Fractal Continual Model of Matter for Classification of Nanostructures, Clusters and Massive Bodies

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It was shown that nanostructures and clusters can be considered as a continuous environment, such crystalline. Solid bodies can be classified by parameter of dimensionality of the vibrational spectrum.

1. MATTERS WITH DIMENSIONALITY OF THE VIBRATIONAL SPECTRUM $d_f = 0$

Introduced in [1, 2] fractal model of the continuum medium generalizes well-known Debye model for heat capacity of solids with exponent of spatial dimensionality of the vibrational spectrum $d_f = 1, 2, 3$ on the full range of integer and fractional values $0 \le d_f \le \infty$. In addition to the Debye temperature $\theta_H = \hbar \cdot \omega_{max}/k_B$ (here $\hbar$ and k_B are Planck and Boltzmann constants correspondingly, ω_{max} is the maximal frequency of the vibrational spectrum) another temperature associated with the lower boundary of the spectrum $\theta_N = \hbar \cdot \omega_{min}/k_B$ was introduced in this model ($\theta_N = 0$ K in the Debye model). Temperature θ_N is essential in studies of the thermal properties of clusters and nanostructures. In this work it focuses on matters having a dimensionality of the vibrational spectra, $d_f = 0$, as well $d_f > 3$. Matters with such dimensionalities of vibrational spectra were not known previously.

Expressions for the density function of the frequency spectrum $g(\omega)$ and the temperature dependence of the heat capacity $C(T)$ in a fractal model have the form [1-3].

$$g(\omega) = \frac{N^*}{\omega \ln(\omega_{max}/\omega_{min})},$$

$$\frac{C(T)}{C_\infty} = \frac{1}{\ln\left(\frac{\theta_H}{\theta_N}\right)} \int_{x_{min}}^{x_{max}} \frac{x\,e^x}{(e^x - 1)^2} dx \quad \text{for } d_f = 0 \tag{1}$$

$$g(\omega) = \frac{N^* d_f \omega^{d_f - 1}}{\omega_{max}^{d_f} - \omega_{min}^{d_f}},$$

$$\frac{C(T)}{C_\infty} = \frac{d_f}{\left(\frac{\theta_H}{T}\right)^{d_f} - \left(\frac{\theta_N}{T}\right)^{d_f}} \int_{x_{min}}^{x_{max}} \frac{x^{d_f + 1}\,e^x}{(e^x - 1)^2} dx \quad \text{for } d_f \ne 0 \tag{2}$$

where $x_{min} = \theta_N/T$, $x_{max} = \theta_H/T$, C_∞ is the heat capacity corresponding to the law of Dulong and Petit, $N^* = 6N-6$ is the number of intermolecular vibrational modes, N is the number of molecules in the analyzed cluster or nanostructure. As it was shown in [3], an average frequency of intermolecular vibrations $\bar{\omega} = \frac{1}{N^*}\sum_{i=1}^{N^k} \omega_i$ for many dimers is closed or almost equal to the average value of the frequency $<\omega>_o$ of the continuous spectrum at $d_f = 0$.

$$\bar{\omega} \approx \langle \omega \rangle_o = \frac{1}{N^*} \int_{\omega_{min}}^{\omega_{max}} \omega\, g(\omega)\, d\omega = \frac{\omega_{max} - \omega_{min}}{\ln(\omega_{max}/\omega_{min})} \tag{3}$$

Furthermore, despite the small number of spectral lines ($N^* = 4$ for dimers of linear molecules and $N^* = 6$ for dimers of nonlinear molecules), the condition of continuity of the spectrum $N^* >> (\theta_H/T)^{d_f}$ at $d_f \approx 0$ and low temperatures T~1K is formally executed. This means that the temperature dependence of the heat capacity, calculated on the total contribution of relevant Einstein oscillators ω_i is

$$\frac{C_e(T)}{C_\infty} = \frac{1}{N^*} \sum_{i=1}^{N^*} \frac{(\theta_i/T)^2 e^{\theta_i/T}}{(e^{\theta_i/T} - 1)^2} \tag{4}$$

where $\theta_i = \hbar\omega_i/k_B$ and is equal to the continuous spectrum formulas (1) should match. Exactly this fact is indicated by results showed in Fig. 1.
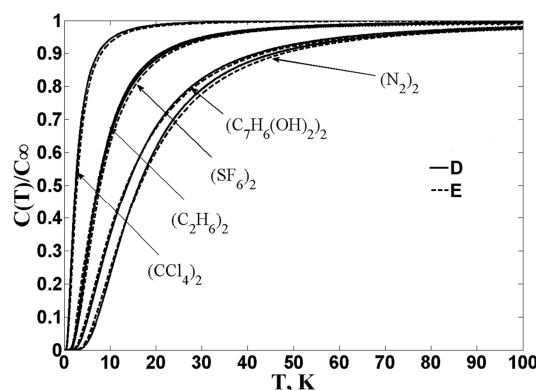

Fig. 1 – Heat capacity of dimers. E is the discrete model (4), D is the continuum model (1)

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The calculations of intermolecular vibrational frequencies were performed using by FIREFLY program package [4] in Hartree-Fock method with 6-311++G(d,p), 6-311G(d,p), and 6-31G(d) basis sets.

Thus, the fractal theory of heat capacity follows that the continuum representation of the state of the substance is possible not only when the number of its constituent atoms or molecules is large, but when it is insignificant, i.e. in nanostructures, clusters and even dimers, representing the smallest possible particle bound state in nature.

2. MATTERS WITH DIMENSIONALITY OF THE VIBRATIONAL SPECTRUM $d_f > 3$

Let us consider further objects having exponent of spatial dimensionality $d_f > 3$, that are so far poorly described. Processing of the experimental data from [5] on low-temperature heat capacity of one of the varieties of diamond using a fractal model (2) shows that the best agreement with experiment gives the dependence of $C(T) \sim T^{3.3}$ rather than Debye law with $d_f = 3$ [1]. Another example is the temperature dependence of the heat capacity of C_{60}-fullerite. Low-temperature ($0.1 \leq T \leq 10$ K) fragment of the experimental dependence of $C(T)$ for C_{60} doped of 15% C_{70} obtained in [6] is represented in linear coordinates as asterisks marked on Fig. 2. Corresponding curves $C(T)$ for fullerite, graphite, and diamond [6] are shown in logarithmic coordinates on inset b of Fig. 2. The angles α_1, α_2, α_3 of inclination of the tangent $C(T)$ at the maximum slope are marked. At low temperatures ($T \ll \theta_H$) using logarithmic coordinates, d_f is determined by a tangent of an angle of inclination to $C(T)$ curve at each temperature point. The presented experimental data shows that this dependence for fullerite at the range $T \approx 1 - 2$ K is steeper than that of diamond, while diamond has heat capacity obeying Debye limiting law. Comparison of experimental data from [6] for fullerite and it processing using a nonlinear least squares with independent variation of parameters d_f, θ_H, and $\theta_N = 0$ K in model (2) revealed (see Fig. 2, inset a) that the maximum value $d_f \approx 4.5$ was achieved at $T \approx 2$ K. Dimensionality of the vibrational spectra satisfy Debye limiting low ($d_f = 3$), only in a neighborhood of the two temperature points $T_1 \approx 1$ K and $T_2 \approx 3$ K.
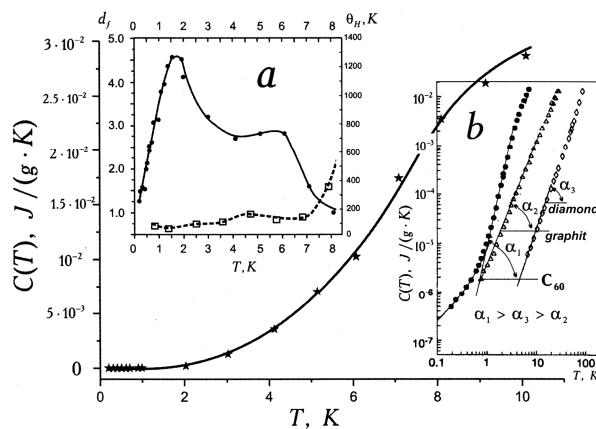
Fig. 2 – Experimental dependence of $C(T)$ in linear coordinates for C_{60} according to [6]. The solid curve corresponds to calculation by model (2). The insets: a - dependences of $d_f(T)$ (upper curve) and $\theta_H(T)$ (lower curve); b - the data $C(T)$ from [6] in logarithmic coordinates

Thus, the fractal continuum model can help classify matters by d_f parameter, since dimers having $d_f \approx 0$. When the amount of particles in the structure increases, exponent of spatial dimensionality also increases [2] and may exceed the value of $d_f = 3$ corresponding matters obeying Debye law.

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