On the Criterion of the Crystal-Liquid Phase Transition for Macro- and for Nano- Systems

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In this work a localization criterion for the solid–liquid phase transition (S-LPT) is suggested. According to this criterion the PT starts when the fraction of delocalization atoms reaches a boundary value: $x_d(S\text{-}L) = 10^{-2}$, above which a liquid phase, and below which, a solid phase is located in the phase diagram. It is shown that this localization criterion is equitable both for macro-, and for nano- systems too. As was shown in [1], the fraction of atoms that pass from the localized state (when an atom vibrates in the cell formed by the nearest environment) into the delocalized state (i.e., acquiring a kinetic energy that is higher than a certain threshold value E_d) is described by the incomplete gamma function of the form:

$$x_d(Y_d) = N_d / N = (2 / \pi^{1/2}) \int_{Y_d}^{\infty} t^{1/2} \exp(-t)\, d\, t \ ,$$

where $Y_d = E_d / k_b T$; E_d is the energy of the delocalization of an atom, which takes on the form:

$$E_d(T, c) = (27 / 128\, \pi^2 k_p^{2/3})\, m f_y (c\, k_b \Theta / \hbar)^2 \ .$$

Here, T is the temperature; c is the distance between the centers of the nearest atoms; k_p is the packing fraction of the structure; k_b and $\hbar$ are the Boltzmann and Planck constants; m is the mass of an atom; Θ is the Debye temperature; $f_y = (2/y)[1 - \exp(-y)] / [1 + \exp(-y)]$; $y = 3\,\Theta/4\,T$. As was shown in [2], at the definite value of Y_d starts both melting of macro-crystal at T_m , and crystallization macro-liquid at T_N:

$$Y_d(S\text{-}L) = E_d(S) / k_b T_m = E_d(L) / k_b T_N \approx 5.67. \qquad (1)$$

Herewith at the solid-liquid border is executed: $x_d(S\text{-}L) \cong 10^{-2}$. It is shown that this criterion extends the Lindemann criterion of melting to the case of crystallization, and the Löven criterion of crystallization to the case of melting. It is shown that the localization criterion suggested is applicable both for the normally melting substances and for the substances melting with a decrease in the specific volume upon the transition into the liquid phase. On the basis of the localization criterion was explained of the temperature hysteresis of S-LPT: a crystal melts always at a certain temperature (T_m), while a liquid can easily be supercooled to below this temperature, so that the temperature of the start of crystallization (T_N) is always lower: $T_m > T_N$. We use for description of nanocrystal with free surface the model of rectangular parallelepiped with a square base, which consists of N atom, and whose shape can be varying by the shape parameter [3, 4]. In the case of "nonquantum" nanocrystals (i.e. where the energy "zero-point oscillations" is smaller than energy of chemical binding) the next expression is received:

$$\{[\Theta(N, f)/\Theta(\infty)][c(N, f)/c(\infty)]\}^2 = [\Theta^*(N, f)\, c^*(N, f)]^2 \cong k_n^*(N, f)\, [c^*(N, f)]^{-2(3\gamma - 1)}, \qquad (2)$$

where $f = N_{ps}/N_{po}$ is the shape parameter, which is defined by the relation of number of atoms on a side edge (N_{ps}) to number of atoms on an square base edge (N_{po}); $k_n^*(N, f) = k_n(N, f)/k_n(\infty)$ is the normalized average (over all atoms) first coordination number; γ is the Grüneisen parameter, which is independent via N or f [3, 4]. Proceeding from Eq. (2), it is shown that functions $E_d(T_m)/k_b T_m$ and $x_d(T_m)$ have not of a size dependencies, whatever herewith the "surface pressure". Therefore, the localization criterion for S-LPT (1) has it the same value, independently neither from size nor from shape of nanocrystal.

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[2] *Magomedov M.N.* // The Physics of Metals and Metallography. 2008. V. 105. N 2. P. 116 – 125.
[3] *Magomedov M.N.* // Physics of the Solid State. 2003. V. 45. N 7. P. 1213 – 1218; 2004. V. 46. N 5. P. 954 – 968.
[4] *Magomedov M.N.* // Technical Physics Letters. 2005. V. 31. N 1. P. 13 – 17; 2007. V. 33. N 3. P. 212 – 215; 2007. V. 33. N 5. P. 954 – 968.