Frequency Spectrum and Low-Temperature Specific Heat of Noncrystalline Solids

Shozo TAKENO and Masaki GODA*

Department of Nuclear Engineering, Kyoto University, Kyoto
**Department of Physics, Hokkaido University, Sapporo[†] and Research
Institute for Fundamental Physics, Kyoto University, Kyoto*

It is shown that an extra phonon density of states associated with the roton-like part of the dispersion of phonon excitations, which is likely to exist in almost all types of noncrystalline solids, gives rise to an excess low-temperature specific heat. This could account for the anomaly in the low-temperature thermal properties observed in a large number of noncrystalline solids and glassy polymers. It is shown that under certain conditions the excess low-temperature specific heat is nearly proportional to absolute temperature.

The thermal conductivity of noncrystalline dielectric solids has long been known to be markedly different from that of crystalline solids.[1],[2] It has also been increasingly apparent that the low-temperature specific heat of solids in the glassy phase is larger than in the crystalline phase:[3]~[6] This difference has often been referred to as an excess specific heat. The characteristic feature here is that such a behavior is insensitive to structural details of a particular noncrystalline sample and therefore that it seems to be rather common in almost all types of noncrystalline solids. This result seems to preclude possible mechanisms arising from structure-sensitive phonon scatterings or quasi-localized phonon modes due to impurities or defects.[7] Fulde and Wagner[8] have proposed a semi-phenomenological model for elementary phonon excitations in noncrystalline solids which can account for the low-temperature anomalies in the specific heat and the thermal conductivity of amorphous solids. Recently Anderson, Halperin and Varma[9] have proposed an alternative possible model, starting from the basic assumption that in any glass system there should be a certain number of atoms which can sit more or less equally well in two equilibrium positions.

In a previous paper, to be referred to as I,[10] the present authors have shown that the structural disorder inherent in noncrystalline solids is likely to give rise to roton-like phonon excitations in the close vicinity of the first peak in the structure factor (see Figs. 1 and 4 in I). In this paper we wish to show that such a behavior of phonon modes does yield an extra phonon density of states in the low-frequency region, thus giving rise to anomalies in the low-temperature thermal properties of noncrystalline solids. For the sake of simplicity, we confine our-

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[†] Permanent address.

selves in this paper to the problem of the low-temperature specific heat.

According to the results obtained in I,[10] the dynamical matrix $\mathscr{D}$ giving the phonon eigenfrequencies as a function of wave vector k in a noncrystalline solid composed of atoms of a single species is given by*)

$$\mathscr{D} = (\rho/M) \int d\mathbf{R} g_2(\mathbf{R}) \nabla\nabla v(\mathbf{R}) \left[1 - \exp(i\mathbf{k}\cdot\mathbf{R})\right]. \tag{1}$$

Here, M and ρ are the atomic mass and the number density of the atoms, respectively, $v(\mathbf{R})$ is the "bare potential" describing the interaction of a pair of atoms, and $g_2(\mathbf{R})$ is a pair correlation function for the distribution of atoms in the solid. Equation (1) may be called a quasi-crystalline approximation. It has been shown that of three branches of phonon modes, one is longitudinal and the other two are transverse, at least the dispersion of the longitudinal phonons has the form of phonon-roton-like excitations[11] as observed in liquid helium.[12] Let $\omega_l(k)$ be the eigenfrequency of such phonon modes with imaginary part $\Gamma_l(\omega^2)$. Within the framework of the harmonic approximation, the factor Γ_l arises if we take into account higher order correlations other than pairs.**) Then, its contribution to the frequency spectrum $\rho_l(\omega)$ can be expressed in the form

$$\rho_l(\omega) = (2\omega/\pi) \mathrm{Im}\left[\int \frac{f_l(\mathbf{k})d\mathbf{k}}{\Omega^2 - \omega_l(\mathbf{k})^2} \right]$$

with

$$\Omega^2 = \omega^2 - i\Gamma_l(\omega^2), \tag{2}$$

where $f_l(\mathbf{k})d\mathbf{k}$ is the number of modes between $\mathbf{k}$ and $\mathbf{k}+d\mathbf{k}$ and $\mathrm{Im}[A]$ denotes the imaginary part of A. In the case of a crystal lattice, the quantity $f_l(\mathbf{k})$ is nonzero and becomes $V_a/(2\pi)^3$ only in the first Brillouine zone, where V_a is the volume of the unit cell. In our present case, however, such a relation can no longer be used since the conventional reduced-zone scheme does not hold. Without any approximation, we cannot proceed from Eq. (2). For the sake of simplicity, we assume in the following that both of $\omega_l(k)$ and $f_l(k)$ are spherically symmetric.***) Equation (2) then reduces to

$$\rho_l(\omega) = 8\omega\, \mathrm{Im}\left[\int_0^\infty \frac{f_l(k)k^2 dk}{\Omega^2 - \omega_l(k)^2} \right]. \tag{3}$$

As in the case of liquid helium, we take $\omega_l(k)$ in the vicinity of $k=k_0$, at which the roton-like minimum takes place, to be of the form[13],[10]

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*) For a detailed discussion of Eq. (1), see Ref. 10), §3.

**) For a discussion on this point, see Ref. 11), the Appendix.

***) This approximation is equivalent to assuming the pair correlation function g_2 to be spherically symmetric. Thus, we are taking into account only those correlations which exist in the case of simple liquids. This may be used as a zero-order approximation. There have been experimental indications that the structure factor of several substances in noncrystalline phase is not very different from that in liquid phase.

$$\omega_l(k) = \Delta_l + \frac{(k-k_0)^2}{2\mu_l}, \qquad\qquad (4)$$

where[10]

$$\Delta_l = \omega_l(k_0)$$

and

$$\mu_l = 2\omega_l(k_0)/[d^2\omega_l(k)^2/dk^2]_{k=k_0}. \qquad\qquad (5)$$

It is shown that the quantities Δ_l, k_0 and μ_l depend on a parameter characterizing the degree of local ordering.[10] As shown in our previous paper[10] and also as in the case of phonon-roton excitations in liquid helium,[13] the quantity k_0 is, in general, slightly smaller than the position of the first peak in the structure factor. The contribution of the roton spectrum, similar to Eq. (4), to the specific heat of liquid helium has been studied by Landau.[18] The present method differs from that employed by him in that the imaginary part Γ_l of the frequency and the wave-number distribution function $f_l(k)$ have been introduced. Insertion of Eq. (4) into Eq. (3) gives

$$\rho_l^{(r)}(\omega) = 8\mu\omega \, \mathrm{Im}\left[\int_0^\infty dx \, \frac{f_l(k_L+k'(x))(k_L+k'(x))^3 + f_l(k_L-k'(x))(k_L-k'(x))^3}{(\Omega^2-x^2)k'(x)} \right]$$

with

$$k'(x) = [2\mu(x-\Delta_l)]^{1/2}, \qquad\qquad (6)$$

where the superscript r denotes the roton-like part of the frequency spectrum. In view of the fact that in the case of a crystal lattice $f_l(k)$ is step-function-like[*] with a cutoff wave vector corresponding to the first reciprocal lattice vector k_L, we take $f_l(k)$ to be of the form as shown in Fig. 1. The underlying fact here is that the uncertainty Δk in wave number k inherent in disordered systems generally increases as k increases and that the integrated value of $f_l(k)$ over the whole wave-number space must be equal to the total number of atoms in the system.
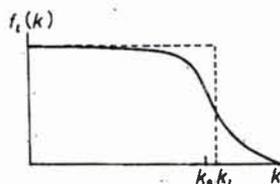

Fig. 1. Schematic behavior of the wave-number distribution function $f_l(k)$. The dotted line corresponds to the case of a crystal lattice.

We then expand the function $f_l(k_L \pm k')$ in Taylor's series:

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[*] The properties of the wave-number distribution function $f_l(k)$ in noncrystalline solids have also been briefly touched upon in a paper by Morgan [G. J. Morgan, J. Phys. C1 (1968), 347]. See also, G. J. Morgan and J. M. Ziman, Proc. Phys. Soc. 91 (1967), 689.

$$f_i(k_L \pm k') = f(k_L) \pm f'(k_L)k' + \cdots. \tag{7}$$

Combining Eq. (7) with Eq. (6), we get

$$\rho_i^{(r)}(\omega) = 16\mu\omega k_L^2 f_i(k_L) \operatorname{Im}\left[\int dx \frac{1}{(\Omega^2 - x^2)k'(x)} \right]$$

$$+ 16\mu\omega \{ f_i(k_l) + 2k_L(\partial f_i/\partial k)_{k=k_L} \} \operatorname{Im}\left[\int \frac{k'(x)}{\Omega^2 - x^2} dx \right]$$

$$\equiv \rho_{i1}^{(r)}(\omega) + \rho_{i2}^{(r)}(\omega). \tag{8}$$

Without detailed calculations, we can obtain the qualitative property of $\rho_i^{(r)}(\omega)$. We observe that by setting $\Gamma_i(\omega^2)$ equal to zero Eq. (6) reduces to

$$\rho_i^{(r)}(\omega) = \frac{16\mu\omega k_L f_i(\omega_L)}{[2\mu(\omega - \Delta_i)]^{1/2}}$$

$$+ 16\mu\omega \left\{ f_i(k_L) + 2k_L\left(\frac{\partial f_i(k)}{\partial k}\right)_{k=k_L} \right\} [2\mu(\omega - \Delta_i)]^{1/2}$$

$$\equiv \rho_{i1}^{(r)}(\omega) + \rho_{i2}^{(r)}(\omega), \tag{9}$$

having the singularity of the form $(\omega - \Delta_i)^{-1/2}$. Introduction of the imaginary part would generally modifies the spectrum as shown in Fig. 2. It also modifies the second term, but this modification is not so pronounced as compared with that due to the first term. Such a result could be obtained by analogy of the energy spectra of electrons or phonons in disordered systems. As is seen from Fig. 2, thus the over-all behavior of $\rho_i^{(r)}(\omega)$ is almost constant in the vicinity of $\omega = \Delta$. The above result, when combined with the formula for the specific heat,
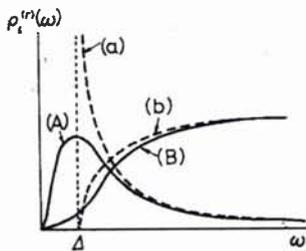

Fig. 2. Schematic behavior of $\rho_i^{(r)}(\omega)$. The solid and the dotted lines correspond to the cases with and without the imaginary part $\Gamma_i(\omega^2)$. Curves (A), (B), (a) and (b) represent $\rho_{i1}^{(r)}(\omega)$, $\rho_{i2}^{(r)}(\omega)$, $\rho_{i1s}^{(r)}(\omega)$ and $\rho_{i2s}^{(r)}(\omega)$, respectively.

$$\Delta C_V^{(r)} = k_B \int d\omega \rho_i^{(r)}(\omega) \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2}$$

$$= (k_B^2/\hbar) T \int dx \rho_i^{(r)}\left(\frac{k_B T}{\hbar}x\right) \frac{x^2 e^x}{(e^x - 1)^2}, \tag{10}$$

gives an excess specific heat $\Delta C_v^{(r)}$. Here, k_B is the Boltzmann constant and $\hbar$ is the Planck constant divided by 2π.

The result obtained here depends on the frequency gap Δ_i in the phonon dispersion curve which, as we have shown in I,[10] characterizes the local ordering in disordered systems. It appears that any model or theory aiming at understanding of the low-temperature thermal properties of noncrystalline solids and glassy polymers as well must be very simple and at the same time

sufficiently general to be equally applicable to a large number, if not even all, of such disordered systems. The result obtained here may be one of possible candidates for such a theory.

A remarkable result obtained by Zeller and Pohl[3] is that the specific heat of noncrystalline solids at very low temperatures is proportional to T. This could be accounted for by the present result. It is seen from Fig. 2 that the excess frequency spectrum $\rho_t^{(r)}(\omega)$ is almost independent of ω above and in the vicinity of Δ_t. To arrive at a result more concrete than Eq. (10), we make an attempt at approximating $\rho_t^{(r)}(\omega)$ by

$$\rho_t^{(r)}(\omega) = \begin{cases} A\omega^n, & \omega < \omega_1, \\ A\omega_1^n, & \omega > \omega_1, \end{cases} \quad (n>1) \tag{11}$$

where A is a constant.*) The quantities n and ω_1 are a positive number greater than unity and a constant close to but smaller than Δ_t, which characterize the behavior of $\rho_t^{(r)}(\omega)$ in the close vicinity of $\omega=0$ and $\omega=\Delta_t$, respectively. Putting Eq. (11) into Eq. (10), we get

$$\Delta C_V^{(r)} = (k_B^2/\hbar) A\omega_1^n T \int_0^{\theta/T} \frac{x^2 e^x}{(e^x-1)^2} dx + (k_B^2/\hbar) AT$$

$$\times \int_{\theta_1/T}^{\theta_1/T} \left[\left(\frac{k_B T}{\hbar}\right)^n x^n - \omega_1^n \right] \frac{x^2 e^x}{(e^x-1)^2} dx, \tag{12}$$

where

$$\theta_1 = \hbar\omega_1/k_B \tag{13}$$

and θ is a temperature corresponding to a cutoff frequency of $\rho_t^{(r)}(\omega)$ in the region $\omega > \omega_1$. At very low temperatures the quantity θ/T is taken to be infinity. Thus, the first term of Eq. (12) gives an excess specific heat proportional to T. The second term depends sensitively on θ_1 and n. We have not yet obtained information on Δ_t from experimental data. For liquid helium, the roton minimum in unit of degree Kelvin is about 8°K. In view of possible ordering in noncrystalline solids higher than in the case of liquid helium, the quantity θ_1 may be smaller than, say, 5°K. For a sufficiently small value of θ_1 the second term in Eq. (12) can be neglected in comparison with the first term. This may hold for noncrystalline solids, in which the linear dependence of the low-temperature specific heat with respect to absolute temperature has been observed.[3] It is, however, to be reminded that more important is probably the existence of excess low-temperature specific heat itself, which may reflect a very general feature of noncrystalline solids and glassy polymers resulting from structural disorder.**)

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*) The discontinuity of the derivative of $\rho_t^{(r)}(\omega)$ at $\omega=\omega_1$ is an artifact of our approximation, which does not affect the essential feature of the excess specific heat discussed here.

**) It has recently been shown that an excess low-temperature specific heat of vitreous selenium is not proportional to the absolute temperature [see, J. C. Lasjaunias, R. Maynard and D. Thoulouz, Solid State Comm. 10 (1972), 215].

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