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Specific heat related to details of the vibrational modes for a 2D nanocrystalline material

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"What – if" analyses of the interfacial component of nanocrystalline materials (NCM), especially at higher temperatures, were performed using a two-dimensional model. What influence would thermal excitations have on the pair distribution function, the vibrational spectra and the specific heat, over the temperature range of 30–1200 K, if the NCM would be stable over this temperature range, i.e. if grain growth cannot occur? It turned out that reduction of the grain size and increase in temperature influenced the pair distribution function, the vibrational spectra and specific heats in a similar manner. The changes in the vibrational spectra and the specific heat with decreasing grain size or increasing temperature could be related to changes in the occupation of the vibrational modes. The so-called participation ratio (PR) proved to be a suitable means of measuring the occupation of the modes and to classify the spectra. The differences in the specific heat could be largely attributed to parts of a subspectrum, filtered out from the complete vibrational spectrum by collecting the modes of a certain participation ratio range.

1. Introduction

Nanocrystalline materials (NCM) are polycrystalline materials with grain sizes below 100 nm. The preparation of nanocrystalline materials of ever finer grain size has been addressed by many active research projects in physics, chemistry and engineering. The research is motivated by the search for materials with new properties and the desire to tailor these materials' properties at will. Among other applications, there is interest in nanostructured chemical sensors, more reactive catalysts, materials with optimised mechanical and thermodynamic properties, new magnetic materials for, e.g. information storage, optoelectronic detectors and lasers, nano-engineered superconductors and interactions of nanoparticles with biological molecules. General introductions to nanocrystalline materials and nm sized clusters can be found in [1–3].

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Knowledge of the atomic-scale structure and its relation to the physical properties of materials is an indispensable prerequisite to understand and predict their properties. Computational materials science aims to give this link between structure and properties. Besides the collection and interpretation of a steadily increasing number of experimental data, gained, e.g. by neutron scattering, a major goal of computational materials science, nowadays, is to predict properties of materials, some of which being difficult to access experimentally. Multiscale simulation of polycrystalline materials could bridge the gap between macroscopic and atomic-scale systems [4]. Introductions to computational materials science and molecular simulations are provided in [5, 6].

The wave functions of electrons and phonons in NCM are modified, in contrast to their counterparts in coarser-grained normal polycrystals, due to the confinement prescribed by the characteristic length scale of microstructure of the order of 10 nm. Several experiments on metallic nanocrystals show interesting lattice dynamical properties [7–12]. A low frequency enhancement of the vibrational density of states (VDOS) was found in, e.g. [8]. In order to gain more insight into the nature of the VDOS changes of nanocrystalline materials as a function of grain size and temperature, as well as how these changes affect the stability and the specific heat of NCM, the molecular-dynamics (MD) simulations, described below, were undertaken. This paper is organised in four sections. In the second section the computational procedure will be explained, in section 3 the results concerning VDOS and specific heat are presented, and finally some conclusions are drawn.

2. Computational procedure

2.1. Boundary conditions

In the case of nanocrystalline materials (NCM) the usual periodic boundary conditions would impose constraint forces on the ensemble of the grains, due to missing translational symmetry of the model system. Therefore, the model system was subdivided in an inner and an outer region, which completely enshrouded the inner region. The thickness of the outer region corresponded to the cutoff radius of the potential. The dynamical matrix (see below) was set up with the atoms of the inner region, whereby the atoms of the outer shell served as additional neighbours for the atoms of the inner region (pseudoperiodic boundary conditions).

2.2. Molecular statics (MS)

Within a single crystal, small hexagonal crystal cores were marked and rotated by a random angle. These cores consisted of about 100–400 atoms. The rest of the atoms (“matrix atoms”) were then displaced randomly and the volume of the matrix increased homogeneously to about that of the fluid material. The energy of this atomic arrangement was then minimised by a conjugate gradient method. During the computation, the atoms of the hexagonal crystal cores were allowed to move only translationally as a whole in order to preserve the given orientation relationships of the nanocrystal. The matrix atoms could move individually.

2.3. Molecular dynamics (MD)

The nanocrystalline structures computed by molecular statics served as the starting configuration to solve the equations of motion using the Verlet algorithm:

$$\mathbf{x}(t+dt)=\mathbf{v}(t)+\left(\mathbf{fx}(t+dt)\right)+f\left(\mathbf{x}(t)\frac{dt}{2}\right)dt \tag{1}$$

$$\mathbf{v}(t+dt)=\mathbf{v}(t)+\left(\mathbf{f}\left(\mathbf{x}(t+dt)\right)+f\left(\mathbf{x}(t)\right)\right)\frac{dt}{2} \tag{2}$$

where **x** is the coordinates vector, **v** – velocities vector, **f** – force vector, t – time.

A Morse pair potential with parameters corresponding to gold was used. The starting velocities were distributed according to the Maxwell Boltzmann distribution. The time step of 0.01 psec was chosen. The system properties were averaged at 30, 150, 300, 600, 900 and 1200 K.

2.4. Computation of the vibrational spectra

The vibrational density of states (VDOS) was computed by determination of the eigenvalues (and eigenvectors) of the dynamical matrix [13].

$$\omega_j^2 e_\alpha(k|j)=\sum_{k'}\sum_{\beta}D_{\alpha\beta}(k,k')e_\beta(k'|j) \tag{3}$$

$$D_{\alpha\beta}(k,k')=\frac{1}{\sqrt{m_k m_{k'}}}\phi_{\alpha\beta}(k,k')=\frac{1}{\sqrt{m_k m_{k'}}}\left(\frac{\partial^2\phi}{\partial x_\alpha(k)\partial x_\beta(k')}\right)_0 \tag{4}$$

where k = 1, 2, …, n indexes the atomic cores, m_k denotes the mass of core k, $D_{\alpha\beta}(k, k')$ denotes the dynamical matrix, Φ is the effective potential, Greek letters serve as coordinate indices, $x_\alpha(k)$, α = 1, 2 [3] are the Cartesian coordinates of the core k and $E(k|j)$ – its eigenvectors, $\Phi_{\alpha\beta}(k, k')$ are effective force constants.The vibrational spectra are obtained from the eigenfrequencies ω by histogram formation.

2.5. Computation of the specific heats

The heat capacity at constant volume (c_v) is obtained by taking the partial derivative of the energy with respect to the temperature [1]:

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = k\sum \frac{(h\nu_i / kT)^2 \, e^{h\nu_i / kT}}{(e^{h\nu_i / kT} - 1)^2} \tag{5}$$

where E is energy, T – temperature, ν_i – i-th eigen frequency, k – Boltzmann's constant, h – Planck's constant. It can therefore be computed directly from the vibrational spectra.

2.6. Participation ratio (PR)

In order to characterise the vibrational spectra of a system more precisely, one can try to determine the degree of their localisation. One possibility is to form an appropriate ratio PR of moments of the kinetic energy [14]:

$$PR(\omega) = \frac{M_1^\varepsilon M_1^\varepsilon}{M_0^\varepsilon M_2^\varepsilon} = \frac{1}{N}\frac{(M_1^\varepsilon)^2}{M_2^\varepsilon}, \qquad M_n^\varepsilon(\omega) = \sum_{i=1}^{N} \varepsilon_i^{2r} \qquad \text{with} \qquad \varepsilon_i = m\left|r_i\right|^2 \tag{6}$$

where $M_n^\varepsilon(\omega)$ is kinetic energy moment of the n-th order, ω – vibrational frequency, ε_i – mean kinetic energy of the i-th atom participating in the normal mode, r_i – vibrational amplitude, N – total number of atoms.

The moments of the kinetic energy $M_n^\varepsilon(\omega)$ are proportional to the moments which can be formed from eigenvectors of the vibrational modes. The proportionality factor hauls out in the definition of the PR and one obtains the following simplified equation:

$$PR(\omega) = \frac{1}{N}\frac{M_1^2}{M_2}, \qquad M_n(\omega) = \sum_{i=1}^{N} u_i^{2r} \tag{7}$$

$M_n(\omega)$ is the moment of the n-th order, ω – vibrational frequency, u_i – eigenamplitude, N – total number of atoms.

The participation ratio lies between 0 and 1. For three known vibrational states, the following participation ratios arise: $PR = 1/N$ – localised mode, only one atom vibrates, $PR = 1$ – extended mode, all atoms are displaced with equal amplitude (pure translation of the system), $PR \approx 0{:}5$ corresponds to the plane waves, characteristic of perfect crystals.

3. Results of the molecular dynamic (MD) simulations

3.1. Vibrational spectra (VDOS)

Figures 1–4 show the vibrational spectra of nanocrystalline materials (NCM) obtained by diagonalization of the dynamical matrix. In addition subspectra are shown,

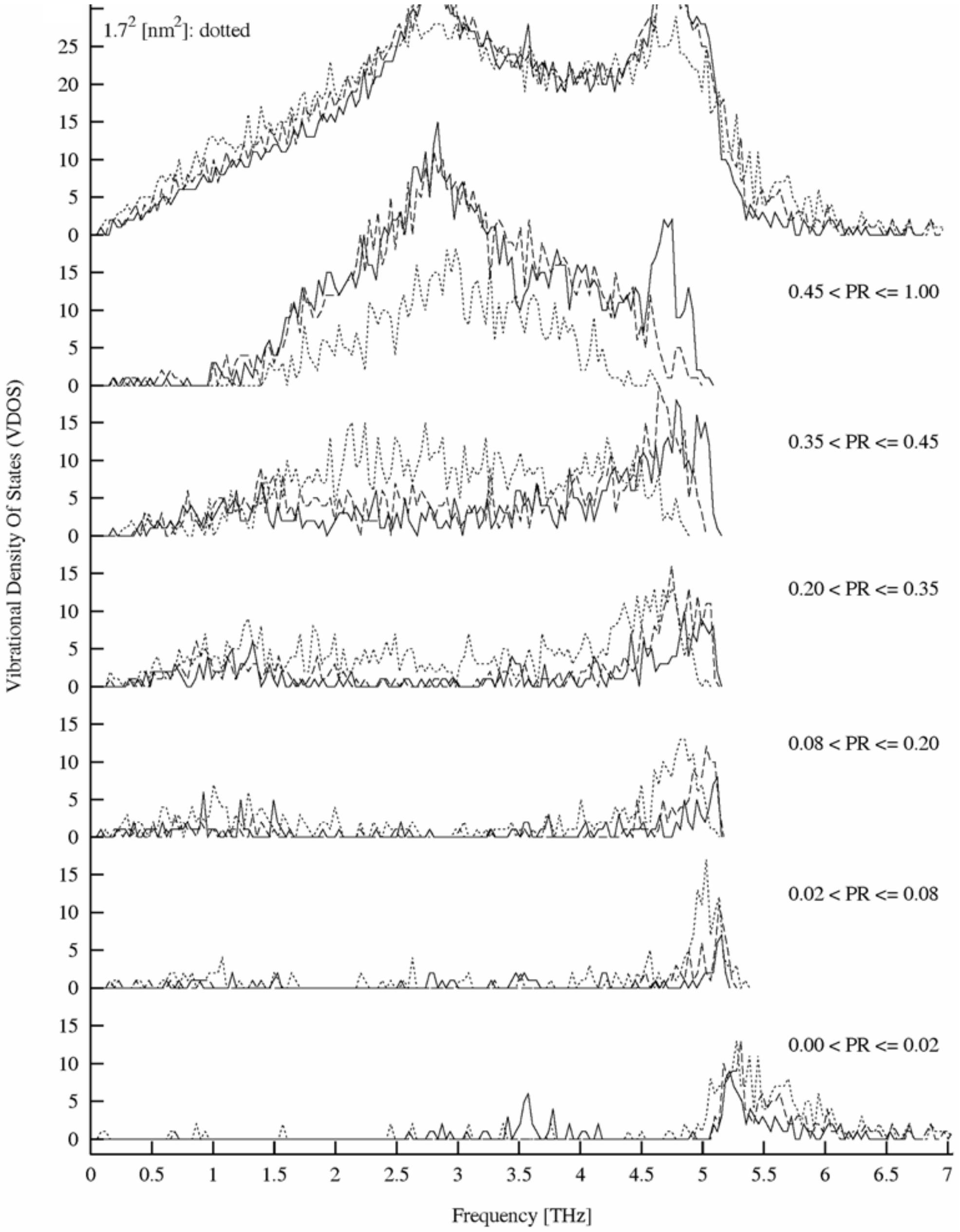

Fig. 1. Vibrational spectra of NCM with an average grain size of 6.5^2 nm^2 (solid curves), 3.3^2 nm^2 (dashed curves) and 1.7^2 nm^2 (dotted curves) for the temperature of 30 K. In addition, the decomposition of the complete spectrum in subspectra according to participation ratio intervals (PRI) of the modes is shown. The topmost array of curves shows the complete spectra of the NCM (PR $\in$]0; 1]), the arrays of curves there under show subspectra with PR $\in$]0.45; 1] until PR $\in$]0; 0.02])

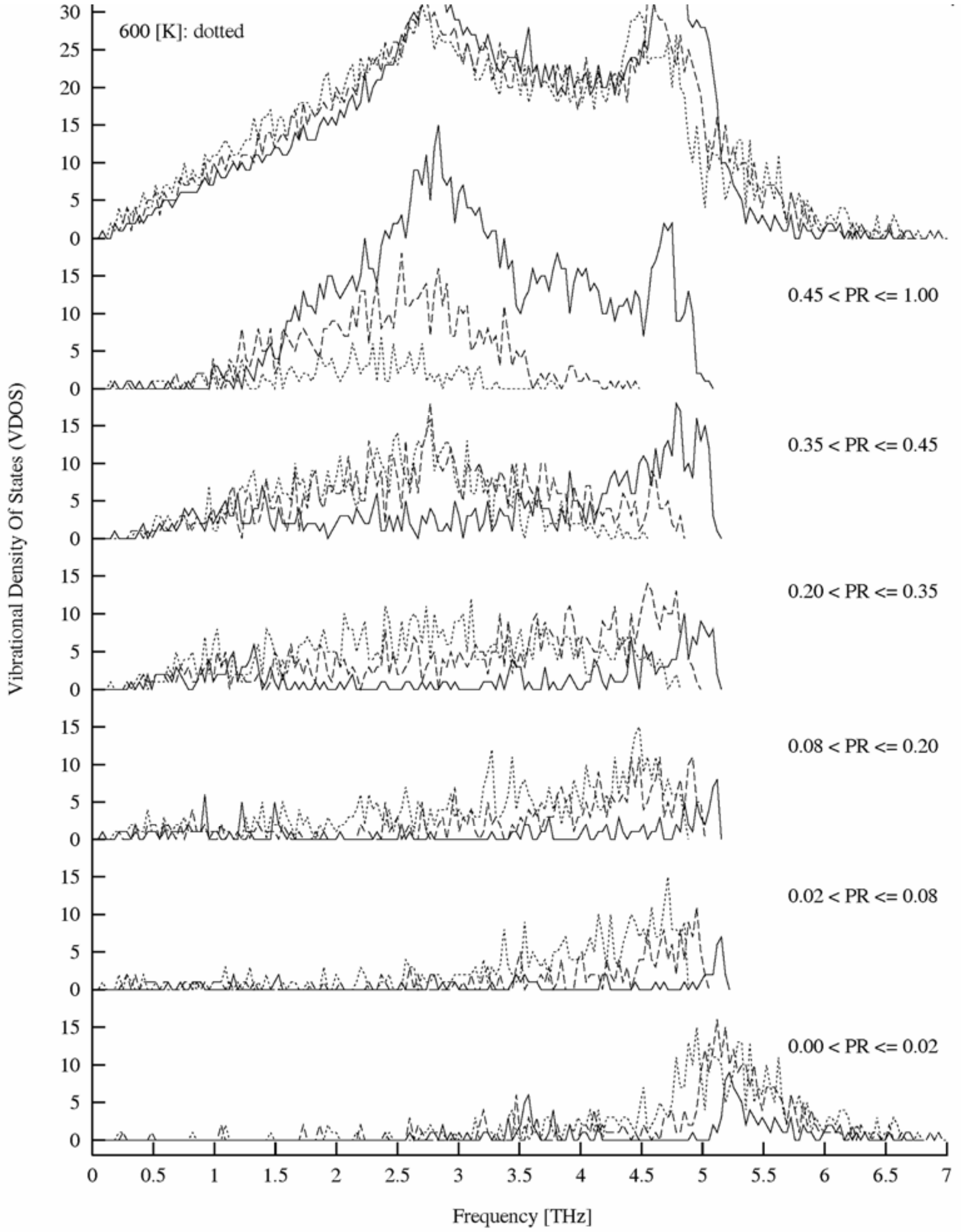

Fig. 2. Vibrational spectra of NCM with an average grain size of 6.5^2 nm^2 for the temperatures of 30 (solid), 300 (dashed) and 600 K (dotted curves). In addition, the decomposition of the complete spectrum in subspectra according to participation ratio intervals (PRI) of the modes is shown. The topmost array of curves shows the complete spectra of the NCM (PR $\in$]0; 1]), the arrays of curves thereunder show subspectra with PR $\in$]0.45; 1] until PR $\in$]0; 0.02])

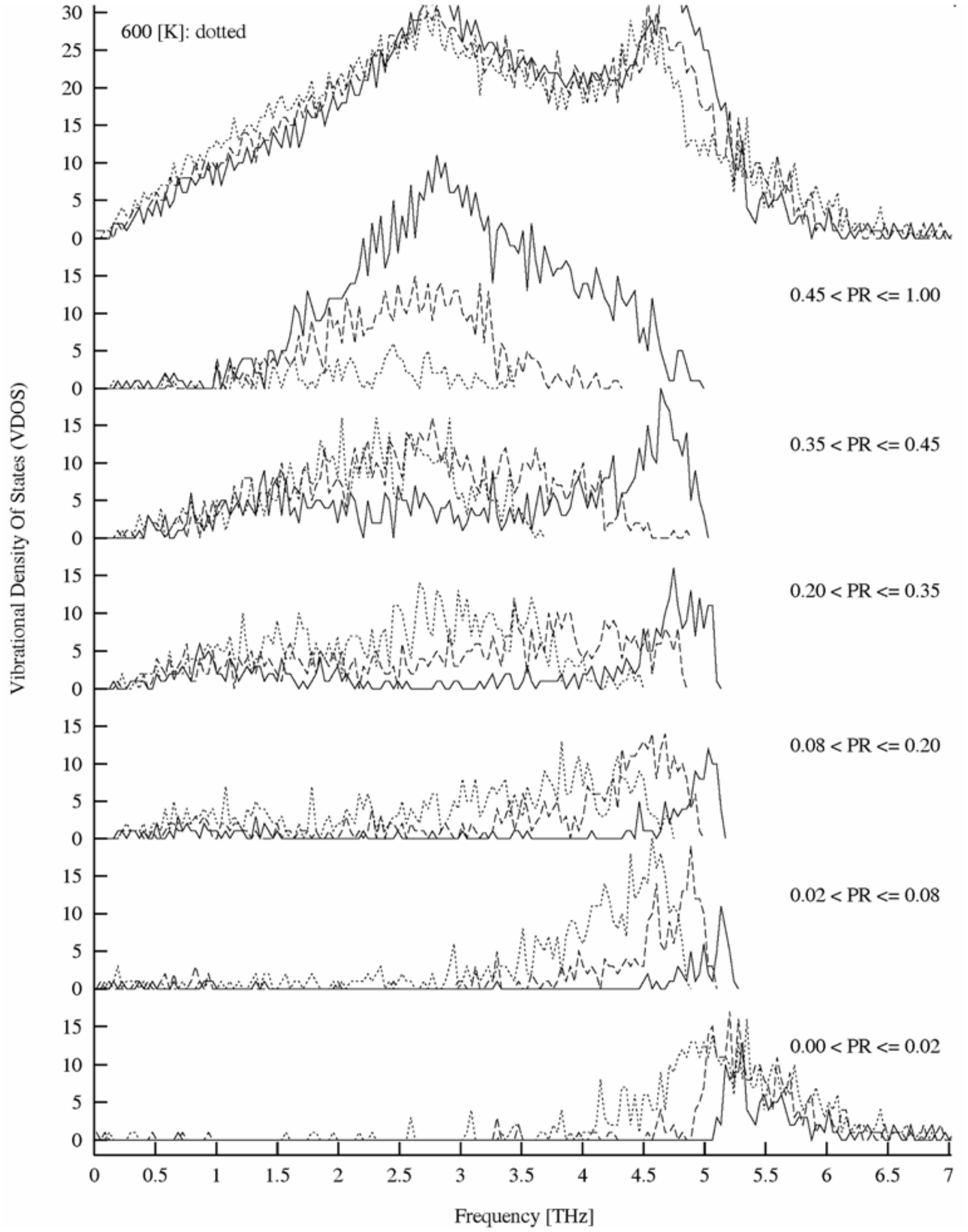

Fig. 3. Vibrational spectra of NCM with an average grain size of 3.3^2 nm^2 for 6 temperatures from 30 to 1200 K. In addition the decomposition of the complete spectrum in subspectra according to participation ratio intervals (PRI) of the modes is shown. The topmost array of curves shows the complete spectra of the NCM (PR $\in$]0; 1]), the array of curves there under show subspectra with PR $\in$]0.45; 1] until PR $\in$]0; 0.02])

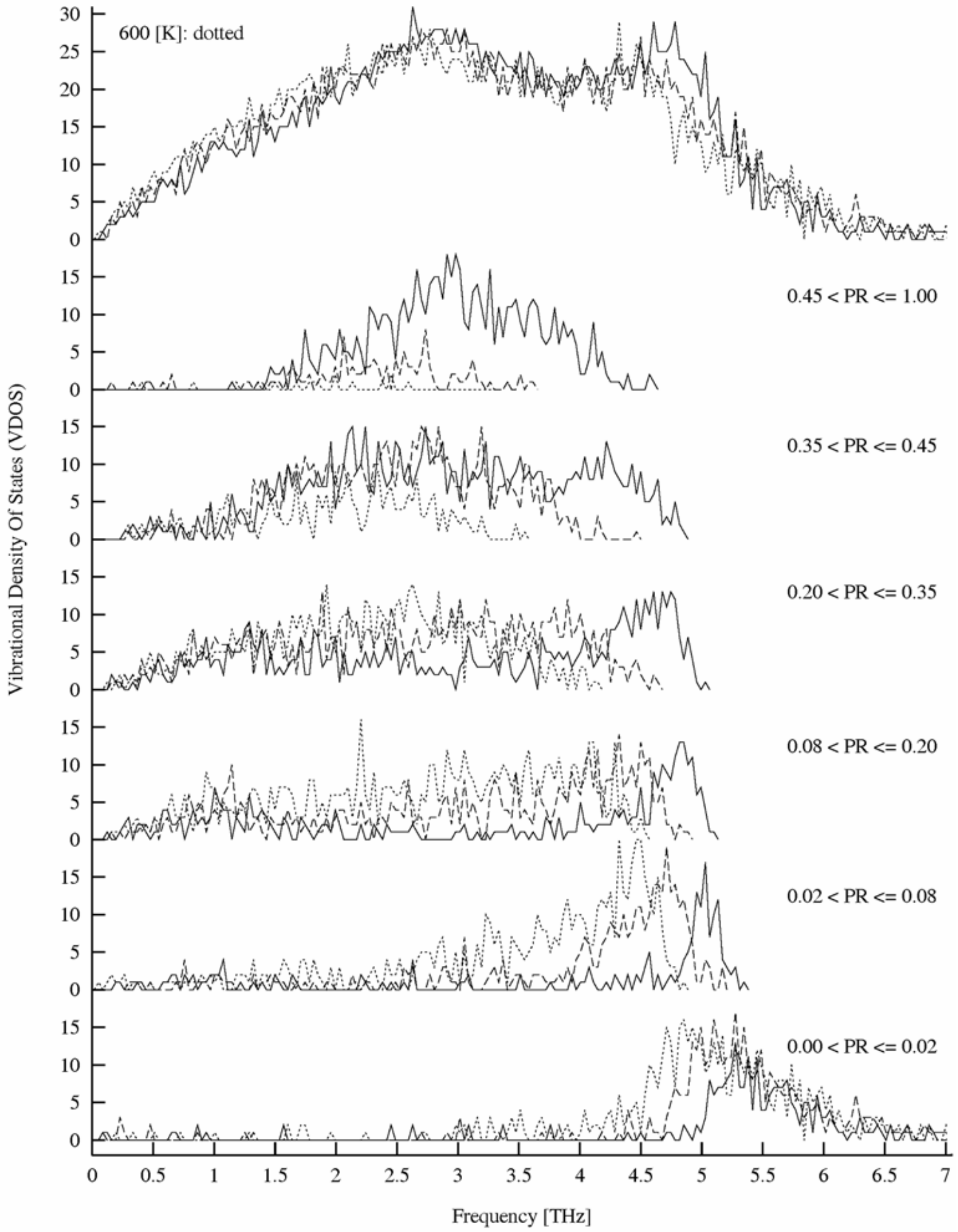

Fig. 4. Vibrational spectra of NCM with an average grain size of 1.7^2 nm^2 for the temperatures of 30 (solid), 300 (dashed) and 600 K (dotted curves). In addition, the decomposition of the complete spectrum in subspectra according to participation ratio intervals (PRI) of the modes is shown. The topmost array of curves shows the complete spectra of the NCM (PR $\in$]0; 1]), the arrays of curves thereunder show subspectra with PR $\in$]0.45; 1] until PR $\in$]0; 0.02])

which result from splitting of the complete VDOS according to participation ratio (PR) intervals. The grain size effect is shown in Fig. 1 for three different grain sizes. The effect of temperature is shown in Figs. 2–4 for 30, 300 and 600 K for the grain sizes of Fig. 1.

In the case of a single crystal the subspectrum, which belongs to the PR interval]0.45; 1], corresponds to all but the over-all spectrum (PR $\in$]0; 1]). Nearly no modes contribute to the subspectra with PR $\leq$ 0.45.

In the case of a NCM, the subspectra with PR $\leq$ 0.45 contribute substantially to the total spectrum. Their contribution increases with decreasing grain size. In particular, modes from the transversal peak shift to subspectra with a lower participation ratio. The high-frequency offshoot of the VDOS, which is peculiar to a NCM (not present in a single crystal), is characterised by very low participation ratios (PR $\leq$ 0.08). These modes are strongly localised. NCM with 6.5^2 nm^2 grain size have vibrational modes similar to those of a single crystal in the medium frequency range (~1.1–5.2 THz), i.e. they have modes with participation ratios $\in$]0.45; 1]. But the subspectra with PR $\leq$ 0.45 of these NCM contain already low- and high-frequency modes, which are not present in a perfect crystal.

With decreasing grain size, the vibrational modes of the medium frequency range of a NCM lose participants to subspectra of lower PR-intervals. More and more modes are shifted from the longitudinal and transversal peak sites to mainly the longitudinal rising peak edge (towards lower frequencies). The transversal peak gets disintegrated from its trailing edge. Also the number of new high-frequency modes in the spectra increases.

The temperature behaviour of the VDOS of NCM is reciprocal to that of their grain size: the low (~0–1.5 THz), medium (~1.5–5.2 THz) and high ($\geq$ 5.2 THz) frequency ranges of the modes experience with increasing temperature similar changes as occur with decreasing grain size.

An example of the similarity of the grain size and temperature effects is given by a comparison of the subspectra of 2 NCM with different grain sizes at different temperatures: The solid curves in Fig. 4, for a grain size of 1:72 nm^2 at 30 K, show a remarkable similarity with the dashed curves in figure 2, which were obtained with a grain size of 6.5^2 nm^2 at 300 K.

The weakening of the transversal modes as a function of decreasing grain size with respect to increasing temperature leads – together with the continuous transition from long to short range order, found in the pair distribution functions – to the following issue: With decreasing grain size (or increasing temperature) the NCM should exhibit an amorphisation by shear instability of the grains.

3.2. Specific heats

Figure 5 shows the specific heats of the NCM with three grain sizes (6.5^2; 3.3^2; 1.7^2 nm^2) and the difference to the specific heat of a perfect crystal with the same number of atoms at 0 K, computed from spectra obtained by diagonalization of the dynamical matrix.

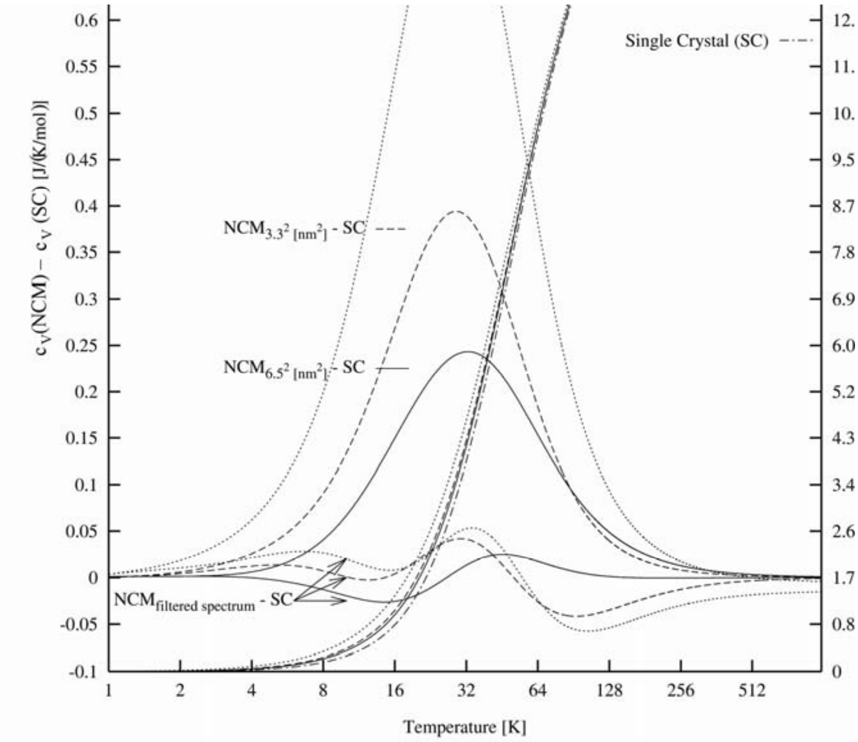

Fig. 5. Specific heats of 3 NCM with different grain sizes (indicated by NCM$_{x\cdot x^2[\mathrm{nm}^2]}$) and their difference to the specific heat of a single crystal (indicated by NCM $_{x\cdot x^2[\mathrm{nm}^2]}$- SC"), as well as the specific heat of the single crystal (indicated by SingleCrystal (SC)). In addition, differences in the specific heat of the same NCM to those the single crystal are drawn, which were computed by filtering from the vibrational spectra of the NCM parts of a subspectrum with PR $\in$]0.2; 0.35] (indicated by NCM$_{\mathrm{filteredspectrum}}$ – SC). The specific heats of the NCM were computed from vibrational spectra, which were obtained by diagonalization of the dynamical matrix of an instantaneous configuration of the MD simulation at 30 K

In the range around 28 K the specific heat of the NCM is increased, compared to that of the perfect crystal. The difference of the specific heat of the NCM and single crystal increases with decreasing grain diameter D, approximately proportional to $1/D$.

The increase of the specific heat of the NCM can be attributed to parts of a subspectrum with PR $\in$]0.2; 0.35] in such a manner that after filtering out of these parts from the complete spectrum of the NCM, the specific heats of NCM and perfect crystal differ only by circa 15% of the value of the original increase.

4. Summary and conclusions

Two-dimensional nanocrystalline materials (NCM) were simulated by molecular static and molecular dynamic methods as a function of grain size and temperature. The vibrational density of states (VDOS) was examined in detail. It was subdivided into subspectra by means of the so-called participation ratio (PR), which measures the fraction of the atoms contributing effectively to a given mode.

The weakening of the transversal modes as a function of decreasing grain size with respect to increasing temperature together with the continuous transition from far to short range order, found in the pair distribution functions suggests that NCM should exhibit an amorphisation because of shear instability of the grains under these conditions.

The specific heat of the NCM was increased in the temperature range of about 28 K compared with that of a single crystal. The increase is broadly reciprocally proportional to the grain diameter. The differences in the specific heat could be largely attributed to parts of a subspectrum of the VDOS obtained by interval formation according to the PR.

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