

## Debye Limiting Law Violation in Clusters and Nanostructures

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(Received 16 April 2013; published online 29 August 2013)

In this work fractal continuum model of condensed matter was used. Calculations of vibrational spectra of molecular clusters were carried out. It was established that temperature changes of heat capacity associated to intermolecular oscillations in clusters does not obey Debye limiting law.

**Keywords:** Nanostructures, Clusters, Debye Limiting Law, Lattice Heat Capacity, Vibrational Spectrum.

PACS numbers: 65.808+n, 61.43.Hv

### 1. FRACTAL CONTINUUM MODEL OF CONDENSED STATE MATTER

Lattice heat capacity  $C(T)$  of solid bodies at low temperatures is considered to depend on temperature as described by Debye limiting law  $C(T) \sim \alpha T^3$  ( $\alpha = \text{const}$ ) for any atomic (molecular) structure and type of chemical bond in solid body. It is actual for continuous distribution of frequency spectrum if  $0 \leq \omega \leq \omega_{max}$  (the model of crystal of infinite wavelengths spectrum) and  $1 \leq d_f \leq 3$ , where  $d_f$  is exponent of spatial dimensionality. The frequency spectrum of most solid bodies satisfies these conditions. However in common case, i.e. if  $d_f > 3$  or  $d_f < 1$  (for example, it has place in clusters and nanostructures) and the spectrum is finite ( $\omega_{min} \leq \omega \leq \omega_{max}$ ), Debye limiting law near  $T = 0$  K doesn't work. In this case, lattice heat capacity depends on temperature in a different way, not like described above.

The fact of Debye limiting law violation can be established using by generalized continuum model of condensed matter [1]. This model requires experimental measured heat capacity of substances or *ab initio* calculated structure of vibrational spectrum. The model contains three parameters: two characteristic temperatures (1, 2) and the exponent of spatial dimensionality.

$$\theta_N = \frac{\hbar \omega_{min}}{k_B} \quad (1)$$

$$\theta_H = \frac{\hbar \omega_{max}}{k_B} \quad (2)$$

Here  $\hbar$  is Planck constant,  $k_B$  is Boltzmann constant,  $\omega_{max}$ ,  $\omega_{min}$  are the minimal and the maximal frequencies in the vibrational spectrum.

The exponent of spatial dimensionality  $d_f$  can accept the whole and fractional values in the range  $0 \leq d_f \leq \infty$ .

The density functions of frequency spectrum can be described as (3, 4), see [1, 2].

$$g(\omega) = \frac{N^* d_f \omega^{d_f-1}}{\omega_{max}^{d_f} - \omega_{min}^{d_f}} \quad \text{for } d_f > 0 \quad (3)$$

$$g(\omega) = \frac{N^*}{\omega \ln \frac{\omega_{max}}{\omega_{min}}} \quad \text{for } d_f = 0 \quad (4)$$

Here  $N^* = 3\mu N^{-6}$  is the number of vibrational modes,  $\mu$  is the number of atoms in a molecule,  $N$  is the number of molecules in a cluster. The expression for temperature dependence of the lattice heat capacity looks like (5, 6), see [1, 2].

$$\frac{C(T)}{C_\infty} = \frac{d_f}{\left(\frac{\theta_H}{T}\right)^{d_f} - \left(\frac{\theta_N}{T}\right)^{d_f}} \int_{x_{min}}^{x_{max}} \frac{x^{d_f+1} e^x}{(e^x - 1)^2} dx \quad \text{for } d_f > 0 \quad (5)$$

$$\frac{C(T)}{C_\infty} = \frac{1}{\ln \left(\frac{\theta_H}{\theta_N}\right)} \int_{x_{min}}^{x_{max}} \frac{x e^x}{(e^x - 1)^2} dx \quad \text{for } d_f = 0 \quad (6)$$

Here  $x_{min} = \theta_N / T$ ,  $x_{max} = \theta_H / T$ ,  $C_\infty$  is the value of a heat capacity corresponding to Dulong-Petit law.

The case corresponding to continuum Debye model has the following parameters:  $\theta_N = 0$  (the model of crystal of infinite wavelengths spectrum), and  $1 \leq d_f \leq 3$  (considering heterodynamism).

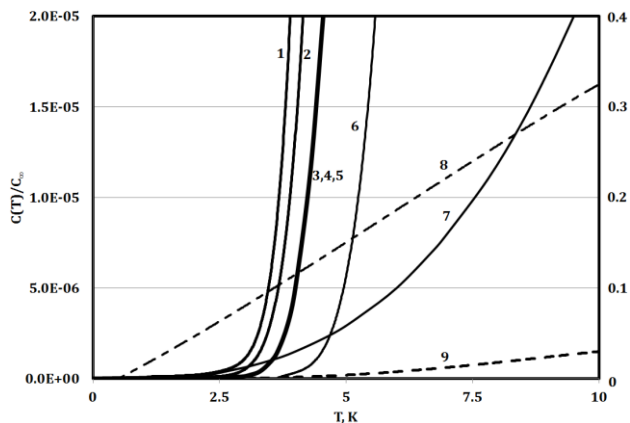
### 2. DETERMINATION OF THE EXPONENTS AND TEMPERATURE CHANGES OF MOLECULAR CLUSTERS HEAT CAPACITY

In massive bodies the relation  $\theta_N / \theta_H$  is much less than 1 because  $\theta_N$  has small value. However for clusters and nanoparticles  $\theta_N / \theta_H$  is about 1, the value of  $\theta_N$  is more or equal 1-50 K. For example, *ab initio* calculations of vibrational frequencies of water cluster [3] revealed for dimer  $(H_2O)_2$ :  $\theta_N / \theta_H \approx 0.2$ , for  $(H_2O)_{10}$ :  $\theta_N / \theta_H \approx 5 \cdot 10^{-2}$ . Similar calculation that we carried out for methane and 5-methylresorcinol revealed the following results:  $\theta_N / \theta_H \approx 0.23$  for  $(CH_4)_3$ ,  $\theta_N / \theta_H \approx 6 \cdot 10^{-2}$

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for  $(\text{CH}_4)_{10}$ ,  $\theta_N / \theta_H \approx 2 \cdot 10^{-2}$  for  $[\text{C}_7\text{H}_6(\text{OH})_2]_6$ . The calculations were performed using by FIREFLY program package [4] in Hartree-Fock method with 6-311G (d, p) and 6-31G (d) basis sets.

On Fig. 1 you can see the diagrams of heat capacity on temperature dependence for water clusters (solid lines) and 5-methylresorcinol hexamer (dotted line, the right scale) obtained from fractal model equations (4-6).



**Fig. 1** – Heat capacity on temperature dependence for water clusters (solid lines) and 5-methylresorcinol hexamer (dotted lines, the right scale)

Curves 1-5 correspond to five allotropic modifications of water clusters, for that  $\theta_H = 1520$ - $1560$  K,  $\theta_N = 40$ - $51$  K,  $d_f = 0.45$ - $0.48$ , 6 – cluster  $(\text{H}_2\text{O})_{16}$  with  $\theta_H = 1520$  K,  $\theta_N = 55$  K (data from [2]), 7 – Debye limiting law ( $\theta_H = 1500$  K,  $\theta_N = 0$  K), 8 – hexamer of 5-methylresorcinol ( $\theta_H = 95$  K,  $\theta_N = 2.2$  K,  $d_f = 0.7$ ), 9 – Debye limiting law ( $\theta_H = 90$  K,  $\theta_N = 0$  K,  $d_f = 3$ ). Discrepancy of dependences  $C(T)$  to viewed clusters and Debye limiting law are obvious. The obtained result is quite general because dimensionality of intermolecular oscillations for most clusters is  $d_f < 1$ , and final temperature values are  $\theta_N \approx 1$ - $50$  K. While values  $d_f = 3$ ,  $\theta_N = 0$  K are necessary to satisfy Debye limiting law. The condition  $N^* \gg (\theta_H / T)^{d_f}$  of the spectrum continuity of intermolecular vibrations at  $d_f < 1$  is performed for

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relatively small clusters. If  $d_f = 0$ , it is true even for the dimers that have  $N^* = 4$  for linear and  $N^* = 6$  for non-linear molecules. Substances with dimensionality of a spectrum  $d_f \ll 1$  and even  $d_f = 0$ , probably is interesting to really exist in the nature. To establish this fact it is enough to obtain data from *ab initio* calculations and compare the medial vibrational frequency of intermolecular oscillations (7) with its analogue for value  $d_f = 0$  of continuum spectrum (8).

$$\bar{\omega} = \frac{1}{N^*} \sum_{i=1}^{N^*} \omega_i \quad (7)$$

$$\langle \omega \rangle_o = \frac{1}{N^*} \int_{\omega_{\min}}^{\omega_{\max}} \omega g(\omega) d\omega = \frac{\omega_{\max} - \omega_{\min}}{\ln \omega_{\max} / \omega_{\min}} \quad (8)$$

In table below you can see the comparison of frequencies for some dimers.

**Table 1** – Intermolecular vibrational frequencies of dimers

Dimer	$\omega_i, \text{cm}^{-1}$ [5]						$\bar{\omega}$	$\langle \omega \rangle_o$	Method, basis set
$(\text{N}_2)_2$	20.0	27.5	40.0	55.0			35	35	HF/6-311(d,p)
$(\text{CO}_2)_2$	16.7	25.9	35.6	49.7			43.5	44	HF/6-311(d,p)
$(\text{H}_2\text{O})_2$	119	138	152	179	334	592	300	296	LCCSD(T)/aVQZ
$(\text{CCl}_4)_2$	2.42	4.90	5.08	6.26	6.82	10.37	6	5.65	HF/6-31(d)
$(\text{SF}_6)_2$	7.5	15.1	15.1	17.4	17.4	29.8	17	15.7	HF/6-311(d,p)
$[\text{C}_7\text{H}_6(\text{OH})_2]_2$	12	17.5	24.3	29.2	41.0	62.0	31	31	HF/6-311(d,p)

Many other dimers are very possible to have dimensionality close to zero. Therefore their heat capacity related to intermolecular oscillations, does not obey Debye limiting law.

## ACKNOWLEDGEMENTS

K.B. Tereshkina is grateful to the Russian Foundation for Basic Research (project No 12-04-31915) for partial support of this work.

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