

Vibrational Behavior of Nanocrystalline Materials

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The elastic and vibrational properties of iron-nickel and aluminum nanoparticles and nanocrystalline materials have been investigated on the basis of molecular dynamics simulations and the embedded atom method for the description of the materials. It is well known that nanocrystalline solids, with grain sizes in the nanometer range, exhibit often unusual properties like increased hardness due to immobilization of dislocations at the grain boundaries known as Hall-Petch effect. However, when reducing the grain size below a critical value, sliding processes between the grains decrease the hardness giving rise to the reverse Hall-Petch effect. Furthermore, the structural transformation of the particles and nanocrystalline materials, including melting of the nanoparticles, as a function of time, temperature or pressure show a distinct size dependence.

I. INTRODUCTION

Clusters, nanoparticles, self-assembly of clusters or large organic molecules, consolidation of nanocrystalline materials by compaction and sintering have become active research fields in chemistry, physics and engineering.^{1,2} Not to forget to mention activities in the areas of biology, biochemistry and pharmaceuticals especially in connection with the problem of rapid onset of drug action by using hollow clusters or organic structures like the cyclodextrins able to accommodate the drugs and transporting them to the locations where needed.^{3,4} The fabrication of nanocrystalline materials of ever finer grain size has become a technological challenge and is, among other interests, motivated by the often novel properties these materials display. In this contribution we concentrate on elastic and vibrational properties of iron-nickel and aluminum nanoparticles by using a microscopic approach. This work has been motivated by the experimental observation of significant enhancements of the yield strength and the hardness of nanomaterials with grain sizes in the nanometer range^{5,6} (known as Hall-Petch effect^{7,8}) and by the crossover to decreasing hardness of systems with even smaller grain sizes (reverse Hall-Petch effect^{9,10}). In particular the question in how far the grain size will effect structural transformations and the solid-liquid transition is addressed. This work is part of an ongoing research project and only preliminary results can be presented.¹¹

The well-known Hall-Petch equation^{7,8} relates the yield strength σ_y to the average grain size d of bulk material by

$$\sigma_y = \sigma_0 + k/d^{1/2},$$

where σ_0 is a friction stress and k a constant. A corresponding relationship exists between hardness and grain size. Figure 1 shows experimental results of the hardness as a function of $d^{-1/2}$ for nanocrystalline Fe, Ni, Cu, Ag and Pd (Fig. 1 has been adapted from Ref. 5 which also gives the references to the original experimental works). The increase of the hardness with increasing inverse square root of d is in particular for Fe and Ni nanomaterials quite large. This behavior is attributed to the increasing interaction of dislocations with grain boundaries leading to a suppression of dislocation motion and a pile-up of dislocations at the grain boundaries. However, it has early been argued that for finest grain sizes a softening mechanism may occur by increasing diffusional accommodation of the grain boundaries and superplastic behavior at elevated temperatures.^{12,13}

We have performed molecular dynamics simulations for an assembly of $\text{Fe}_{80}\text{Ni}_{20}$ nanoparticles arranged with arbitrary crystallographic orientations on an fcc lattice.^{14,15} Sintering of the particles (each containing approximately 10^3 atoms) at elevated temperatures or under pressure leads to nanophase material which allows for easy sliding of the grains and superplastic behavior under further stress. The crossover from these grain sizes (showing kind of reverse Hall-Petch behavior) to grain sizes for which the Hall-Petch effect should be detectable has so far not been simulated. For computational details of the present simulations we refer to Ref. 14. With respect to superplastic behavior of nanophase materials we would like to draw the attention to recent molecular dynamics simulations of Cu.¹⁶

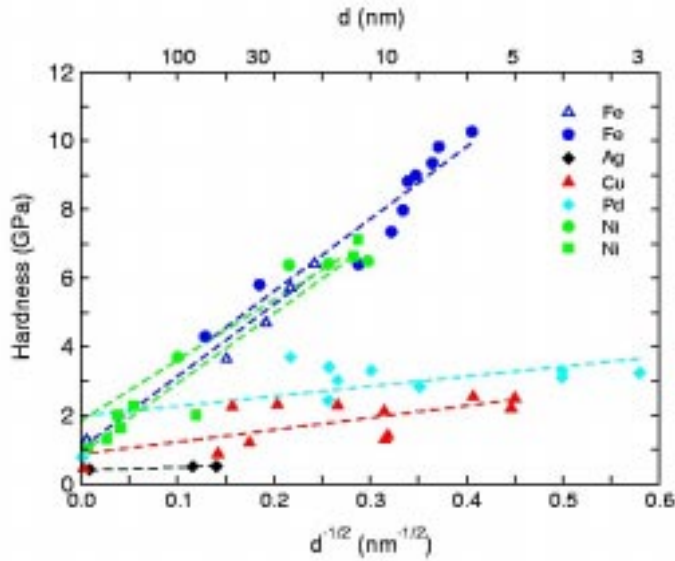


Figure 1: Variation of the hardness with $d^{-1/2}$, where d is the grain size, for a selected class of nanophase metals synthesized from gas-condensed clusters compared with their coarse-grained counterparts (values at $d^{-1/2}$ close to zero). Data have been taken from Ref. 5.

II. VIBRATIONAL DENSITY OF STATES OF NANOPHASE MATERIALS

It is well known that the vibrational density of states (VDOS) of nanophase materials shows an enhancement at low and high energies.¹⁷ We have recently obtained the VDOS of nanocrystalline Ni and Cu with grain diameters between 5 and 12 nm from molecular dynamics simulations.¹⁸ Because of the decomposition of the VDOS into grain and grain boundary components, the low-frequency region could be investigated for the first time in detail. It was found that the anomalous increase of the VDOS is mainly caused by the high number of grain boundary atoms and that a power-law behavior of the low-frequency grain boundary VDOS exists, suggesting a reduced dimensionality effect. The results show an $\omega^{1.5}$ behavior which has to be compared with the usual low-frequency scaling of ω^{d-1} , where d is the spatial dimension. We also found that the integrated pair distribution function of the grain boundary atoms varies as $r^{2.5}$ at distances $r < 4$ nm (which is close to the result for nanocrystalline Pd for which a spatial dimension of $d = 2.4$ for the grain boundaries was reported¹⁹). For further discussion we refer to Ref. 18.

Here we present new results for aluminum nanoparticles. Figure 2 shows the structures of the solid (at $T = 300$ K) and liquid (at $T = 900$ K) particles. The corresponding VDOS are shown in Fig. 3. The nonvanishing VDOS (for $\omega = 0$) of the liquid particle can be attributed to diffusional processes or diffusional modes, which, however, have not yet been analyzed in detail. When we approach the melt-

ting point of the particles with increasing temperature, we practically do not observe any overheating but a sudden transition to the liquid state accompanied by a nearly complete loss of crystalline facets at the surface and enhanced diffusion of the surface atoms.²⁰

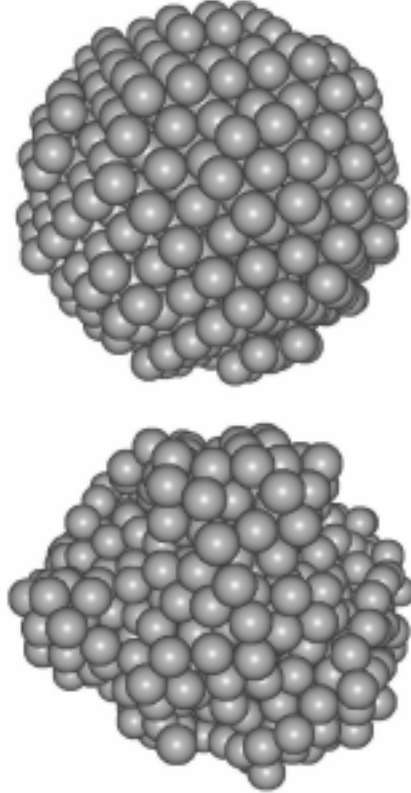


Figure 2: Solid (top) and liquid (bottom) phase of an aluminum particle containing 791 atoms (at a temperature of $T = 300$ K and 900 K, respectively).

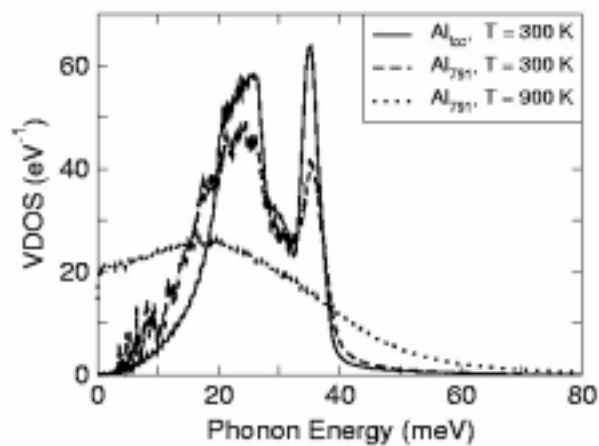


Figure 3: Vibrational density of states of an aluminum particle consisting of 791 atoms at $T = 300$ K (where the particle is solid) and at $T = 900$ K (where the particle is liquid) in comparison to the bulk density of states of aluminum in the face centered cubic structure at $T = 300$ K (solid line).

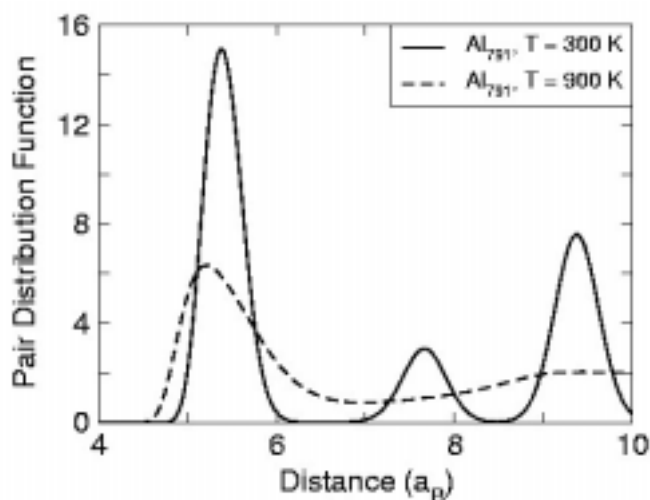


Figure 4: Radial distribution function for the aluminum particle at two different temperatures as a function of the distance (in units of a_B). Note that in the liquid state at $T = 900$ K there are, besides the peak for the first nearest neighbor shell, no marked peaks for the further neighbor shells.

III. MELTING OF NANOPARTICLES

The melting of the particles is a very interesting subject since the phenomenological melting theory predicts a scaling of reduction of the melting temperature with the inverse of the particle diameter d (see, for example, Ref. 21; the first prediction for the behavior of the melting temperature of clusters was formulated by Pavlov, Ref. 22):

$$1 - T_M(d)/T_B \approx 1/d,$$

where $T_M(d)$ and T_B are the melting temperature for the cluster and the corresponding bulk system, respectively. In the molecular dynamics simulations, when approaching the melting temperature, we observe increasing fluctuations of structural changes of the particles with a sudden first-order type of transition to the liquid state confirming early experimental and theoretical works (for general aspects of melting of low-dimensional systems compare Ref. 23 and 24). Figure 5 shows the change of the energy of the particles with different sizes as a function of the temperature. The sudden increase of the energy may be used to define the melting temperature. Figure 6 shows that the decrease of the melting temperature as given by the above formula is indeed fulfilled down to smallest cluster sizes. This is remarkable in view of the many conformational changes the particles undergo prior to melting. Of further interest is the seemingly complete loss of crystalline order of the liquid particle. The pair correlation function in Fig. 4 shows already that a given atom of the cluster sees dominantly the first nearest neighbor shell. With respect to melting in general the associated change of local symmetry is much at debate at present, see, for example, Ref. 25, in which a fivefold symmetry in the surface melt of lead was detected.

In order to account for the symmetry changes one needs more detailed information about symmetry aspects related to the neighbors. An appropriate tool is the so called common-neighbor analysis by which the environment of neighbored pairs of atoms is characterized by three indices defining the number of common nearest neighbors, the number of neighbor relations (bonds) and the length of the longest chain of bonds between the neighbors of this pair of atoms.²⁶ For further discussion we refer to the literature.

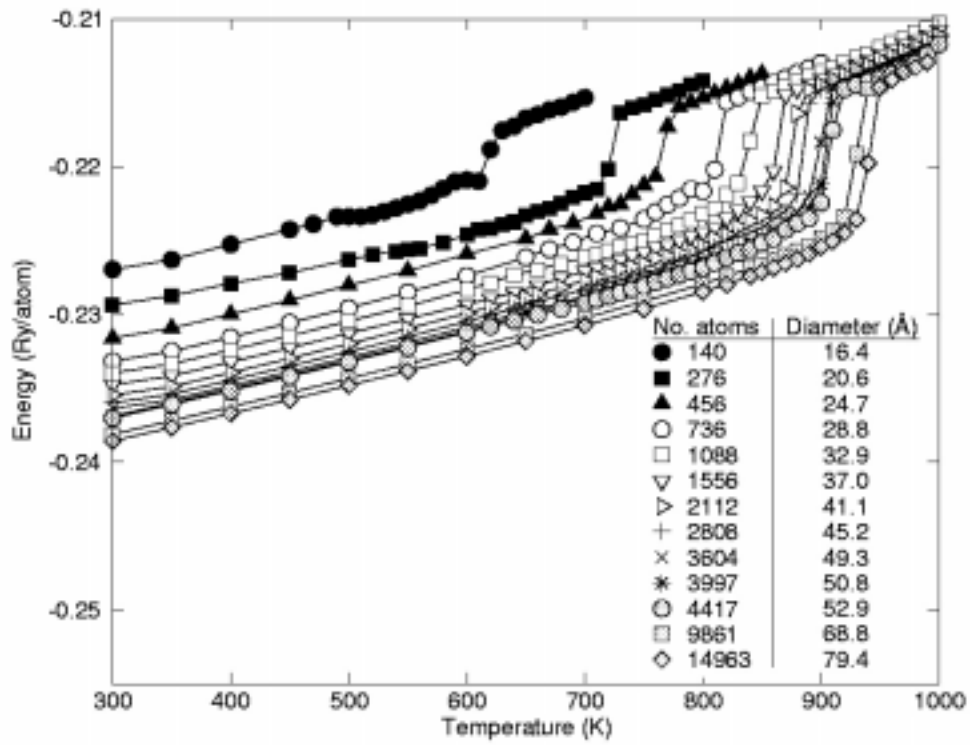


Figure 5: The variation of the energy of free aluminum nanoparticles with different numbers of atoms as a function of the temperature.

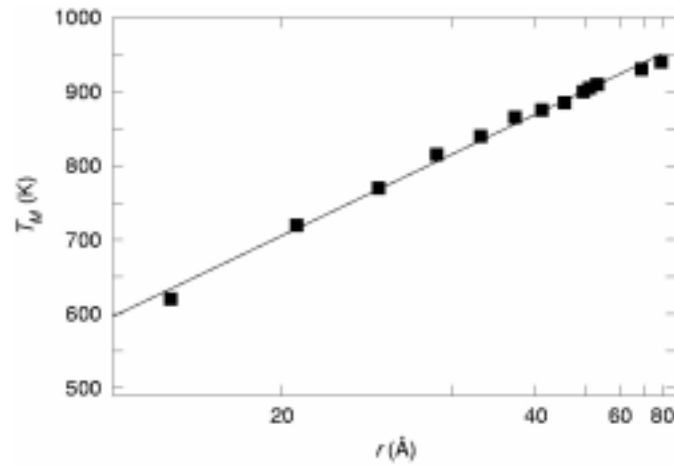


Figure 6: Variation of the melting temperature (taken from Fig. 5) as a function of the cluster radius.

IV. CONCLUSIONS

We have discussed vibrational properties of nanoparticles and shown that the scaling of the low-frequency part of the spectrum is related to the increasing number of atoms in the grain boundaries

(with decreasing particles sizes) compared to the number of atoms in the inner part of the particles. The melting temperature of the particles exhibits a different scaling behavior which was predicted by a phenomenological melting theory. But also structural changes of the particles (solid-solid transformations) scale with the inverse of the particle size. This is, for example, the case for the austenitic transformation temperature not shown here.²⁷

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