familiar in the theory of phase transitions and various other critical phenomena, where they describe the behavior near the critical point in complex systems with many degrees of freedom. From our point of view, double-well potentials arise in an amorphous structure because the form of a certain class of local potentials is unstable to fluctuations of the microscopic parameters, and in this sense one may also speak of manifolds of critical points separating the regions in which the single-well and double-well potentials can occur. It is important to stress that the possibility of describing the vicinity of a transition point by a function of a single variable is a general feature of the problem under consideration. In what follows we give a brief argument to substantiate formula (2.1) on the basis of the ideas of catastrophe theory (see, for example, Ref. 7).

Let us first mention some formal relations of a mathematical nature. The ensemble of subsystems under consideration can be described by a distribution function $P(X)$, with $\int P(X)dX = 1$, in the phase space of the variables X . In this space there is a hypersurface S bounding a region Ω of values of X such that the potential $V\{x|X \in \Omega\}$ is a single well; on the other side of this surface are points corresponding to many-well potentials. Far from the hypersurface S , the potential $V(x)$ can be represented in the neighborhood of its extrema by a quadratic form:

$$\sum_{i,j} A_{ij}x_i x_j = \sum_i \tilde{A}_i \tilde{x}_i^2.$$

On the hypersurface itself, the matrix A_{ij} is degenerate, i.e., at least one of its eigenvalues \tilde{A}_i is zero (or becomes arbitrarily small in absolute value near S). In this case the quadratic approximation for the potential $V(x)$ is inadequate. In its mathematical aspects the problem of the local description of a function in the neighborhood of an extremum near a degeneracy of the matrix of its second derivatives is solved by means of the so-called splitting lemma (see, for example, Ref. 7), which enables one to write $V(x)$ in the form

$$V(x) = \tilde{V}(\tilde{x}_1, \dots, \tilde{x}_r) + \sum_{i>r} \tilde{A}_i \tilde{x}_i^2, \quad (2.2)$$

where \tilde{V} is a function only of the modes $\tilde{x}_1, \dots, \tilde{x}_r$, corresponding to the nearly degenerate eigenvalues \tilde{A}_i , which by definition are such that $|\tilde{A}_i| \ll \tilde{A}_j$ at $i < r$ and $j > r$; the coordinates \tilde{x}_i are related to the modes \tilde{x}_i by a transformation which is, generally speaking, nonlinear. The coefficients \tilde{A}_i in (2.2), just as the parameters occurring in the expression for $V(x_1, \dots, x_r)$, are functions of the fluctuating variables X .

It is convenient furthermore to characterize the smallness of \tilde{A}_i by a small parameter $\alpha \ll 1$ and to say that the proximity of the potential $V(x)$ to degeneracy in one mode corresponds to a phase volume $v_1 \propto \alpha$ in a narrow layer of thickness α near the hypersurfaces S . It is important that the dimensionalities d_n of the manifolds of those points on the hypersurface S at which $n > 1$ linearly independent eigenvalues of the matrix A_{ij} vanish simultaneously are related by $d_n - d_{n+1} = n + 1$ (this is the difference between the numbers of independent terms of the quadratic forms of $n + 1$ and n variables). Consequently, the ratio of the phase volumes v_n and v_{n+1} in which n and $n + 1$ values \tilde{A}_i are small is $v_n/v_{n+1} \propto \alpha^{n+1}$. We now assume that $V(x)$ is degenerate only with respect to one mode (x_1) and represent $\tilde{V}(x_1)$ near hypersurface S by the expansion

$$\tilde{V} = \tilde{A}_1 \tilde{x}_1^2 + B_1 \tilde{x}_1^3 + C_1 \tilde{x}_1^4 + \dots \quad (2.3)$$

Considering the phase space of the coefficients \tilde{A}_1 , B_1 and C_1 , we see that the smallness of the coefficient \tilde{A}_1 in this space corresponds to a phase volume $v' \propto \alpha$ (along the plane $\tilde{A}_1 = 0$), while the simultaneous smallness of the coefficients \tilde{A}_1 and B_1 corresponds to a phase volume $v'' \propto \alpha^2 \gg v_2$. The simultaneous smallness of the three coefficients \tilde{A}_1 , B_1 and C_1 would correspond already to a phase volume of the same order as $v_2 \propto \alpha^3$.

Using the relations mentioned above, we can substantiate (2.1) in the following way. On empirical grounds we can assume that the relative concentration of many-well potentials in the material is small, $n_0 \ll 1$ (say, $n_0 \lesssim 10^{-2}$). In terms of our approach, this means that the many-well potentials are realized on the rapidly decaying tail of a distribution function $P(X)$ centered in the region Ω around some point $X = \bar{X}$ corresponding to single-well potentials with parameters close to those of the unusual atomic potentials in crystals. Because of the random nature of the disorder, the tail of

the distribution $P(X)$ should, generally speaking, cross the boundary of the region Ω over many dimensions, as a rule far from the relatively small phase volumes v_n for $n \geq 2$. In this sense one can say that the typical critical behavior of the potential $V(x)$ corresponds to an instability with respect to only a single mode, i.e., the typical many-well potentials in an amorphous structure are double wells, potentials with $z_0 \geq 3$ wells occur with a significantly lower probability, in accordance with the smaller phase volume in the space of the fluctuating variables X . At the same time, however, the vanishing of the coefficient B_1 is still not atypical, since it corresponds to a phase volume $v'' \gg v_2$. A typical many-well potential in a glass should thus be described by an expansion of the form (2.3) or, equivalently, (2.1), where for obvious reasons one should assume $C > 0$. Since $P(X)$ falls off rapidly outside region Ω , the major fraction of double-well potentials correspond to points in phase space near the boundary of this region, where expansion (2.3) is valid.

To avoid misunderstandings, we should point out that in this approach we exclude from consideration right from the start the trivial kind of many-well character that results from features in the short-range order of an undistorted structure, such as that which arises when an atom is displaced from a lattice site to interstitial positions. A many-well character of this kind, which also occurs in a crystalline phase, is not due to fluctuations of the structural parameters and is typified by very large values of Δ and/or λ , which are at odds with the values estimated from the empirical data on the low-temperature anomalies in amorphous materials. Our scheme also excludes the many-well character due to the possible presence of defects of the off-center type in crystals with well-defined (practically nonfluctuating) parameters. We are thus discussing exclusively the kind of many-well character that result from fluctuations in the parameter of the ideal (far from defects in the short-range order) structure of the amorphous material.

It will be convenient to express the displacement x in (2.1) in dimensionless units, introducing as a length scale the characteristic atomic radius $a_0 \sim 1 \text{ \AA}$. Then the constants A , B , and C have dimensions of energy, while the parameters η and t are dimensionless. Since for $\eta \sim 1$ and $t \sim 1$ the expansion (2.1) should correspond to atomic potentials of the usual form, we can assume $A \sim B \sim C \sim m\omega_D^2 a_0^2 \sim 10\text{--}30 \text{ eV}$, where m is a typical atomic mass and ω_D is the Debye frequency.

In accordance with what we have said, the probability distribution $H(\eta)$ for the parameter η should be consistent with a mean value $\bar{\eta} \sim 1$, corresponding to single-well potentials with nearly nominal parameters (Fig. 2a). It is easy to-

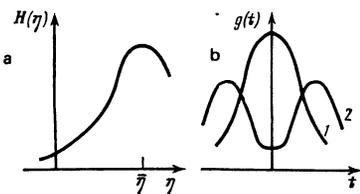


FIG. 2. The distribution for the parameters of the atomic double-well potentials in amorphous systems.

show that expression (2.1) describes a double-well potential for

$$\eta < \eta_0 = \frac{1}{32} B^2 t^2 / AC = t^2 / r, \quad r \sim 1.$$

The empirical requirement that the concentration of the double wells be small is therefore equivalent to the condition $\eta_0 \ll 1$ for the overwhelming majority of subsystems in the ensemble, i.e., the distribution $g(t)$ for the parameter t should have a rather small width. Since there are no preferred directions in glass and asymmetries in $V(x)$ of opposite signs are equally probably, the distribution $g(t)$ should be even as well. Shown schematically in Fig. 2b are two qualitatively different types of distributions $g(t)$ which satisfy these requirements. The first type of distribution (curve 1) is characterized by the fact that $g(t=0) \simeq g_{\max} \equiv \max[g(t)]$, while for the second type (curve 2) one has $g(t=0) \simeq \ll g_{\max}$. In addition to $g(t)$, we shall also make use of the distribution for the parameter η_0 :

$$H_0(\eta_0) = \frac{1}{2} g((r\eta_0)^{1/2}) (r/\eta_0)^{1/2}.$$

In taking this approach, we must assume that the characteristic decay scales η_c and η_{0c} for the distributions $H(\eta)$ and $H_0(\eta_0)$ are rather small, in any case appreciably smaller than unity. At the same time, as we shall see, to match the experimental data these quantities should not be smaller than a certain characteristic value $\eta_L \sim 10^{-2}$ determined from the dynamics of a particle in a double well. The specific form of the distributions $H(\eta)$ and $g(t)$ turns out to be unimportant here, and in regard to these distributions we need only the information given in Fig. 2.

Turning now to the Hamiltonian of an atomic system with typical double-well potentials, we notice that the quadratic form corresponding to the kinetic energy can, without loss of generality, be assumed to be diagonalized by the same transformation that diagonalizes the matrix A_{ij} . The Hamiltonian we seek can therefore be represented in the form

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{int}},$$

$$\mathcal{H}_1 = -\frac{\hbar^2}{2m_i} \frac{d^2}{d\tilde{x}_i^2} + \bar{A}_i \tilde{x}_i^2 + B_i \tilde{x}_i^3 + C_i \tilde{x}_i^4,$$

$$\mathcal{H}_2 = \frac{1}{2} \sum_{i \neq 1} (m_i \dot{\tilde{x}}_i^2 + 2A_i \tilde{x}_i^2), \quad \bar{A}_i \gg |\bar{A}_i| \quad \text{for } i \neq 1, \quad (2.4)$$

where the terms \mathcal{H}_1 and \mathcal{H}_2 correspond to the double-well potentials (the critical mode that is singled out) and to the surrounding medium, and \mathcal{H}_{int} describes their interaction. The Hamiltonian \mathcal{H}_2 is characterized by a wide spectrum of frequencies $\{\omega_2\}$ corresponding to the various modes of atomic motion. These include modes which describe vibrations encompassing small spatial configurations (the quasi-molecular type), whose frequencies, by virtue of the condition $\bar{A}_i \gg |\bar{A}_i|$, conform to $\omega_2 \gg \omega_1$, where ω_1 is the characteristic frequency scale of the Hamiltonian \mathcal{H}_1 . On the other hand, the spectrum $\{\omega_2\}$ also contains low frequencies $\omega_2 \lesssim \omega_1$ corresponding to collective modes—long-wavelength acoustical phonons, $\bar{A}_i \rightarrow \frac{1}{2} m_q \omega_q^2(q$ is the wave

vector) for $\omega_q \ll \omega_D, m_q \gg m$. The interaction of a particle in a double well with surrounding-medium modes for which $\omega_2 \gg \omega_1$ does not alter the essential form of \mathcal{H}_1 and can be taken into account in the adiabatic approximation by a renormalization of the parameters \tilde{A}_1, B_1 , and C_1 . Hereafter we shall assume that this renormalization has already been done. The interaction with long-wavelength acoustical phonons, on the other hand, whose coordinates are not involved in this renormalization, will be treated in Sec. 5.

3. ATOMIC TUNNELING STATES IN DOUBLE-WELL POTENTIALS

In this section we shall consider the energy levels of an isolated (not interacting with the surroundings) double well. The problem involves finding the first interlevel gap u as a function of the parameters η and η_0 . In accordance with what we have said above, we shall assume that the Hamiltonian of an isolated double well is of the form

$$\mathcal{H}_1 = -\frac{\hbar^2}{2m_1 a_0^2} \frac{d^2}{dx^2} + A\eta x^2 + Btx^3 + Cx^4, \quad (3.1)$$

where m_1 is of the order of an atomic mass, the effective parameters η and t are small in absolute value, $|\eta| \ll 1, |t| \ll 1$.

For $|\eta| \ll 1$, expression (3.1) is in fact the Hamiltonian of a highly anharmonic oscillator. In the general case it is a difficult problem to determine the energy spectrum of such a Hamiltonian, and there is no analytical solution. However, a solution can be obtained by the methods of perturbation theory in the case of a small parameter $u/E_1 \equiv (E_2 - E_1)/E_1 \ll 1$, which, as we shall see, corresponds to precisely the case of low temperatures (say, $T \lesssim 1$ K), the actual situation for the phenomena considered here.

In what follows it will be convenient to start from symmetric double wells ($\Delta_0 = 0$). Then the asymmetry can be taken into account by perturbation theory. One is readily convinced by direct calculations that expression (3.1) describes a symmetric double well in two cases:

$$\xi_1 \equiv \eta/\eta_0^{-3/2} = 0 \quad \text{for } 0 < \eta < \eta_0, \quad (3.2a)$$

$$\xi_2 \equiv (\eta_0/\eta_L)^{1/2} = 0 \quad \text{for } \eta < 0. \quad (3.2b)$$

In (3.2b) we have introduced a parameter η_L which characterizes the scale of η and η_0 in the problem; the value of this parameter is defined in (3.7) below. For the actual weakly asymmetric double wells obtained from the symmetric configuration at small but finite values of the parameter ξ_1 in case (3.2a) or ξ_2 in (3.2a), the potentials of the individual wells are described by expressions of the form

$$V_1(x) = A\eta_0^{2/3} (\xi_1 x^2 + (r\eta_0)^{1/2} Bx^3 + Cx^4),$$

$$V_2(x) = A\eta_0^{2/3} (-5\xi_1 x^2 - (r\eta_0)^{1/2} \times (1 - \eta_0^{3/2} \xi_1) Bx^3 + Cx^4 + \eta_0^{2/3} \frac{A^2}{C} \eta_0^2 \xi_1)$$

(3.3)

or

$$V_{1,2}(x) = 2A\eta_0 (\gamma \pm \gamma^{1/2}) x^2 + (r\eta_0)^{1/2} \times (-1/2 \mp 3/2 \gamma^{1/2}) Bx^3 + Cx^4 + \eta_0^{2/3} \frac{A^2}{C} \eta_0^2 \gamma^{1/2} \delta_{j,2},$$

$$\gamma \equiv (1 - \eta/\eta_0), \quad i=1, 2. \quad (3.4)$$

In (3.3) and (3.4) the displacement x is measured from the minima of the respective wells. The shape $V_B(x)$ and height δV_B of the interwell barrier are described for symmetric double wells by

$$V_{Bj}(x) = -A_j' x^2 + Cx^4, \quad \delta V_{Bj} = A_j'^2/4C,$$

$$A_1' = \eta_0 A, \quad A_2' = A|\eta|. \quad (3.5)$$

Here and below we label expressions corresponding to cases (3.2a) and (3.2b), where necessary, by the indices $j=1$ or $j=2$.

Let us first consider the energy level of a particle in an isolated well of a symmetric double-well potential, neglecting the cubic anharmonicity in the well. The potential of such a well is of the form

$$V_j^{(0)}(x) = A_j'' x^2 + Cx^4,$$

where the displacement x is measured from the minimum, and A_j'' can easily be determined from (3.3) for $j=1$ or from (3.4) for $j=2$. The energy of the lower level, measured from the bottom of the well, is

$$E_j^{(0)} \equiv E^{(0)}(A_j'', C) \gg E^{(0)}(0, C) \sim w = C^2 \epsilon^2, \quad \epsilon \equiv \hbar^2/2m_1 a_0^2. \quad (3.6)$$

The harmonic component $A_j'' x^2$ turns out to be important only for rather large values $A_j'' \gg \epsilon^{1/3} C^{2/3}$, in which case

$$\xi_j \gg 1, \quad \xi_1 \equiv \eta_0/\eta_L, \quad \xi_2 \equiv -\eta/\eta_L, \quad \eta_L \equiv (\epsilon/A)^{1/2} (C/A)^{2/3}. \quad (3.7)$$

The characteristic quantities we have introduced have the following scales: $\epsilon \sim 1$ K, $w \sim 10$ – 30 K, $\eta_L \sim 10^{-2}$. The condition that at least one energy level exists in each of the wells can be written

$$E_j^{(0)} < \delta V_{Bj}, \quad E_j^{(0)} \approx w [8j\xi_j / (10-j)]^{1/2}$$

where δV_{Bj} is given in (3.5). This condition corresponds to the predominance of the harmonic component in each of the wells; the corresponding restrictions on the parameters are

$$\xi_1 > \xi_1 \equiv 9 \cdot 2^{-1/2}, \quad \xi_2 > \xi_2 \equiv 2^{3/2}. \quad (3.8)$$

If the interwell barrier were high enough for each well to have several levels, the energy difference between the levels would be of order w or larger. Consequently, the actual small energy spacing $u \ll w$ can only come about by the appropriate splitting of the levels in a double well (and not within a single well).

Allowance for the cubic anharmonicity of the wells of a symmetric double-well potential leads only to a rather insignificant change in the numerical coefficients in the expressions for $E_j^{(0)}$ and ξ_j . In particular, the correction to the energy levels is approximately $\xi_j^{-3/2} E_j^{(0)}$. Therefore, the conclusions about the restrictions on the parameters ξ_j and about the impossibility of obtaining small interlevel gaps within a single well of a symmetric double well remain valid when the cubic anisotropy of this single well is taken into account.

In view of what we have said, it is natural to choose for the zeroth approximation the states of a symmetric double well:

$$|\pm; j\rangle = \psi_j^{(\pm)}(x) = 2^{-1/2} [\psi_j^{(1)}(x) \pm \psi_j^{(2)}(x)], \quad u = u_j^{(0)} = J_j^{(0)} \ll E_j^{(0)}, \quad (3.9)$$

where $\psi_j^{(1)}$ and $\psi_j^{(2)}$ are the wave functions of a particle in an individual well, taken in the harmonic approximation. In the first order of perturbation theory (for nearby levels) we have⁸

$$u = [(J_j^{(0)} + V'_{j,++} - V'_{j,--})^2 + 4|V'_{j,+}|^2]^{1/2} = (J_j^2 + \Delta_j^2)^{1/2},$$

$$V'_{j,++} = \langle j; + | V' | +; j \rangle, \quad V'_{j,--} = \langle j; - | V' | -; j \rangle,$$

$$V'_{j,+} = \langle j; + | V' | -; j \rangle,$$

$$V'_{j,+-} - V'_{j,-+} = 0, \quad \text{i.e., } J_j = J_j^{(0)}, \quad (3.10)$$

where $V'_{j,++}$, $V'_{j,--}$, and $V'_{j,+}$ are the matrix elements of the excitation potential, which is here the contribution of the cubic anharmonicity to the potential. These matrix elements have familiar expressions (see, for example, Ref. 8), through the use of which we find

$$\Delta_j = w |\xi_j| f_j(\zeta_j),$$

$$f_1(\zeta) = \left| \frac{9}{\sqrt{2}} \zeta^{5/2} - \frac{891}{64} \zeta^{-1} - \frac{8}{9} \zeta^2 \right|,$$

$$f_2(\zeta) = \sqrt{\zeta} \left| 2\sqrt{2} \zeta^{5/2} - \frac{11}{6} \zeta^{-2} - \frac{4}{3} \zeta \right|. \quad (3.11)$$

In the expressions for the $f_j(\zeta)$ the first terms are due to the difference between the harmonic components of the individual wells of the double-well potential, the second terms are due to the difference between their anharmonic components, and the third terms represent the classical asymmetry Δ_0 (recall that Δ_0 is the energy difference between the minima of the wells); it follows from (3.8) that these last terms are the dominant ones: $\Delta \approx \Delta_0$. In regard to $J^{(0)}$, we may use the well-known expression⁸

$$J^{(0)} \approx \frac{\hbar \omega_0}{\pi} e^{-\lambda}, \quad \lambda = \frac{1}{\hbar} \int_{-x_0}^{x_0} |p| dx,$$

where ω_0 is the classical frequency of motion in an individual well, $-x_0$ and x_0 are the turning points, and p is the momentum. Integration yields

$$\lambda_j = \frac{2(2mC)^{1/2}}{\hbar} \left(\frac{|A_j'|}{2C} + \frac{E_j^{(0)}}{C} \right)^{1/2}$$

$$\times \left\{ \frac{|A_j'|}{C} K_2(y_j) - 2 \left(\frac{E_j^{(0)}}{C} \right)^{1/2} K_1(y_j) \right\}, \quad (3.12)$$

$$y_j = [(\delta V_{Bj})^{1/2} - (E_j^{(0)})^{1/2}] (\delta V_{Bj} - E_j^{(0)})^{-1/2}, \quad \delta V_{Bj} = \delta V_{Bj}(\zeta_j),$$

$$E_j^{(0)} = E_j^{(0)}(\zeta_j),$$

where $K_1(y)$ and $K_2(y)$ are complete elliptic integrals of the first and second kind. For future purposes the exact functions are not very important, and we will have in mind the expression

$$J_j^{(0)} = 2 \frac{E_j^{(0)}}{\pi} \exp[-\lambda_j(\zeta_j)] \quad \text{for } \lambda_j(\zeta) = \beta_j \zeta^{1/\nu_j},$$

$$\beta_j \approx 1, \quad 1/2 \leq \nu_j \leq 2/3; \quad (3.13)$$

here, in particular, $\nu_j \approx 2/3$ for $E_j^{(0)} \ll \delta V_{Bj}$.

In concluding this section we point out that the tunneling states in the cases $j = 1$ and $j = 2$ exist in different regions of the parameter space of η and η_0 , separated by a discontinuity. In other words, there is no possibility of going between these regions by a continuous change of parameters while preserving the condition $u \ll w$. The physical reason for this is that the double-well character of the potential is rather pronounced for $0 < \eta < \eta_0$ or $\eta < 0$, but not in the vicinity of the point $\eta = 0$, where the interwell barrier is very small ($\delta V_{Bj} = 0$ at $\eta = 0$). In this sense we shall speak of two types of tunneling states for $j = 1$ and $j = 2$.

4. LOW-TEMPERATURE SPECIFIC HEAT OF THE TUNNELING STATES

The tunneling states considered above give the following contribution to the specific heat (see Ref. 3):

$$c_{TS} = \int_0^{\infty} n(u) \left\{ \left(\frac{u}{T} \right)^2 \frac{\exp(-u/T)}{[1 + \exp(-u/T)]^2} \right\} du, \quad (4.1)$$

where $n(u)$ is the density of the u distribution. If the function $n(u)$ is sufficiently smooth,

$$\frac{T}{n(u)} \left| \frac{dn(u)}{du} \right|_{u \rightarrow T} \ll 1, \quad (4.2)$$

this specific heat becomes

$$c_{TS} \sim 1/6 \pi^2 n(T) T \quad \text{for } n(T) \approx \text{const} \quad (4.3)$$

in agreement with experiment. Our next problem is to determine the form of $n(u)$. Using the results of the previous sections, we may write

$$n(u) = \sum_{j=1,2} n_j(u) = \sum_{j=1,2} \int_{-\infty}^{\infty} dt g(t) \int_{-\infty}^{\infty} d\eta H(\eta) \delta(u - u_j(\eta, t)), \quad (4.4)$$

where $u_j(\eta, t)$ is the expression for u in terms of the parameters of a double well of the j -th type. Going over the variables ξ_j and ζ_j and integrating with the aid of the delta function, we obtain after some manipulation an expression for $n_j(u)$ of the form

$$n_1 = \int_{\zeta_1^{(0)}}^{\infty} \Phi_1(\zeta) d\zeta$$

$$\equiv \frac{\eta_L^{1/2}}{w} r \int_{\zeta_1^{(0)}}^{\infty} H(\theta/\theta_0 \eta_L \zeta) g((r\eta_L \zeta)^{1/2}) \Phi_1^{-1/2}(\zeta) f_1^{-1}(\zeta) \zeta^{1/2} d\zeta, \quad (4.5a)$$

$$n_2 = \int_{\zeta_2^{(0)}}^{\infty} \Phi_2(\zeta) d\zeta$$

$$\equiv \frac{\eta_L^{1/2}}{w} r \int_{\zeta_2^{(0)}}^{\infty} H(-\eta_L \zeta) g\left(\left(\frac{r\eta_L u^2 \Phi_2(\zeta)}{f_2^2(\zeta) w^2}\right)^{1/2}\right) \Phi_2^{-1/2}(\zeta) f_2^{-1}(\zeta) d\zeta, \quad (4.5b)$$

where the limits $\zeta_j^{(0)} \equiv \zeta_j^{(0)}(u)$ are determined from the conditions

$$\varphi_j(\zeta) \equiv 1 - (J_j^{(0)}(\zeta)/u)^2 = 0 \text{ at } \zeta = \zeta_j^{(0)} \quad (4.6)$$

(the main contribution to the integrals in (4.5) is from the region $\eta \ll 1$); $\zeta_j^{(0)}(u)$ is a logarithmically weak function of u . For purposes of estimation we can assume [cf. (3.14)]

$$\zeta_j^{(0)} = \left[\frac{1}{\beta_j} \ln \frac{E_j^{(0)}(\bar{\zeta}_j)}{u} \right]^{1/\nu_j} \quad (4.7)$$

Condition (4.2) is satisfied if

$$\left| \frac{u}{n_j(u)} \frac{dn_j(u)}{du} \right|_{u=r} \ll 1 \quad (4.8)$$

for both n_j when $n_1 \sim n_2$ or for the larger of them when n_1 and n_2 are substantially different. The quantities on the left-hand side of (4.8) are determined by the form of the functions $\Phi_j(\zeta)$ in (4.5), i.e., by the specific features of the distribution $H(\eta)$ and $g(t)$. For the distributions in Fig. 2 there are two qualitatively different cases possible. In the first case $\Phi_j(\zeta)$ has a pronounced maximum at some $\zeta_{j, \max} > \zeta_j^{(0)}$. Then the integral for $n_j(u)$ is determined mainly by the region near $\zeta_{j, \max}$ and depends only weakly on the limit (i.e., on u). In the second case $\Phi_j(\zeta)$ is a monotonically decreasing function in the integration region,¹⁾ but the scale for its decay is rather large. As a result, the logarithmically weak shift of the lower limit $\zeta_j^{(0)}$ upon a change in u has a relatively small effect on the integral for $n_j(u)$. The restrictions on the parameters of the distributions $H(\eta)$ and $g(t)$ are set here by conditions (4.8) and are of the form

$$\eta_L \left(\frac{1}{\eta_c} + \frac{r}{\eta_{oc}} \right) \ll (\zeta_1^{(0)})^{(1-\nu_1)/\nu_1} \text{ for } n_1(u), \quad (4.9a)$$

$$\eta_L \left[\frac{1}{\eta_c} + \frac{r}{\eta_{oc}} \frac{u^2}{w^2} \frac{\mu_2(\zeta_2^{(0)})}{f_2^2(\zeta_2^{(0)})} \right] \ll (\zeta_2^{(0)})^{(1-\nu_2)/\nu_2} \text{ for } n_2(u). \quad (4.9b)$$

In (4.9b) we have made use of the fact that

$$\varphi_j(\zeta_j^{(0)} + \delta\zeta) \approx \mu_j(\zeta_j^{(0)}) \delta\zeta \text{ for } \delta\zeta \ll \zeta_j^{(0)}, \quad (4.10)$$

$$\mu_j(\zeta) = \left| \zeta^{-1} - 2 \frac{d}{d\zeta} \lambda_j(\zeta) \right|.$$

Conditions (4.9) can be interpreted to mean that in the region of interest, $u \ll w$, the characteristic scale for changes in the dynamical properties of a particle in a double well are governed primarily by the size of η_L . Accordingly, $n_j(u)$ is little different from a constant if the distributions $H(\eta)$ and $g(t)$ change slowly enough on this scale. The quantities $(\zeta_j^{(0)})^{(1-\nu_j)/\nu_j}$ in (4.9) reflect the logarithmically weak dependence of this scale on the parameters of the double well.

We note that although the expressions for $n_1(u)$ and $n_2(u)$ are similar, there are differences between them of a quantitative nature: The scale for changes in the function $g(t)$ in the expression for $n_2(u)$ is greater by a factor of

$$(w/u) f_2(\zeta_2^{(0)}) \mu_2^{-1/\nu_2}(\zeta_2^{(0)}) \gg 1.$$

Therefore, for given distributions $H(\eta)$ and $g(t)$, both the identical and the alternative cases mentioned above for $n_1(u)$ and $n_2(u)$ can be realized.

The relationship of $n_1(u)$ and $n_2(u)$ also depends on the form and parameters of the distributions $H(\eta)$ and $g(t)$. Cases with both $n_1(u) \sim n_2(u)$ and $n_1(u) \gg n_2(u)$ or $n_1(u) \ll n_2(u)$ are possible. In particular, in the case where $\Phi_j(\zeta)$, $j = 1, 2$, are monotonically decreasing functions in the integration region and

$$\eta_L \left(\frac{1}{\eta_c} + \frac{r}{\eta_{oc}} \right) \ll (\zeta_1^{(0)})^{-1} \text{ for } n_1(u), \quad (4.11)$$

$$\eta_L \left[\frac{1}{\eta_c} + \frac{r}{\eta_{oc}} \left(\frac{u}{w} \right)^2 \frac{\mu_2(\zeta_2^{(0)})}{f_2^2(\zeta_2^{(0)})} \right] \ll (\zeta_2^{(0)})^{-1} \text{ for } n_2(u),$$

and for a distribution $g(t)$ of the type shown by curve 1 in Fig. 2b, we have the relations

$$\begin{aligned} n_1(u) &\approx \eta_L^{\nu_1} w^{-1} f_1^{-1}(\zeta_1^{(0)}) (\zeta_1^{(0)})^{\nu_1} r g(0) H(0), \\ n_2(u) &\approx \eta_L^{\nu_2} w^{-1} f_2^{-1}(\zeta_2^{(0)}) \zeta_2^{(0)} r g(0) H(0), \end{aligned} \quad (4.12)$$

and so $n_1(u) \approx n_2(u)$. If conditions (4.11) hold and $g(t)$ is of the form shown by curve 2 in Fig. 2b, then $n_2(u) \ll n_1(u) \approx n(u)$. Finally, if $\eta_c < \eta_L$ and $\eta_{oc} < \eta_L$, but

$$(w/u)^2 f_2^2(\zeta_2^{(0)}) \mu_2^{-1}(\zeta_2^{(0)}) \eta_{oc} \gg \eta_L,$$

then we have the relation $n_1(u) \ll n_2(u) \approx n(u)$.

Thus the behavioral features of $n(u)$ depend on the specific form and parameters of the distributions $H(\eta)$ and $g(t)$, and several different cases are possible. It is seen, however, that in the majority of these cases $n(u)$ is a weakly varying function and differs little from a constant (it is, generally speaking, a logarithmic function). In fact, in accordance with what we have said, $n(u)$ can depend appreciably on its argument only if $\Phi_j(\zeta)$ is a monotonically decreasing function for both the $n_j(u)$ or for the larger of the two, and, simultaneously, the conditions opposite to those of (4.9) hold. In terms of our approach, the experimental behavior $c_{TS} \propto T$ is evidence that this latter possibility is not commonly realized.

Naturally, it would be desirable to have independent estimates of the parameters of the distributions $H(\eta)$ and $g(t)$ that would demonstrate that the relations for which $n(u) \approx \text{const}$ can be satisfied. One can obtain rough estimates of this kind from the experimental data on the concentration of tunneling states given the form of the distributions $H(\eta)$ and $g(t)$ shown qualitatively in Fig. 2. A simple example is

$$H(\eta) \sim N^{\nu_h} \eta_c^{-1} \exp \left[- \left(\frac{\bar{\eta} - \eta}{\eta_c} \right)^2 \right],$$

$$g(t) \sim N^{\nu_h} t_c^{-1} \exp \left[- \left(\frac{t}{t_c} \right)^2 \right],$$

where N is the total concentration of the subsystems described by the distributions $H(\eta)$ and $g(t)$. On the basis of the results of Sec. 2, the total concentration of double wells can be estimated as

$$N_{DW}=2 \int_{-\infty}^{\infty} d\eta H(\eta) \int_0^{\infty} dt g(t) \theta\left(\frac{t^2}{r} - \eta\right) \\ \sim N \exp\left[-\left(\frac{\bar{\eta} - \eta_{0c}}{\eta_c}\right)^2\right].$$

This quantity should obviously not be smaller than the concentration of tunneling states with $u \lesssim T$ measured in low-temperature experiments, typical values of which are in turn not smaller than $10^{17}-10^{18} \text{ cm}^{-3}$ at $T \sim 10 \text{ K}$.^{1,2} Considering also that N should not be greater than the total concentration of atoms in the material, we obtain the estimate $\eta_c \gtrsim 0.1$. If η_{0c} is of the same order of magnitude or larger, conditions (4.9) will be satisfied and $n(u) \approx \text{const}$. If, on the other hand, $\eta_{0c} \ll \eta_c$, then it is not hard to see that $n(u) \approx n_2(u) \gg n_1(u)$, where $n_2(u) \approx \text{const}$ for sufficiently small $u \ll w$, and, hence, $n(u) \approx \text{const}$ also. One can directly show that estimates such as the one just made are rather insensitive to the specific choice of the functional form of the distributions $H(\eta)$ and $g(t)$ shown qualitatively by the curves in Fig. 2. In fact, such estimates show that the decay scale of the distribution $H(\eta)$ cannot be very small, i.e., $\eta_c \gg \eta_L$, since the measured concentration of tunneling states is not too small, and this circumstance ensures the practical constancy of $n(u)$, at least for sufficiently small $u \ll w$.

5. THE ROLE OF TUNNELING STATES IN THE LOW-TEMPERATURE THERMAL CONDUCTIVITY

The low-energy excitations that we have been studying, tunneling states with $u \ll w$, are scatterers of low-frequency acoustical phonons³ and thus contribute to the thermal conductivity. At the actual phonon frequencies ω , which are not too low, resonant scattering is predominant over relaxational scattering and plays the governing role.^{3,9} In this case the thermal conductivity is related in the usual way to the corresponding phonon free path $l(\omega)$:

$$\chi(T) \approx \frac{1}{3} c_{ph} s l(\omega) \Big|_{\omega=T/\hbar}, \quad c_{ph} \propto T^3, \quad T \ll \hbar \omega_D,$$

where s is the speed of sound. The behavior $\chi \propto T^2$ observed experimentally in amorphous structures corresponds to $l(\omega) \propto \omega^{-1}$.

In accordance with Ref. 3 we may write

$$l^{-1}(\omega) = \sum_{j=1,2} l_j^{-1}(\omega), \quad l_j^{-1}(\omega) = \sigma(\omega) n_{eff}^{(j)}(\omega) \text{cth}(\hbar\omega/2T), \quad (5.1)$$

where the resonant scattering cross section is $\sigma(\omega) \approx 4\pi s^2 \omega^{-2}$. The effective density of resonant scatterers in (5.1) is

$$n_{eff}^{(j)} = \langle 2\pi \hbar^{-1} g_D(\omega) |M_j|^2 \rangle = \langle \Gamma_j(\omega) \rangle, \quad (5.2)$$

where M_j is the matrix element for a real transition of the particle between the levels of the tunneling states of type j on account of the interaction with the phonons, which have a density of states $g_D = 9\omega^2/\omega_D^3$ in the Debye approximation, and Γ_j is the corresponding level width of the tunneling states. The angle brackets in (5.2) denote an ensemble average over the tunneling states of type j ; in the present approach, this average is given by the relations [cf. (4.4)]:

$$\langle \Gamma_j \rangle = \int_{-\infty}^{\infty} d\eta H(\eta) \int_{-\infty}^{\infty} dt g(t) \delta(u(\eta, t) - \hbar\omega) \Gamma_j \\ = \int_{\zeta_j^{(0)}(\omega)}^{\infty} \Phi_j(\zeta_j) \Gamma_j(\zeta_j, \tilde{\xi}_j, \omega) d\zeta_j, \quad (5.3)$$

$$\tilde{\xi}_j \equiv \tilde{\xi}_j(\zeta_j) = \hbar\omega w^{-1} \varphi_j^{1/2}(\zeta_j) f_j^{-1}(\zeta_j), \quad \zeta_j^{(0)}(\omega) \equiv \zeta_j^{(0)}(u) \Big|_{u=\hbar\omega}.$$

In (5.3) we have gone over from the variables η and η_0 to the variables ζ_j and ξ_j ; the value $\tilde{\xi}_j$ is determined by the condition $u(\zeta_j, \tilde{\xi}_j) = \hbar\omega$. We note that over and above the different notation used, expressions (5.1)–(5.3) differ from the corresponding expressions of Ref. 3 in that here we have allowed for the existence of two types of tunneling states, and the average is taken over the distributions of the fluctuating parameters η and t (and not Δ_0 and λ as in Ref. 3).

To calculate the matrix elements $M_j \equiv M_j(\eta, \eta_0, \omega)$ one must establish the form of the coupling between the tunneling states and the phonons, i.e., specify the Hamiltonian \mathcal{H}_{int} in (2.4). In the general case of an arbitrary tunneling particle it is difficult to determine \mathcal{H}_{int} , and a complete solution of the problem may involve the specific structure of the particle. For the tunneling states considered here, the main role in the interaction \mathcal{H}_{int} , as we mentioned in Sec. 2, is played by long-wavelength acoustical phonons. This circumstance permits us to go over to the continuum approximation, introducing the strain tensor e_{ik} . Keeping only the first nonvanishing term in the expansion of $\mathcal{H}_{int}(x, e_{ik})$ in powers of x and e_{ik} , one can assume, as in the theory of the deformation potential, that

$$\mathcal{H}_{int} \approx x \kappa_{ik} e_{ik}, \quad (5.4)$$

where κ_{ik} is a tensor coupling parameter. Since the tensor character of these quantities is not important in the present problem, let us for simplicity consider only a scalar interaction ($\kappa_{ik} \rightarrow \kappa, e_{ik} \rightarrow e$):

$$\mathcal{H}_{int} = x e \approx \kappa x \sum_{\mathbf{q}\alpha} \left(\frac{\hbar \mathbf{q}}{2m s}\right)^{\alpha} \frac{\mathbf{q}\alpha}{q} (b_{\mathbf{q}} + b_{-\mathbf{q}}^+), \quad (5.5)$$

where \mathbf{n} denotes the (unit) polarization vectors, and $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^+$ are the annihilation and creation operators for phonons with wave vector \mathbf{q} .

With the Hamiltonian (5.5) we obtain

$$M_j^2 \approx \vartheta^2 D_j^2 \frac{\hbar \omega J_j^2}{2m s^2 u_j^2}, \quad D_j = \kappa_j \delta x_j, \quad j=1, 2, \quad (5.6)$$

where we have made use of the fact that

$$\langle +j | x | -j \rangle \approx \frac{J_j}{u_j} \delta x_j \approx \frac{2j-1}{2j} \left(\frac{e}{C}\right)^{1/2} \zeta_j^{1/2} \frac{J_j}{u_j},$$

where δx_j is the spatial separation between the minima of a double well of type j ; the factor $\vartheta \sim 1$ comes from the averaging over the polarization directions. The coupling parameters κ_j can in general be different for tunneling states of type $j=1$ and $j=2$ and may also depend on η and η_0 , i.e., $\kappa_j = \kappa_j(\zeta_j)$ in (5.6)

In principle, relations (5.1)–(5.3) and (5.6) determine a solution to the problem of the phonon thermal conductivity and the mean free path of acoustical phonons for the case when their dominant scattering mechanism is resonant scattering by tunneling states. The detailed behavior of $l(\omega)$ and $\chi(T)$ depend on the specific structure of the coupling parameters κ_j . After straightforward manipulations, the result of the averaging in (5.2) can be written

$$l_j^{-1} = 36\pi^2 \theta^2 \frac{\omega}{m\omega_D^3} \int_0^1 \Phi_j[\xi_j(\Lambda)] D_j^2[\xi_j(\Lambda)] \frac{\xi_j(\Lambda)}{\mu_j[\xi_j(\Lambda)]} d\Lambda, \quad (5.7)$$

where we have introduced the variable $\Lambda = [J_j(\xi_j)/\hbar\omega]^{1/2}$; the functional dependence $\xi_j(\Lambda)$ logarithmically weak. It can be assumed (and this agrees with the assumption of the phenomenological model³) that $D_j(\eta, \eta_0)$ is a rather slowly varying function, at least in comparison with an exponential. Then the integral in (5.7) differs from those in the expressions for $n_j(u)$ only by the logarithmically slow factors

$$D_j^2[\xi_j(\Lambda)] \xi_j(\Lambda) \mu_j^{-1}[\xi_j(\Lambda)]$$

in the integrand, and the analysis of the dependence of this integral on the form of the distributions $H(\eta)$ and $g(t)$ is the same as that given in Sec. 4. In particular, it can be stated that the different possible cases are $l_1(\omega) \sim l_2(\omega)$ and $l_1(\omega) \gg l_2(\omega)$ or $l_1(\omega) \ll l_2(\omega)$. It must be stressed, however, that generally speaking

$$l_1(\omega)/l_2(\omega) \neq n_2(\hbar\omega)/n_1(\hbar\omega),$$

even for $\kappa_1 = \kappa_2$ [see (5.6)–(5.7)], i.e., tunneling states with $j = 1$ and $j = 2$ interact differently with phonons. This circumstance may be important in the experimental aspects of the problem (see Sec. 7). Based on what we have said, it is generally true that to logarithmic accuracy $l(\omega) \propto \omega^{-1}$, i.e., $\chi \propto T^2$, under the same conditions for which $n(u) \approx \text{const}$, i.e., $c_{TS} \propto T$. The empirical data show that such a relationship is generally obeyed for a wide class of amorphous structures.

In concluding this section let us touch upon the problem of the scale of the constants in the deformation potential D_j . The change in the energy splitting of the tunneling states upon a dilation $\delta u_j \sim D_j e$ and also D_j itself can be estimated crudely as the value of δu_j for $e \sim 1$. This approach leads, in particular, to reasonable values of the constants in the deformation potential D for ordinary single-well atomic potentials: $D \sim D^{(0)} \equiv \hbar\omega_D (\sim 10^{-2})$ eV. However, the empirically determined values $D \sim 1$ eV for the tunneling states are anomalously large on the scale of $D^{(0)}$. The nature of these rather large anomalies remains an open question. They can be given a reasonable explanation based on the critical properties of the double-well potentials that we predicted earlier in this article.² For this purpose we note that in an estimate of the type (see Ref. 10)

$$D \sim \frac{du}{dk} \frac{dk}{de} \sim \frac{u}{k} \frac{dk}{de}$$

the derivative dk/de is not anomalously small (unlike the quasielastic constant k itself). In point of fact,¹⁰ the small-

ness of k is the result of a cancellation of a number of large terms, each of which depends on e in the same way as do the terms appearing in $k^{(0)}$, and consequently, $dk/de \sim dk^{(0)}/de$. This circumstance permits us to estimate the value of D for the critical potential as

$$D \sim D^{(0)} k^{(0)}/k \sim D^{(0)} \eta_L^{-1} \sim 10^2 D^{(0)}, \quad k^{(0)} \equiv k(\eta=1) \sim m\omega_D^2,$$

where we have used the fact that for the double wells in question the characteristic values of k are of the order of $k^{(0)} \eta_L^{-1}$ (see Sec. 3); the quantity $D^{(0)}$ here refers to a hypothetical double well having the same energy splitting u but lacking critical properties. Our estimate thus yields a value $D \sim 1$ eV in good agreement with experiment.

6. DEPENDENCE OF THE MEASURED LOW-TEMPERATURE SPECIFIC HEAT ON THE MEASUREMENT TIME

In Sec. 4 we considered a specific heat defined in accordance with ordinary equilibrium thermodynamics. However, if the interwell barrier strength λ is large enough, the relaxation time $\tau \sim \hbar/\Gamma$ of the tunneling states will be comparable to or larger than the measurement time τ_{exp} . The tunneling states available for tunneling are only those with $\tau \lesssim \tau_{\text{exp}}$, with the result that the measured low-temperature specific heat depends on the measurement time, i.e., $c_{TS} = c_{TS}(\tau_{\text{exp}})$, as was first predicted in Ref. 3. For sufficiently smooth distributions $\rho_\lambda(\lambda)$, the function $c_{TS}(\tau_{\text{exp}})$ should have a logarithmic character. In particular, for the uniform distribution $\rho_\lambda(\lambda) = \lambda_c^{-1} \theta(\lambda_c - \lambda)$ used in Ref. 3, we obtain¹¹

$$c_{TS} \propto T \ln(\tau_{\text{exp}}/\tau_{\text{min}}), \quad (6.1)$$

where the minimum relaxation time τ_{min} for tunneling states with a given $u (\approx T)$ corresponds to the maximum tunneling amplitude $J = u$. Repeated attempts have been made to verify law (6.1) experimentally (see the recent papers of Refs. 12 and 13). It was found that the behavior of $c_{TS}(\tau_{\text{exp}})$ is in fact logarithmic, but is more complex than (6.1) and does not reduce to it.

Our theory leads to a $c_{TS}(\tau_{\text{exp}})$ dependence that is different from (6.1). The functional form can be established by determining the conditional probability density $\rho_j(\tau|u)$ that a tunneling state of type j with a given u is characterized by relaxation time τ . Using the results given above, we find

$$\rho_j(\tau|u) \approx \left[\ln \left(\frac{w^2}{u^2} \frac{\tau}{\tau_{\text{min},j}} \right) \right]^{-1/2} \left(1 - \frac{\tau_{\text{min},j}}{\tau} \right)^{-1/2} \tau^{-1}, \quad (6.2)$$

$$c_{TS,j}(\tau_{\text{exp}}) \approx c_{TS,j}(\infty) \left\{ 1 - \left[1 + \mathcal{L}^{-1} \ln \left(\frac{\tau_{\text{exp}}}{\tau_{\text{min},j}} \right) \right]^{-1/2} \right\}, \quad (6.3)$$

$$\mathcal{L} = \mathcal{L}(T) \equiv 2 \ln \frac{w}{T},$$

$$\tau_{\text{min},j} \approx \frac{\hbar n_j(u)}{\langle \Gamma_j(\omega) \rangle} \Big|_{\substack{u=\tau \\ \hbar\omega=T}} \left(\infty \left(\frac{\hbar\omega_D}{T} \right)^3 \right).$$

It follows from (6.3) that law (6.1) obtains only for $\tau_{\text{exp}} \ll \bar{\tau}_j \equiv (w/T)^2 \tau_{\text{min},j}$, whereas for $\tau_{\text{exp}} \gg \bar{\tau}_j$ the dependence $c_{TS}(\tau_{\text{exp}})$ is substantially weaker and tends toward a satura-

tion which is unrelated to the boundary of the spectrum of λ values (for the actual values of the parameters we estimate that $\bar{\tau}_j \sim 10^{-5}$ s).

In papers on the study of the dependence of c_{TS} on τ_{exp} , law (6.1) is usually interpreted as an inevitable consequence of the model of Ref. 3. In regard to this we note the following. The possible predictions of that model are accurate only up to logarithmic corrections. This is due both to the use of a quasiclassical formula for the tunneling amplitude and to the actual neglect of the logarithmically weak deviation of the distributions of the parameters Δ and λ from strict uniformity (which, however, do not alter the main conclusions of Ref. 3 as to the existence of the dependence $c_{TS} \propto T$ and $\chi \propto T^2$). The dependence given in (6.1) can be refined by including logarithmic corrections³⁾ to the theory of Ref. 3. Therefore, on the basis of Ref. 3 one can only state that c_{TS} does depend on τ_{exp} , but one cannot determine its exact functional form [in this sense (6.3) in no way contradicts the general ideas of the phenomenological model of Ref. 3]. For this reason the usual attempts to compare the empirical results with law (6.1), and also attempts to determine the specific physical causes of the deviation from this law (see Refs. 12 and 13), would appear groundless.

7. CONCLUSION

The proposed theory is based on a general description found for the typical local many-well atomic potentials in amorphous materials in terms of a function of a single variable, corresponding to the critical mode of motion. The typical many-well potentials turn out to be the double-well and critical potentials, and the tunneling states in them are two-level states. The ensuing conclusions about the nature of the low-temperature anomalies of $c(T)$, $\chi(T)$ and $I(\omega)$ in amorphous materials agree with the experimental data. The proposed theory thus provides a foundation for the postulate of Ref. 3 attributing the anomalies observed in the low-temperature properties of amorphous structures to the presence of two-level tunneling states in double-well potentials, and reveals the definite physical content of this hypothesis. On the other hand the theory explains certain properties which have hitherto seemed anomalous of two-level systems of this kind. In particular, the anomalously large phonon-tunneling-state coupling parameters $D \sim 1$ eV determined empirically can be explained by invoking the critical properties of the double wells (see Sec. 5). We note that the anomalously high sensitivity to internal strains has been known earlier and was perceived as a general circumstance for defects with small values of the local quasielastic constants in crystals (see Ref. 10). This circumstance, however, was never related to the observed values of D for the tunneling states, since there was no understanding of the critical properties of double-well potentials. From this standpoint the values $D \gg D^{(0)}$ observed for the tunneling states can be regarded as experimental support for the critical properties predicted above for the double wells.

The anomalously large values of D also bear upon the question of the changes in the spectral structure of the tunneling states on account of their interaction with phonons.

The lowest-order correction to the "bare" interlevel energy u for the tunneling states, to account for the interaction with phonons, corresponds to the second order of perturbation theory and, on the basis of the results obtained above, can be estimated as

$$|\delta u^{(2)}| \sim \frac{D^2}{ms^2} \left(\frac{J}{u}\right)^2 \frac{u}{\hbar\omega_c} \int_0^{\omega_c} \frac{\omega^2 d\omega}{\omega_D^3} \\ \sim \frac{D^2}{ms^2} \left(\frac{J}{u}\right)^2 \left(\frac{\omega_c}{\omega_D}\right)^3 \frac{u}{\hbar\omega_c} \text{ at } T=0,$$

where ω_c is the maximum frequency of the phonons involved in the interaction. In the model of Ref. 3, $\omega_c = \omega_D$, leading to values $|\delta u^{(2)}| \gg u$ for the actual values $J \sim u$ (in this sense the model of Ref. 3 is internally inconsistent). In the proposed theory the rapid modes of motion with $\hbar\omega \gg u$ are included in the definition of the "bare" splitting of the tunneling states upon adiabatic renormalization of the parameters of the double well, and it should be assumed that $\omega_c \sim u/\hbar \ll \omega_D$, so that

$$|\delta u^{(2)}| \sim \frac{D^2}{ms^2} \left(\frac{w}{\hbar\omega_D}\right)^3 \left(\frac{J}{u}\right)^2 \frac{u}{w} \ll u.$$

The high-order corrections are negligibly small; for example

$$|\delta u^{(4)}| \ll \left(\frac{D}{ms^2}\right)^2 \frac{D^2}{\hbar\omega_D} \left(\frac{w}{\hbar\omega_D}\right)^8 \frac{u}{w} \ll u,$$

etc. Therefore all of the results obtained above remain valid if u is taken to mean its unessentially renormalized value in the various expressions.

We should also stress in this regard that the proposed theory can also include the dynamical aspects of the nature of the double wells with adiabatic allowance for the fast modes of motion. For example, in the simplest model of a single-mode Hamiltonian for the surrounding medium,

$$\mathcal{H}_2 = p_2^2/2m_2 + 1/2 m_2 \omega_2^2 \tilde{x}_2^2 \text{ with } \omega_2 \gg w/\hbar$$

(see Sec. 2), the adiabatic renormalization is of the form

$$\eta \rightarrow \eta + \delta\eta, \quad \delta\eta = -D^2/2Ams^2,$$

i.e., a potential which would be a single well if the surrounding atoms were at rest can be transformed into a double well when their rapid motion is taken into account. We note, however, that this effect is not of practical importance at the actual values $|\delta_\eta| \lesssim 10^{-2}$ and $|\eta| \sim \eta_L \zeta_j^{(0)} > \eta_L \bar{\zeta}_j$ for the relevant potentials in amorphous systems (cf. Ref. 14).

In conclusion, we can point out several circumstances which follow from the above discussion and might be of experimental significance. In the theory, the idea arises that there are two different types of tunneling states, which interact differently with phonons. This prediction may correspond to the hypothesis that both normal and anomalous tunneling states exist, which was made by Black and Halperin¹⁵ on the basis of analysis of the experimental data. Also, the predicted dependence of the measured specific heat on the measurement time found in the present differs from that indicated earlier by Jäckle.¹¹ Finally, the phenomenon

of local attraction between charge carriers of the same sign, which was predicted earlier¹⁶ by two of us in their analysis of a specific model for the critical potential described by expression (2.1), can be said to be extremely general. This assertion follows from the general grounds for expression (2.1) given in the present paper and the derivation given in Ref. 16. In other words, local attraction between carriers of the same sign and the anomalies in the low-temperature thermal properties, both being due to the critical properties of the structure of amorphous materials, can be observed in the same substances.

We wish to thank M. A. Krivoglaz, V. L. Gurevich, and D. A. Parshin for helpful discussions.

¹¹The case of a monotonically increasing function $\Phi_j(\zeta)$ need not be considered here, since it follows from Sec. 2 that $\Phi_j(\zeta)$ must fall off at sufficiently large values of ζ .

¹²Without going into details, we remark that attempts to explain the large values of D as being due to a strong change in the barrier penetrability J upon dilation have not been successful at the actual values $\lambda \lesssim 10$ and are at odds with the observed dependences $l \propto \omega^{-1}$ and $\chi \propto T^2$.

¹³We note that (6.2) differs from the corresponding expression in Ref. 11 by the presence of a logarithmic factor.

- ¹⁴S. Hunklingen and W. Arnold, *Phys. Acoustics* **12**, 155 (1976).
¹⁵W. A. Phillips (ed.), *Amorphous Solids: Low Temperature Properties*, Springer-Verlag, Heidelberg (1980).
¹⁶P. W. Anderson, B. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972); W. A. Phillips, *J. Low Temp. Phys.* **7**, 351 (1972).
¹⁷V. G. Karpov and M. I. Klinger, *Pis'ma Zh. Tekh. Fiz.* **6**, 1478 (1980) [*Sov. Tech. Phys. Lett.* **6**, 636 (1980)]; M. I. Klinger and V. G. Karpov, *Solid State Commun.* **37**, 975 (1981).
¹⁸M. H. Cohen and G. S. Crest, *Phys. Rev. Lett.* **45**, 1271 (1980).
¹⁹J. C. Phillips, *Phys. Rev. B* **24**, 1744 (1981).
²⁰T. Poston and I. N. Stuart, *Catastrophe Theory and its Applications*, Pitman, London (1978).
²¹L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, 3rd ed., Pergamon Press, Oxford (1977).
²²P. Doussinedu, C. Frenois, R. G. Leisure, A. Levelut, and V. J. Preiur, *J. Phys. (Paris)* **41**, 1193 (1980).
²³A. M. Stoneham, *Theory of Defects in Solids: Electronic Structure of Defects in Insulators and Semiconductors*, Oxford Univ. Press (1975).
²⁴J. Jäckle, *Z. Phys.* **257**, 212 (1972).
²⁵M. Meissner and K. Spitzmann, *Phys. Rev. Lett.* **46**, 265 (1981).
²⁶M. T. Loaponen, R. C. Dynes, V. Narayanmurit, and F. P. Garno, *Phys. Rev. B* **25**, 1161 (1982).
²⁷J. P. Sethna, *Phys. Rev. B* **24**, 698 (1981).
²⁸J. L. Black and B. I. Halperin, *Phys. Rev. B* **16**, 2879 (1977).
²⁹M. I. Klinger and V. G. Karpov, *Zh. Eksp. Teor. Fiz.* **82**, 1687 (1982) [*Sov. Phys. JETP* **55**, 976 (1982)].

Translated by Steve Torstveit