Size-Dependent Specific Heat of Nanoclusters

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The contribution of surface energy to overall thermodynamic properties of the system is crucial for small, finite size phases [1]. A very telling example is the experimental evidence of size-dependent heat capacity of nanoparticles, recently reported for metallic nanoclusters and nanostructured dielectrics [2,3]. Despite of its clear physical background this phenomenon is still subject to a limited number of theoretical models. This is the reason to focus our study on the impact of the interface energy on specific heat of nanocrystals. In the framework of classical Gibbs thermodynamics, the Einstein-Debye model for heat capacity of solids is extended to clusters with comparable number of bulk and surface atoms. We introduce surface heat capacity that accounts for surface free energy contribution. Defined as a difference, between the surface and bulk terms, the excess heat capacity reveals temperature gap and size limits of nanoclusters where the contribution of surface energy is essential. Considering the role of surface Debye temperatures, we evaluate the deviation of specific heat for nanoclusters having different surface atomic density and surface orientation. We found that specific heat of nanocomposite systems can be enlarged by: (i) decreasing the size of nanocrystals and (ii) increasing the relative part of high index surfaces that facet the nanocrystal. Being in agreement with recent experimental findings, the present model opens up a way to predict basic, size-dependent thermodynamic properties of nanocomposite systems [4,5].

References

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