

Nonlocal effects on the thermal behavior of non-crystalline solids

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We argue that nonlocal effects represented by fractionary terms in the kinetic energy can be relevant to achieve a satisfactory phenomenological description of the thermal behavior of the specific heat of non-crystalline solids at very low temperature. We propose a simple model formed by the direct sum of two Hamiltonians, one of which is obtained by incorporating fractional derivatives in the kinetic energy of a conventional Hamiltonian, and the other one accounts for the presence of phonons in the system. Some experimental data are used to support the proposed description.

Keywords: Non-crystalline solids; Thermal behavior; Nonlocal effects; Green function

1. INTRODUCTION

In the crystalline order, the atoms forming the solid suppress their individual displacements in favor of collective movements whose quantum manifestations are the phonons. In a crystal system, this order is enough to describe its thermal behavior at very low temperature. If the system is metallic, another contribution, coming from the Exclusion Principle, has to be taken into account, but the global picture is found from the collective movements of the system. The case of a non-crystalline solid is surely more complicated, because, since the pioneer work of Zeller and Pohl, it is well known that the thermal properties of these materials are very different from the crystalline ones [1]. In fact, after several decades of research on the problem, two features of the specific heat and of the thermal conductivity in these materials have been considered as universal: An approximated linear dependence on the temperature below 1 K and the presence of a *boson peak* above this temperature for the specific heat; a quadratic dependence on the temperature, below 1 K, and a plateau (in correspondence to the boson peak) for the thermal conductivity [2, 3]. Although the two-level or tunnelling states model has been very successful in accounting for the thermal behavior of the specific heat (see e.g., Ref. [2] for a review), a satisfactory microscopic description of these phenomena, in terms of a simple applicable model, is still to be achieved. For that reason, it is highly desirable to have a unified (and hopefully simple) point of view to analyze the data on the specific heat of glassy samples in the low-temperature region. Along these lines, some efforts have been made in the past in order to establish the physical nature of the elementary excitations present in these systems. By following an analogy to what happens in the physics of superfluid helium, Takeno and Goda [4, 5], and in a similar way Tanttila [6–8], proposed a new contribution to the specific heat of a glassy system from the extra density of state produced by rotonlike excitations. In particular, Tanttila [6] has proposed that all liquids and glasses possess a new fundamental excitation. This excitation is a localized region of somewhat lower or higher density than the host matrix. These localized regions have the property that they are free to propagate throughout the crystal. In this manner, the glassy system should be composed of a “gas” of excitations. These excitations are supposed to explain most of the properties of the liquids and glasses.

Despite these important contributions, a complete explanation starting from the elementary excitations for the specific heat data in the low temperature region is still lacking. To explore in more details this analogy with the physics of superfluid helium, the possibility to build a simple, but general framework to understand the temperature behavior of the specific heat at very low temperatures has been recently discussed [9]. The starting point was Landau’s fundamental idea to consider the quantum liquid at low temperature as a gas of elementary excitations, or quasi-particles. To check the possible validity of a similar strategy for glassy systems, we assume that the low temperature specific heat of a glassy sample is formed by two terms: the first term corresponds to the temperature dependence of the specific heat of an ideal Bose gas, whereas the second one corresponds to a Debye contribution, i.e., coming from a phonon gas. Therefore our hypothesis is that the low temperature spectrum of elementary excitations is composed of two gases of quasiparticles: the phonon gas and an ideal gas of quasiparticles coming from a specific Hamiltonian. In this framework, we show that it is possible to obtain a temperature dependence for the specific heat in good agreement with some well known experimental data.

2. NONLOCAL EFFECTS AND GREEN FUNCTION

To investigate a possible source for these quasiparticles, we assume that the system is described by a Hamiltonian that can be written in the form

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_F \oplus \hat{\mathcal{H}}_D, \quad (1)$$

where $\hat{\mathcal{H}}_F$ is a conventional Hamiltonian incorporating fractional derivatives in the kinetic energy term (as we discuss below) and $\hat{\mathcal{H}}_D$ is related to the presence of phonons in the system, also incorporating an excess term, typical of glasses. The form (1) can be justified if we admit the existence of two kinds of decoupled elementary excitations governing the behavior of the system at very low temperature, as discussed above. In this manner, the partition function factorizes and the specific heat is shown to be a sum of two contributions: $C(T, V, N) = C_F(T, V, N) + C_D(T, V, N)$.

For the fractionary part we can consider the following effective Hamiltonian

$$\begin{aligned} \hat{\mathcal{H}}_F = & \frac{1}{2m_\alpha} \int d\mathbf{r} \psi^\dagger(\mathbf{r}, t) (-\hbar^2 \nabla^2)^{\alpha/2} \psi(\mathbf{r}, t) \\ & + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \psi^\dagger(\mathbf{r}, t) \psi^\dagger(\mathbf{r}', t) V(|\mathbf{r} - \mathbf{r}'|) \psi(\mathbf{r}, t) \psi(\mathbf{r}', t), \end{aligned} \quad (2)$$

where $\psi^\dagger(\mathbf{r}, \mathbf{t})$ and $\psi(\mathbf{r}, \mathbf{t})$ are second quantized operators, m_α is an effective constant, the last term is the interaction between the components of the system, and

$$(-\hbar^2 \nabla^2)^{\alpha/2} \psi(\mathbf{r}, t) \equiv \int \frac{d\mathbf{p}}{(2\pi\hbar)^3} e^{i\mathbf{p} \cdot \mathbf{r} / \hbar} |\mathbf{p}|^\alpha \psi(\mathbf{p}, t)$$

is the quantum Reiz operator [10], which introduces a nonlocal character in the kinetic energy term. A remarkable characteristic of this procedure is that the solutions of the equation of motion (see below) remind us the Lévy distribution form instead of the Gaussian one. Another direct consequence, via Heisenberg equation for $\psi(\mathbf{r}, \mathbf{t})$, verified from Eq. (2) concerns the dynamical equation for $\psi(\mathbf{r}, \mathbf{t})$, which is actually given by

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = & \frac{1}{2m_\alpha} (-\hbar^2 \nabla^2)^{\alpha/2} \psi(\mathbf{r}, t) \\ & + \int d\mathbf{r}' V(|\mathbf{r} - \mathbf{r}'|) \psi^\dagger(\mathbf{r}', t) \psi(\mathbf{r}', t) \psi(\mathbf{r}, t). \end{aligned} \quad (3)$$

Equation (3) is a Schrödinger-like equation with fractional derivatives applied on the spatial variable, instead of the usual ones. This equation, without the interaction term but incorporating an external potential, was analyzed in several scenarios, in a first quantized perspective [10–12]. In fact, it has been applied to analyze the energy spectra of a hydrogenlike atom, a fractional oscillator in the semiclassical approximation, the parity conservation law [11], quark–antiquark $q\bar{q}$ bound states treated within the on-relativistic potential picture [12] and the quantum scattering problem [10]. In particular, in this context for the free case (i.e., absence of interaction) with $\psi(\mathbf{r}, 0) = \delta(\mathbf{r})$, the solution of Eq.(3) is a Lévy-like distribution, i.e., it is given by

$$\psi(\mathbf{r}, t) = \int \frac{d\mathbf{p}}{(2\pi\hbar)^3} e^{i\mathbf{p} \cdot \mathbf{r} / \hbar} e^{-i|\mathbf{p}|^\alpha / (2m_\alpha \hbar) t}. \quad (4)$$

The quantum statistics which emerges from the above scenario by using the thermal Green function approach may be related to the dynamical aspects of the $\psi(\mathbf{r}, \mathbf{t})$. In fact, following [13], we define the one-particle Green function as

$$\mathcal{G}(1, 1') = \frac{1}{i} \langle \mathbf{T}(\psi(1) \psi^\dagger(1')) \rangle \quad (5)$$

where the thermodynamic averages, $\langle \dots \rangle$, are evaluated by taking the grand canonical ensemble into account, \mathbf{T} is the Dyson time-ordering operator and 1 and 1' correspond to the variables $\mathbf{r}_1, \mathbf{t}_1$ and $\mathbf{r}_{1'}, \mathbf{t}_{1'}$, respectively. From this equation, we can define the correlation functions

$$\begin{aligned} \mathcal{G}^>(1, 1') &= \frac{1}{i} \langle \psi(1) \psi^\dagger(1') \rangle, \\ \mathcal{G}^<(1, 1') &= \pm \frac{1}{i} \langle \psi^\dagger(1') \psi(1) \rangle, \end{aligned} \quad (6)$$

where $>$ and $<$ represent the Green function to $t_1 > t_{1'}$, $\mathcal{G} = \mathcal{G}^>$ and $t_1 < t_{1'}$, $\mathcal{G} = \mathcal{G}^<$. The upper (lower) sign corresponds to the bosonic (fermionic) case and from Eq. (2) and Eq. (6) it is possible to show that $\mathcal{G}^<(1, 1')|_{t_1=0} = \pm e^{\beta\mu} \mathcal{G}^>(1, 1')|_{t_1=-i\beta}$, by using the cyclic invariance of the trace ($\text{Tr}(\hat{A}\hat{B}) = \text{Tr}(\hat{B}\hat{A})$). This result shows that the above Green function satisfies the same periodic boundary condition of the usual one [13], in contrast to the one [14] formulated within the Tsallis formalism [15]. Similar to what is done in the usual case, we may introduce the spectral function, $\mathcal{A}(\mathbf{p}, \omega)$, defined as $\mathcal{A}(\mathbf{p}, \omega) = \mathcal{G}^>(\mathbf{p}, \omega) \mp \mathcal{G}^<(\mathbf{p}, \omega)$ and express $\mathcal{G}^<$ and $\mathcal{G}^>$ as follows:

$$\begin{aligned} \mathcal{G}^>(\mathbf{p}, \omega) &= (1 \pm f(\omega)) \mathcal{A}(\mathbf{p}, \omega), \\ \mathcal{G}^<(\mathbf{p}, \omega) &= f(\omega) \mathcal{A}(\mathbf{p}, \omega), \end{aligned} \quad (7)$$

i.e., in terms of the spectral function, with $f(\omega) = 1/(e^{(\omega-\mu)} \pm 1)$. Using these green functions, we may obtain thermodynamics quantities such as the average of particle density with momentum \mathbf{p} and energy ω , i.e., $\langle n(\mathbf{p}, \omega) \rangle = \mathcal{G}^<(\mathbf{p}, \omega)$, the pressure $P(\beta, \mu) = \int_{-\infty}^{\mu} d\mu' \langle n(\mathbf{p}, \omega) \rangle$ and the average of energy

$$\langle H \rangle = \frac{V}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int \frac{d^3\mathbf{p}}{(2\pi\hbar)^3} \left(\omega + \frac{|\mathbf{p}|^\alpha}{2m_\alpha} \right) \mathcal{G}^<(\mathbf{p}, \omega). \quad (8)$$

The details of the formalism presented above can be found in Ref. [16].

From the phenomenological point of view, the nonlocality, represented by the fractional derivative present in kinetic term, may be useful to take unusual aspects of the spectrum of the elementary excitation into account, e.g., non-conventional density of states, which emerge due to the structure of the glass material and are manifested by the thermodynamic quantities at low temperature as the specific heat. In fact, the specific heat is generally fitted at low temperature by the expression $C = \mathcal{A}T^n + \mathcal{B}T^3$ which is expected to arise from the phenomenological model investigated here, in contrast, e.g., to the tunnelling states [17]. In order to check its potentiality, we investigate the specific heat obtained from the Hamiltonian (1) and its agreement to the experimental data.

3. THERMAL BEHAVIOR

As highlighted above, the specific heat can be written as a sum of two independent contributions which after some calculations, by considering the previous formalism with $\hat{\mathcal{H}}$ given by Eq. (1) and low temperature limit, may be written in the simplified form

$$C = \mathcal{A}T^{3/\alpha} + \mathcal{B}T^3. \quad (9)$$

The first contribution comes from the kinetic term present in Eq. (2). It is reduced to the contribution of an ideal Bose gas when the kinetic energy term is the usual one, i.e., for $\alpha = 2$. The second term is the usual Debye contribution. In Fig. 1, the specific heat behavior of three non-crystalline samples is shown for very low temperatures. The agreement between the predictions of our model is very good for SiO₂

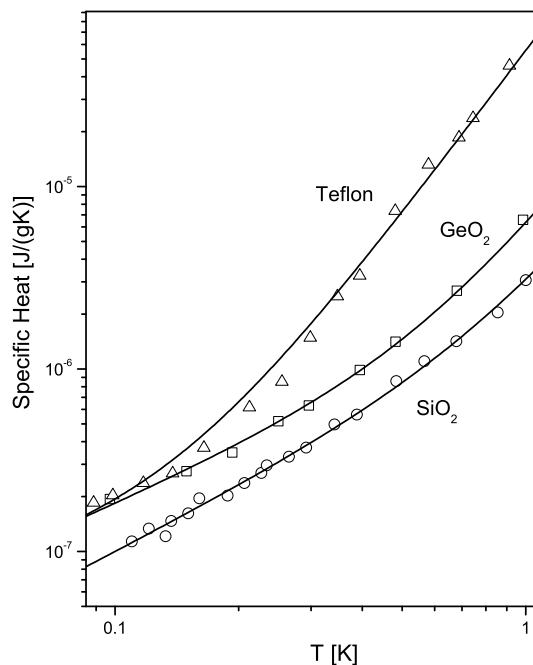


FIG. 1: Specific heat for three non-crystalline samples vs T . The values of parameters \mathcal{A} , \mathcal{B} and α for SiO_2 are $1.40 \cdot 10^{-6} [\text{J}/(\text{g K}^{1+3/\alpha})]$, $1.70 \cdot 10^{-6} [\text{J}/(\text{g K}^4)]$ and 2.60, respectively. For GeO_2 , we have that $\mathcal{A} = 1.74 \cdot 10^{-6} [\text{J}/(\text{g K}^{1+3/\alpha})]$, $\mathcal{B} = 4.63 \cdot 10^{-6} [\text{J}/(\text{g K}^4)]$ and $\alpha = 3.05$. Finally, for Teflon [18], we have $\mathcal{A} = 6.45 \cdot 10^{-7} [\text{J}/(\text{g K}^{1+3/\alpha})]$, $\mathcal{B} = 5.50 \cdot 10^{-5} [\text{J}/(\text{g K}^4)]$ and $\alpha = 4.5$.

($C_F \approx T^n$, $n \approx 1.15$) and GeO_2 ($C_F \approx T^n$, $n \approx 0.98$), and quite satisfactory for Teflon. The same good agreement is found with the measured values for ethanol, shown in Fig. 2. In this case, the contribution coming from the fractionary Hamiltonian is of the form $C_F \approx T^{1.1}$. Except for the ethanol, the exponents lies between 1.0 and 1.5, approximately, i.e., the temperature behavior of the specific heat is not linear at all.

For what concerns $\hat{\mathcal{H}}_D$ one can use an effective Hamiltonian [19]

$$\hat{\mathcal{H}}_D(r, p, T) = p^2 + ar^2 - b\sqrt{T}r^3 e^{-c\sqrt{T}r}, \quad (10)$$

where p and r are the re-scaled momentum and position variables, respectively; a , b , and c are constantes and T is the absolute temperature. Notice that Eq. (10) has an anharmonic term and was used to investigate the boson peak which can be related to the transverse phonons [20]. In terms of these re-scaled variables, it was shown that the specific heat for Eq. (10) can be written as

$$C = E_0 T^3 \int_0^{r^*} dr \int_0^{p^*} dp \left(\frac{pr \hat{\mathcal{H}}_D(r, p, T)}{e^{\hat{\mathcal{H}}_D(r, p, T)} - 1} \right)^2 e^{\hat{\mathcal{H}}_D(r, p, T)}, \quad (11)$$

where $E_0 = (4\pi k_B^2)^2 (2m/\hbar^2)^{3/2}$, $r^* = r_0/\sqrt{k_B T}$, and $p^* = p_0/\sqrt{2mk_B T}$, with r_0 and p_0 being the cut-off values for the variables. Written in the form (10), it is evident that the anharmonic contribution may be negligible for very low tempera-

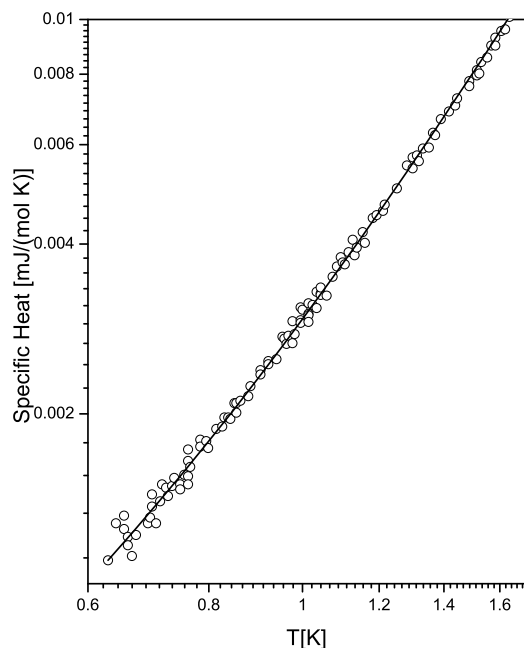


FIG. 2: Specific heat of the ethanol [3] vs T . The values of parameters A_0 , B_0 and α for SiO_2 are $1.05 \cdot 10^{-3} [\text{J}/(\text{mol K}^{1+3/\alpha})]$, $1.89 \cdot 10^{-3} [\text{J}/(\text{mol K}^4)]$ and 2.70, respectively.

ture and consequently the specific heat obtained from Eq. (11) at low temperature is $C \sim T^3$.

4. CONCLUSIONS

The complete scenario could be, then, as follows. At very low temperature, the dynamics of the glassy system is governed by a Hamiltonian in the form (1), with $\hat{\mathcal{H}}_F$ given by the kinetic term of (2), and $\hat{\mathcal{H}}_D$ having a form similar to (10). At low temperature, i.e., near the temperature of the boson peak (between 5 and 50K), the dynamics is still governed by (1), but the contribution coming from (2) being negligible, and the term represented by $\hat{\mathcal{H}}_D$, with its anharmonic part, playing the dominant role. In this framework, the specific heat of the system can be well described by a Hamiltonian written in the general form (1), with each term contributing more significantly or not according to the ranges of temperatures considered. To put this approach on a more firm ground, it is necessary to justify the assumption of a decoupling between the different elementary excitation, permitting us to assume the form (1) and to also justify the physical basis of a fractionary kinetic energy term. The gain with this kind of approach lies on the nonlocal character of the low temperature Hamiltonian, represented by fractionary terms in the kinetic energy. This new element can be the source of a very rich spectral distribution of energies and can indicate a possible mechanism to explain the non-conventional thermal behavior of glasses. If this picture holds true, each glass system will find the more appropriated value of α to express the importance of non-local effects on its dynamics.

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