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Fractal model of heat capacity for substances with diamond-like structures[☆]

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Abstract

Low temperature heat capacity models for substances with diamond-like structures have been considered on the basis of the Debye model and fractal states filling at fixed characteristic temperature. It was shown that low temperature calorimetry is an efficient tool for scanning the distribution of the atomic vibrational states in real substances. Fractal dimension and Poisson's ratio in the elastic–isotropic multifractal model are related by a simple interdependence, which enables estimation of the fractal dimension from elastic properties of solids.

Keywords: Fractal dimension; Heat capacity; Low-temperature calorimetry; Multifractal elasticity

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1. Introduction

The development of models which enable description of the temperature-dependence of heat capacity by using the real physico-chemical properties of a substance, is of great importance both from the point of view of solving the applied problems (for example, determination of thermodynamic properties in the temperature range in which experimental data weren't measured), and for revealing the correlation between physico-chemical properties.

At present there are different models based on the concept of a solid as an elastic continuum. We assume that it would be interesting to consider the temperature-

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dependence of a parameter, which can be obtained both from elastic and thermodynamic properties. In this paper we suggest application of the fractal dimension [1] as such a parameter. To check this suggestion it is quite natural to use the well studied diamond-like substances (diamond, silicon and germanium) as they possess a highly symmetric crystal structure and contain a minimum amount of impurities and defects. The models, which are based on different assumptions about the form of phonon density of vibration states vs. frequency curves, are used for modeling the temperature-dependence of heat capacity.

2. History

Great progress was achieved by the work of Einstein [2], Debye [3], Born and Coworkers [4, 5], Blackman [6], Tarasov [7], Sirota [8] and Lifshits [9]. The most important was the Debye model. In the Debye model the heat capacity (at a given frequency distribution of the number of vibrations) can be represented as:

$$C_V = \int_0^{\nu_{\max}} (h\nu/k_B T)^2 \exp(h\nu/k_B T)\,(\exp(h\nu/k_B/T) - 1)^{-2}\, g(\nu)\,d\nu. \tag{1}$$

To determine the continuous function $g(\nu)$, Debye assumed that a solid body can be considered as a continuous elastic medium, the thermal vibrations in which are the superposition of elastic vibrations similar to sound waves. Moreover, the continuum is considered to be isotropic, so that the velocities of the longitudinal and tranverse vibrations are direction-independent. In this medium, the total number of vibrational modes in the interval from ν to $\nu + d\nu$ is given by

$$g(\nu)\,d\nu = 4\pi V(1/v_l^3 + 2/v_t^3)\,\nu^2\,d\nu. \tag{2}$$

where V is the sample volume, and v_l and v_t are the longitudinal and transverse velocities of sound. Because the number of fundamental vibrations of the continuum is limited to $3N$ vibrations with frequencies between zero and $\nu_{\max}$ the spectral density is proportional to the square of the frequency:

$$g(\nu)\,d\nu = 9N\nu_{\max}^{-3}\nu^2\,d\nu. \tag{3}$$

whereas the heat capacity is given by

$$C_V = 9RT(T/\Theta_D)^3 \int_0^{\Theta_D/T} x^4 \exp(x)\,(\exp(x) - 1)^{-2}\,dx \tag{4}$$

where $x = h\nu/kT$ and $\Theta_D = h\nu_{\max}/k$. At high temperatures, the heat capacity approaches a value close to $3R$; at low temperatures, it is proportional to temperature cubed: $C_V = AT^3$.

The Debye theory related the elastic properties of solids to their thermodynamic properties; however, the experimental data (as derived from the heat capacity) showed that Θ_D was temperature-dependent. We emphasize this fact because we will return to it below in considering the multifractality of vibrational states in solids.

3. Theory

To date, numerous attempts have been undertaken to construct a simple and convenient model for the phonon distribution function. The kieffer model [10] is based on analysis of the vibrational contributions. The distribution function is divided into three frequency groups (one acoustic and two optical).

Westrum and Komada [11] developed a new model of the phonon distribution, which involves one characteristic temperature as a parameter for describing the heat capacity. It was assumed that, irrespective of structure, a solid possesses one longitudinal and two degenerate transverse acoustic modes, in this case the dispersion ratios for longitudinal and transverse modes are similar. In treating the optical branches within this model, it is assumed that the distribution function differs from the Debye function as a consequence of discrete atomic positions in real crystals, so that the cut-off frequency diminishes by a value proportional to the square of the frequency. The distinguishing feature of this model is that it takes account of atomic masses in determining the frequency range and the distribution function for the optical modes. The interamolecular vibrations are described within this model by the Dirac δ-function.

The above models of $C_V(T)$ are based (to various extents) on the specific features of the atomic structure of crystalline substances.

One can to assume that in "quasi-linear" and "quasi-layered" structure substances the $C_p(T)$ dependencies can be expressed by the exponential functions, and the exponent is determined by the crystallochemical features of the structure. This would be related to a strong anisotropy of substances under study. In this case, the noninteger exponent in the $C_V = f(T^D)$ dependence might be interpreted as some effective value. The frequency distribution of the number of vibrational states was described by continuous exponential functions. It resulted in a discrepancy between theory and experiment.

Now we turn to the Debye model once more. The characteristic temperature introduced by Debye defines the temperature at which all of the vibrational states of a crystal (substance) are excited. In some publications the value Θ_D was assumed (see, for example, Ref. [12]) to be temperature-dependent (without any strict substantiation) in order to fit the low-temperature calorimetry data to the theoretical predictions.

The variations of the characteristic Debye temperature with temperature are inherent to the great majority of substances, irrespective of the dimension of the interatomic bonds within the above crystallochemical approach to the "quasi-linear", and "quasi-layered", or high-symmetric structures, which can be fairly illustrated by the experimental data on diamond [13], silicon [14] and germanium [15].

The contradiction between the Debye assumption "Θ_D = const" and the experimentally studied dependence $\Theta_D(T)$ can be easily eliminated.

The suggested approach to modeling of $C_V(T)$ dependence is based on the assumption of the fractality of vibrational states in the substance (solid). From the viewpoint of the formulation (filling the space of quasi momenta) of the "phonon cloud" (which corresponds to the heating of a solid), this is a process of "multifractal growth". As is supported by the above models and available experimental data, the distribution of the atomic vibrational frequencies (phonons) obeys the scaling relationship $C_V \sim \nu^0$, where D is the fractal dimension that takes effective, comprehensive account of the fractal dimension of all the series of vibrations. The magnitude of D can take nonlinear values; it characterizes the degree of filling of the vibration space (in reciprocal space, it is the space of the phonon quasi momenta). Note that the scaling relationship between the number of particles and the aggregate radius (in this case, $C_V \sim \nu^D$) supports the approach suggested. And finally, the third distinctive feature of the fractality of the phonon cloud is that a decrease in density (the number of the vibrational states—phonons) with increasing distance from the fractal center is described by the well-known formula from Bose–Einstein statistics [12]; this formula suggests that the number of phonons in a given state diminishes with increasing frequency (energy) of phonons.

So in modeling the temperature-dependence of heat capacity, one can adopt Debye's assumptions and modern concepts about the fractal character of the filling of vibrational states.

From this point of view low-temperature calorimetry may be used as one of the methods for estimating the fractonic dimension $D(T)$ of the phonon cloud of the occupancy of the "vibrational space". The temperature-dependence of the fractonic dimension $D(T)$ is related, via the structure of the vibrational states, to special features of the filling of real space with atoms. So it may also contain information about the degree of imperfection of a real substance and thus provide some indirect characterization of the topology of the atomic structure of materials.

4. Results

Let us turn our attention to the known, reliable experimental data obtained for C [13], Si [14] and Ge [15].

On the basis of the formula for calculation of vibration states density

$$G(\nu) = 3N\nu_{\max}^{-D}\nu^{D} \tag{5}$$

we solved the following equation:

$$C(T, D) = 3D(D+1)Nk_{B}r\left[\frac{T}{\Theta}\right]^{D}\int_{0}^{\Theta/T}\frac{x^{D}}{\exp(x)-1}\,dx - 3Dk_{B}Nr\frac{\Theta/T}{\exp\Theta/T-1}$$
$$= C_V(T) \tag{6}$$

where N is the Avogadro number, k_B is the Boltzmann constant, r is the number of atoms per formula unit, and C_V is the isochoric heat capacity obtained as a difference between the experimental value of C_p and the contribution from the work of lattice expansion ($C_p - C_V$).

We sought a value of D for $0 \leq T \leq \Theta$ such that the termination error for D would not increase with decreasing T. To do so, Eq. (6) was replaced by the equation:

$$C(D)_{T=\mathrm{const}} = C_V(T=\mathrm{const}) \tag{7}$$

the solution for which was sought for each pair of experimental values of T and $C_V(T)$. We used dichotomy. Integration was performed numerically first over a small, fixed number of points, gradually increasing their number as long as the integral over $n+1$ points differed from that for n points by a magnitude higher than 10^{-8}.

The results obtained are presented in Fig. 1.

On the basis of the assumptions adopted by Debye and the fractonic character of filling of the vibrational states, analysis of the topology of the real atomic structure of substances of varied physicochemical origin becomes possible. The fractonic dimension, its temperature-dependence as derived from the low-temperature data on heat capacity, can serve as a more meaningful characteristic of a material than the temperature-dependence of the Debye temperature because this quantity is directly related to the degree of filling of vibrational space and, therefore, indirectly related to the degree of filling of real space, that is, to the atomic arrangement in the structure of the substance. So it may also contain information about the degree of imperfection of a real substance and thus provides indirect characterization of the topology of the atomic structure of solids according to the physicochemical analysis formula: "composition—structure—fractal topology—properties".

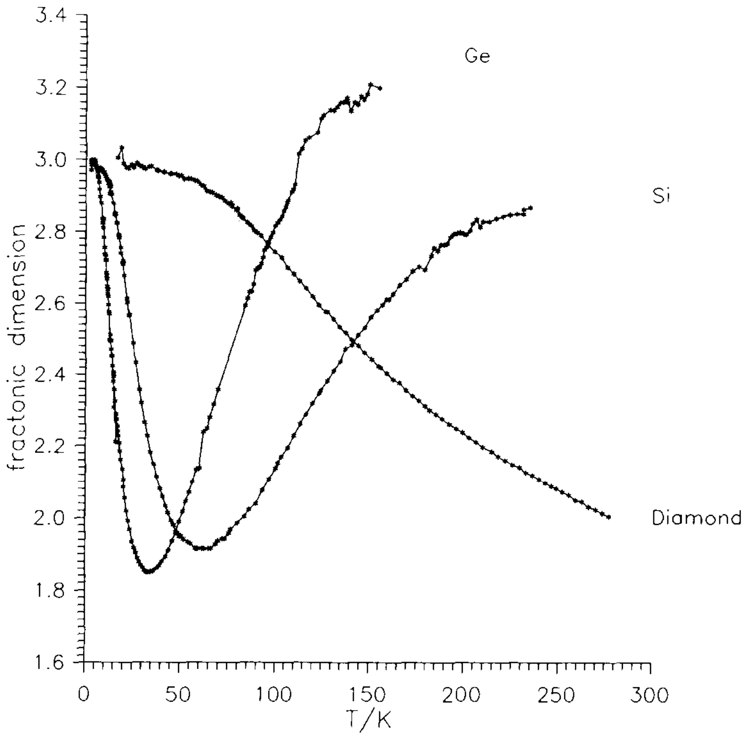

Fig. 1. Low temperature dependence of the fractonic dimension for diamond, silicon and germanium.

From the analysis of low temperature heat capacity data one can envisage the solid not as an elastic continuum, but as an elastic–isotropic multifractal. In this case the fractonic dimension must have a constant noninteger value in the particular temperature range.

A self-consistent thermodynamic theory of multifractal elasticity was constructed in Refs. [16, 17] on the basis of two postulated laws (see Table 1) by analogy with classical theory of the elasticity of solids. These laws enable description of the elastic deformation of statistically self-similar structures and the effect of lateral deformations. In the limit of infinitely small deformations, all relations of the thermodynamic theory lead to the corresponding relations of the theory of the elasticity of solids, which postulates the effect of lateral deformations (see Table 1) in the absence of lateral strains (this, apparently, runs counter to Hooke's law, which is a particular case of Newton's second law).

Deformations λ_i, $i = 1, 2, \ldots, d$ (where d is the topological dimensionality of Euclidean space) appear under the elastic stresses; in this case the density is

$$\rho = \rho_0/(\textstyle\prod_1^d \lambda_i) \tag{8}$$

When a multifractal is uniaxially deformed (with the fractal dimension d_f) under the influence of a stress $\sigma_\parallel$ (deformation $\lambda_1 = \lambda_F$) the structure develops lateral stresses $\sigma_\perp$, which caused lateral deformations $\lambda_{j=2,\ldots,d} = \lambda_\perp$. From the density equation, Eq. (8), and data from Table 1 it follows that

$$\ln(\lambda_F) + (d-1)\ln(\lambda_\perp) = \alpha \ln(\lambda_\perp). \tag{9}$$

Table 1

Comparison of the postulates and certain results of the linear theory of the elasticity of solids and thermodynamic theory of elasticity multifractals

Linear theory of the elasticity of solids	Thermodynamic theory of elasticity of multifractals
1. Hooke's law: relative deformation $\varepsilon_\parallel$ is proportional to the stress $\sigma_\parallel$	1. Reversible deformation of an elastic multifractal under the force F generates only one new characteristic L_F.
2. Poisson's effect: lateral deformations $\varepsilon_\perp = -\nu\varepsilon_\parallel$ developed in the absence of the corresponding stresses, i.e. when $\sigma_\perp = 0$	2. Deformation of a multifractal is self-affine, i.e. density values ρ with L_F in the same fashion as ρ varies with geometrical size change $\rho \sim \lambda_F^{-\alpha}$; $\lambda_F = L_F(F)/L_F(0)$; $\alpha = d - d_f > 0$
3. Expression for the stress σ: $\sigma_{ii} = \frac{1}{V}\left(\frac{\partial U}{\partial \varepsilon_{ii}}\right)$	3. Expression for the force F: $F = \left(\frac{\partial U}{\partial L_F}\right) - T\left(\frac{\partial S}{\partial L_F}\right)$
4. Ratio between elastic moduli (E, G, B are the Young's, shear and bulk moduli): $\nu = -\varepsilon_\perp/\varepsilon_\parallel$, $G = \frac{E}{2(1+\nu)}$, $B = \frac{E}{3(1-2\nu)}$	4. $\nu = \frac{d_f}{d-1} - 1\ [d_f = (\nu+1)(d-1)]$ $G = \frac{d-1}{2d_f}E$, $B = \frac{E}{d(d-d_f)}$

Table 2
Approximation of the temperature-dependence of the heat capacity by the Debye model and fractonic model: D is the fractonic dimension from the experimental data

Substance	ΔT/K	max $\Delta C_V^{\mathrm{Deb}}$/(rel. units)	max ΔC_V^{D}/(rel. units)	D
Li[a]	3–28	0.0043	0.0013	2.82
Cu[a]	14–44	0.091	0.060	2.40
B	40–92	0.025	0.016	2.82
Al[a]	15–55	0.0063	0.0004	2.69
C	13–300	0.034	0.016	2.43
Ge	4–250	0.037	0.026	2.59
Si	4–150	0.057	0.033	2.51
BN	16–63	0.022	0.011	2.16
α-Al_2O_3	5–100	0.81	0.69	2.49
NaCl	10–50	0.32	0.14	2.41

[a] For these metals the electron heat capacity was taken into account.

Table 3
The Debye temperature, calculated from the Debye model (Θ_{Deb}) and, from the fractonic model, Θ_{max}, calculated from the heat capacity temperature-dependence, the fractonic dimension D and the fractal dimension of elastic isotropic fractal d_f

Substance	Θ_{Deb}/K	Θ_{max}/K	D	d_f
Li	344	407	2.82	2.56
Cu	343	358	2.40	2.65
B	1510	1577	2.82	2.46
Al	428	451	2.69	2.70
C	2230	2465	2.43	2.20
Ge	374	364	2.59	2.45
Si	645	639	2.51	2.40
BN	~1550	1453	2.16	2.20
α-Al_2O_3	~1100	1045	2.49	2.46

In this case

$$\nu = \frac{\ln(\lambda_\perp)}{\ln(\lambda_F)} = \frac{d_F}{d-1} - 1 \tag{10}$$

where the logarithmic relationship is the lateral-deformation ratio, which coincides with Poisson's ratio $\nu_0 = \varepsilon_\perp/\varepsilon_\parallel$ only within the limit of infinitely small deformations $\varepsilon_\perp$, $\varepsilon_\parallel \ll 1$.

5. Conclusion

So, the fractal dimension and Poisson's ratio in the model of the elastic–isotropic multifractal are related by the simple interdependence. It gives the ability to estimate the fractal dimension from dilatometric and ultrasonic studies. In addition, it is interesting to compare data obtained from elastic properties and from thermodynamic ones. The results from Tables 2 and 3 testify to good agreement of fractonic (obtained from $C_V(T)$ data) and fractal dimensions (calculated for substances with known Poisson's ratio).

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