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Size-induced thermal thermodynamic hysteresis in nanopowder undergoing structural transitions – from particular case to general behaviour

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We present the analysis for the description of a structural transition of Fe-nanoparticle ensemble subjected to temperature change. The existence of a size-induced hysteresis for the volume fraction of the new phase is demonstrated. It is shown that this may be thermodynamic effect existing under the limitations to realization of the ergodic hypothesis. The thermodynamic hysteresis arises from the nonsymmetry of transforming path of the nanosystem with respect to the initial conditions that is due to the dependence of the phase transformation on the mechanisms of nucleation of a new phase. Moreover, it is argued here that in nanosystems it is required to differentiate the kinetic hysteresis and 'thermodynamic' hysteresis in the first order phase transition.

Keywords: Gibbs free energy; nanoparticle; nucleation; temperature change; structural phase transition; size-induced thermodynamic hysteresis

1. Introduction

Many physical systems naturally exhibit hysteresis. Among materials demonstrating hysteresis phenomena the Fe-nanoparticles and nanopowders have a specific significance, which is due to their wide practical applications. It is well known that the hysteresis is exploited commercially, for example, it provides the element of memory (see, e.g. [1]).

If the system has hysteresis, then one cannot predict the output without looking at the history of the output. In order to predict the output, one must look at the path that the output followed before it reached its current value.

In the usual treatment of hysteresis in bulk materials, it is assumed that this is the kinetic phenomena and considered as the lag in the variable property of a system with respect to the effect producing it as this effect varies, especially the phenomenon in which the magnetic flux density of a ferromagnetic material lags behind the changing external magnetic field strength. In nanosystems phase transformations of materials in confined volumes can deviate considerably from the respective course as observed in the bulk. It has been shown that the usual language of first order phase transition theory becomes invalid in this case due to the fact that the nucleation process might differ from the usual bulk case

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[2–9]. As we shall see here, new size-induced rules and behaviours give new notions and give origin of new language in nanoscience [10].

As example of first-order phase transitions, where size-induced hysteresis phenomena occur, one can mention capillary condensation [11,12]. Capillary condensation is the phase transition in pores or capillaries important for the understanding of the properties of porous materials. It represents the surface driven phase change accompanied by shifts in the phase coexistence curves. By plotting the pressure (or temperature) *versus* the total number of moles adsorbed in such materials it is possible to construct the size-dependent phase diagram similar to bulk equilibrium coexistence curves. Hereby three aspects are important: (1) one can see different shapes of hysteresis loops in the adsorption isotherms, (2) hysteresis effects vanish above some hysteresis critical temperature which is lower than the bulk critical temperature of the corresponding transition and (3) there is some shift in the hysteresis critical temperatures, they increase with the decreasing pore width.

As another example, one can mention the phase separation of a binary alloy taking into account the concentration redistribution which demonstrates the existence of size-induced thermal hysteresis effects in kinetics of phase transitions [13,14]. The melting behaviour of nanoparticles of Pb–Bi alloys, observed by hot stage transmission electron microscopy, shows similar size-induced hysteresis loops [15].

The theoretical consideration of structural phase transitions in nanomaterials undergoing temperature changes still remains an open question. In this respect, one can mention the recent experimental analyses performed by Alivisatos et al. where the kinetic hysteresis width for structural transition in the CdSe nanostructured system turns out to be almost independent of nanocrystal size [16,17]. At the same time the previous kinetic models and simulations predict a considerable increase in the width of the hysteresis loop with increasing particle size (see, in particular [13]). Why? – that is the question for which we want qualitative answer, which is already in this article.

Our analysis performed here is based on the idea of the symmetry of possible evolution paths, which seem to be very simple, but so far are not taken into account generally in the analysis of the thermodynamics and kinetics of phase transitions in nanoparticles. In this article, we analyse the first-order phase transitions in ensembles of nanoparticles (Section 2) from the thermodynamic point of view (Section 3), specifically targeting α-Fe to γ-Fe structural transitions at different fixed temperatures (Section 4). Section 5 contains the summary and conclusions.

2. States of ensemble of nanoparticles at different fixed temperatures

Under experimental conditions, one generally deals with a large number of particles. In order to be able to interpret the behaviour of such ensemble, we assume that the nanoparticles are characterized by a monodisperse size distribution (Figure 1).

In order to develop a detailed theoretical description of the mentioned hysteresis effects we perform a thermodynamic analysis of formation of a nucleus in a single nanoparticle and apply the thermodynamic approaches to the study of phase transition in a nanopowder at different fixed temperatures. Hereby our particles are assumed to be relatively large, the number of atoms, N_0, in each particle is of the 10^3–10^7 order and above, so that their radius is equal or is larger than about 2 nm and hence thermodynamic arguments remain valid.

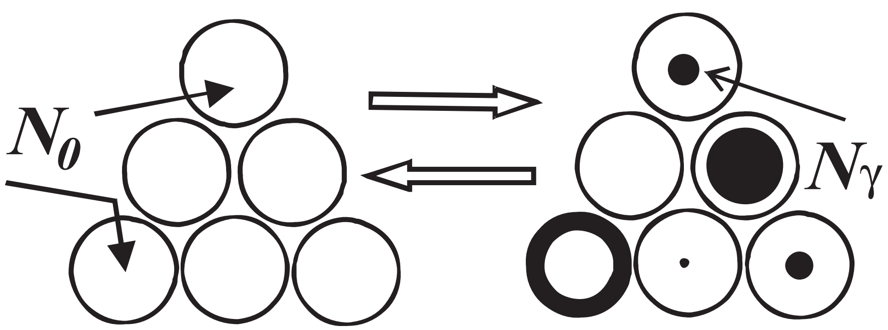

Figure 1. Schematic representation of a structural transition in nanopowder during temperature change: on the left–ensemble of particles of N_0 size before α-Fe to γ-Fe transformation, on the right–the same particles after the transition at another temperature. $N\gamma$ is the number of the atoms in the new-born γ-phase (shown in black colour); it is assumed that in each nanoparticle only one aggregate of the new γ-phase can be formed.

2.1. *Basic models of nucleation*

When the temperature is changed, the first order phase transitions generally start from nuclei of a new phase. In accordance with this, our analysis is based on the argument, which is important for nanosystems but usually disregarded, is related to nucleation, i.e. formation of a new phase inside the initially supersaturated ambient phase.

Let us assume that each small isolated initially supersaturated particle of a given powder (Figure 1) exists as α-phase and then is quenched into the two-phase region (say, α-phase is stable at low temperatures whereas the γ-phase exists at higher ones). Then a phase transition may take place from the single α-phase state to: (1) the γ-phase state, say at some temperature T_1; (2) to a two-phase $\alpha+\gamma$ one, say at temperature T_2. A single nucleus of a new phase can form in the particle as shown in Figure 2. Hereby for simplicity we show only two possibilities among others (shown further) differing from one another only by first step of 'forth' phase transformation – by the nucleation mechanism – homogeneous (path 012 in Figure 2a) or heterogeneous (path 012 in Figure 2b).

This small difference in the possible evolution paths of each particle may take place in Fe-nanopowder and is quite enough to see the principal results and understand the idea of this article.

Commonly, we must calculate all possibilities for a new phase formation and consider general situation of transforming powder (Figure 3).

In the following, we shall realize and distinguish between all the mentioned cases for the Fe powder (Figure 1) at different temperatures: with evolution path 01234 for the mode 2a (Figure 2a), with path 01234 for the mode 2b (Figure 2b) and with path 01234 for the combined mode 3 (Figure 3).

3. Basic thermodynamic approach and the quantity under investigation

Let us discuss the energy related issue of nucleation and α-phase to γ-phase transformation related to the temperature change. Nucleation implies the reconstruction of the structure of the system and yields the appearance of a new interface (between α-phase and γ-phase) with corresponding value of specific surface energy $\sigma_{\alpha\gamma}$. Owing to the competition between bulk driving force and surface terms, the Gibbs free energy required to form a nucleus of a

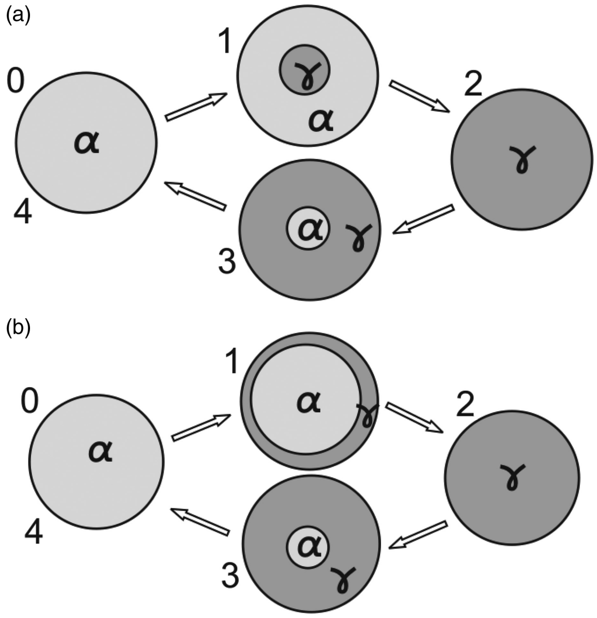

Figure 2. Schematic representation of two different nucleation modes for complete temperature cycle 01234 in a single particle of the powder: (a) Homogeneous nucleation of γ-phase inside α-phase particle during the 'forth' phase transition and homogeneous formation of α-phase inside γ-phase particle during the 'back' phase transition; (b) Heterogeneous nucleation of γ-phase at the wall of α-phase particle during the 'forth' phase transition and homogeneous formation of α-phase inside γ-phase particle during the 'back' phase transition.

new phase goes through a maximum ΔG^* also called nucleation barrier. Hereby the size of the nucleus – corresponding to the maximum is called the critical size of the new phase nucleus. If the value ΔG^* is very high as compared with the energy of thermal motion kT (k – is the Boltzmann constant, T – is the temperature of the system), then the phase transition is impossible. Since there exist the interface and external surfaces at the transition, they will affect the value of ΔG^* and it is expected that surface energies, entering the evaluation of the size-dependent transition temperature, play an important role in the transition of nanoparticles.

3.1. *Thermodynamic model*

It is now possible to evaluate Gibbs free energy of the corresponding transition. The reasoning is based on the calculation of the temperature variation of the Gibbs free energy for the involved phases, $G(T)$, performed under isobaric conditions. Let N_0 be the number of atoms in one particle (Figure 1). At fixed temperature T, the total energy, G_α of the initial α-phase nanoparticle is given by

$$G_\alpha = N_0 g_\alpha + f_\alpha N_0^{2/3} \sigma_\alpha. \tag{1}$$

In this equation, g_α is the bulk Gibbs free energy density of the α-phase, σ_α is the specific surface energy (related to one surface atom), $f_\alpha\ N_0{}^{2/3}$ is the number of surface atoms, and

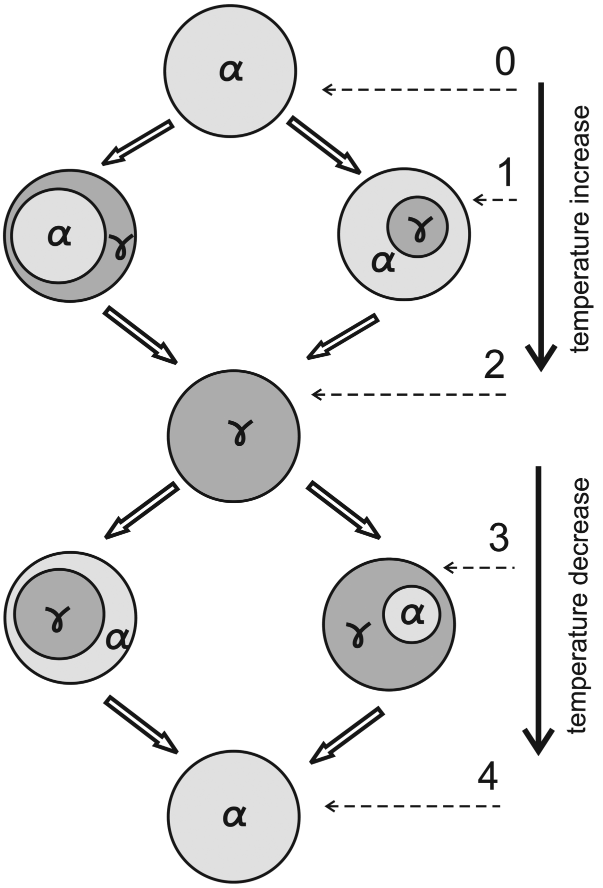

Figure 3. General picture of possible nucleation modes for complete temperature cycle 01234 in the nanopowder. Each particle has two possibilities for the nucleation: homogeneous formation inside the particle and heterogeneous formation on the walls. 01 – two ways of 'forth' transition, 12 – the result of 'forth' transitions: fully transformed γ-phase particles, 23 – 'back' direction with different choices of new transformation ways, 34 – completion of circle.

f_α is the shape factor. In a similar way, one can write the Gibbs free energy of the transformed (into γ-phase) nanoparticle:

$$G_\gamma = N_0 g_\gamma + f_\gamma N_0^{2/3}\sigma_\gamma. \tag{2}$$

Here, the symbol γ refers to the γ-phase.

On the other hand, if such first-order phase transition (from α-phase to γ-phase) takes place it should proceed via nucleation. It means that when the new phase crystal nucleates, the Gibbs free energy dependence has to be written for $\alpha+\gamma$ configuration shown in Figures 1–3.

We get for homogeneous nucleation (configuration 1 in Figure 2a)

$$G_{hm} = N_\alpha g_\alpha + N_\gamma g_\gamma + f_\alpha N_0^{2/3}\sigma_\alpha + f_\gamma N_\gamma^{2/3}\sigma_{\alpha\gamma}, \tag{3a}$$

and for heterogeneous nucleation (configuration 1 or 3 in Figure 2b)

$$G_{ht} = N_\alpha g_\alpha + N_\gamma g_\gamma + f_\gamma N_0^{2/3}\sigma_\gamma + f_\alpha N_\alpha^{2/3}\sigma_{\alpha\gamma}. \tag{3b}$$

Here, N_α and N_γ are the number of atoms in the α- and γ-phases, respectively; g_γ is the bulk energy density (per atom) of the γ-phase; $\sigma_{\alpha\gamma}$ is the specific interfacial energy at the boundary of the α-phase and γ-phase. In addition, one has to take into account the conservation of matter in the considered finite system, i.e.

$$N_\alpha + N_\gamma = N_0. \tag{4}$$

For the following thermodynamic discussion, we need to specify the specific interfacial energy $\sigma_{\alpha\gamma}$ between the two phases. In experiments, $\sigma_{\alpha\gamma}$ is a poorly determined quantity. For Fe system, the qualitative estimations from different experimental data give the relation [18–20]:

$$\sigma_{\alpha\gamma} \approx \left|\sigma_\gamma - \sigma_\alpha\right|.$$

The change in Gibbs free energy ΔG of the nanoparticle related to the formation of a new nucleus is then represented by the bulk driving force for the phase transition g_γ–g_α and surface energy term. For homogeneous nucleation (configuration 1 in Figure 2a) it yields:

$$\Delta G_{hm}(N_\gamma, T) = G_{hm} - G_\alpha = N_\gamma(g_\gamma - g_\alpha) + f_\gamma N_\gamma^{2/3}\sigma_{\alpha\gamma}, \tag{5a}$$

where as for heterogeneous nucleation (configuration 1 or 3 in Figure 2b)

$$\Delta G_{ht}(N_\gamma, T) = G_{ht} - G_\alpha = N_\gamma(g_\gamma - g_\alpha) + f_\gamma([N_0 - N_\gamma]^{2/3} - N_0^{2/3})\sigma_{\alpha\gamma}. \tag{5b}$$

For the following quantitative analysis one has to know the temperature dependence of transformation parameters.

3.2. *Equilibrium statistical distribution*

We introduce a size distribution function $f(N_\gamma, t)$ being equal to the number of new phase nuclei consisting of N_γ atoms at temperature T. At equilibrium, when the temperature T in the nanopowder is fixed, some particles will be in single-phase states and the others – in two-phase states (Figures 1–3). The corresponding number of particles, $f(N_\gamma, T)$, may be found by Boltzmann distribution in statistical mechanical sense.

Again, for homogeneous configurations (1 in Figure 2a)

$$f_{hm}(N_\gamma, T) = \frac{Z}{\sum_{N\gamma=N_{\min}}^{N_{\max}} \exp(-\Delta G_{hm}(N_\gamma, T)/kT)} \cdot \exp(-\Delta G_{hm}(N_\gamma, T)/kT), \tag{6a}$$

and for heterogeneous configurations (1 or 3 in Figure 2b)

$$f_{ht}(N_\gamma, T) = \frac{Z}{\sum_{N\gamma=N_{\min}}^{N_{\max}} \exp(-\Delta G_{ht}(N_\gamma, T)/kT)} \cdot \exp(-\Delta G_{ht}(N_\gamma, T)/kT), \tag{6b}$$

where $N_{\min}$ is the minimal number of atoms in the nuclei, $N_{\max} = N_0$ is the maximal possible number of atoms in each particle, Z is the number of particles in a given nanopowder. The formulae (6) due to the probability factors can be written as: $p_{hm}(N_\gamma, T) = f_{hm}(N_\gamma, T)/Z$, $p_{ht}(N_\gamma, T) = f_{ht}(N_\gamma, T)/Z$ – the probabilities for a given powder to be in a homogeneous or heterogeneous state, respectively, with nuclei consisting of N_γ atoms at temperature T.

3.3. *Volume fraction of the new phase*

The main task we would like to solve is to describe the volume fraction of the new phase during the temperature change in the noninteracting nanoparticle ensemble. In this case, the thermodynamic observables of the system become averaged over the equilibrium distribution Equation (6). From this, one can find the equilibrium value for the volume fraction $\rho(T)$ of the new phase at any fixed T by averaging procedure. That is for homogeneous configurations (1 in Figure 2a) one can calculate:

$$\rho_{hm}(T) = \frac{\sum_{N_\gamma=N_{\min}}^{N_{\max}} N_\gamma \cdot f_{hm}(N_\gamma, T)}{N_0 Z} = \frac{\sum_{N_\gamma=N_{\min}}^{N_{\max}} N_\gamma \cdot p_{hm}(N_\gamma, T)}{N_0}, \tag{7a}$$

and for heterogeneous configurations

$$\rho_{ht}(T) = \frac{\sum_{N_\gamma=N_{\min}}^{N_{\max}} N_\gamma \cdot f_{ht}(N_\gamma, T)}{N_0 Z} = \frac{\sum_{N_\gamma=N_{\min}}^{N_{\max}} N_\gamma \cdot p_{ht}(N_\gamma, T)}{N_0}. \tag{7b}$$

Actually, we shall compute the value of the volume fraction $\rho(T)$ at fixed different temperatures assuming different sizes N_0 of the particles in the ensemble where the transition due to different nucleation modes occurs.

3.4. *Specification of the parameter values*

We assume in agreement with experimental data that $\sigma_{\alpha\gamma}$ is only slowly dependent on temperature and we neglect such dependence. In contrast to $\sigma_{\alpha\gamma}$, we use a quadratic temperature dependence of the bulk driving force for the phase transition $g_\gamma - g_\alpha = AT^2 + BT + C$, where the parameters A, B and C are fit constants, which can be determined from the experimental data. Such relation is the direct consequence of a Taylor expansion with respect to temperature, including second order terms and it can be employed, in particular, for the description of a polymorphic transforming Fe system discussed here ([18] and references therein). Using the experimental data, we approximated the bulk driving force by the dependence (Shirinyan et al. 2001):

$$\Delta g = g_\gamma - g_\alpha = k(-0.00365 \cdot T^2 - 10.3952 \cdot T + 7191.1424)J.$$

It is well known that in the bulk solid state pure Fe can exist in three crystallographic modifications: α-phase (bcc) and γ-phase (fcc), δ-phase (also called by some authors α-phase, bcc). The α-Fe phase appears within the temperature interval $T < 1183$ K. For $1183\,\text{K} < T < 1665$ K, the γ-Fe is more preferable and for $T > 1665$ K until the melting point the δ-phase appears. It means that in the bulk case the energy of α-Fe at $T < 1183$ K is lower than the γ-Fe phase one. In the results presented here, we deal with the case of α-Fe to γ-Fe phase transformations in the vicinity of 1183 K. The corresponding set of parameters of the Fe system have been obtained and employed in the thermodynamic computations: atomic density $n = 8.58 \times 10^{28}\,\text{m}^{-3}$, $\sigma_{\alpha\gamma} = 0.04\,\text{J m}^{-2}$, $\sigma_\alpha = 2.21\,\text{J m}^{-2}$, $\sigma_\gamma = 2.17\,\text{J m}^{-2}$, $f = 2.486 \times 10^{-19}$ J, $N_{\min} = 7$ ([18, 19] and references therein, [20–22]).

4. Size-induced thermal hysteresis

One can expect some interesting possibilities if the nanoparticles transform due to different modes. Generally, different possibilities (Figures 2) give different values of new phase volume fractions (7a, 7b) at the same initial set of parameters.

In the common case (Figure 3) we must calculate all possibilities for a new phase formation. The nucleation mode can change the very result of phase transformation. The mechanism of nucleation has an influence on the nucleation barrier height, on probability of transformation. In this respect, the problem is similar to the competitive formation of two phases [23,24]. In another words, if two modes (or phases) have the driving force to nucleate, the competition between them is inevitable. The question of different phases appearing in bulk materials was formulated by Ostwald in the end of 19th century due to empirical research. According to Oswald's rule, instead of thermodynamically most stable phase modifications, the nearest possible metastable ones are initially formed. In other words, the phase with the smallest potential energy difference in the ambient phase has the highest chance to be initially formed. Later, in the framework of the classical theory of nucleation, Stranski and Totomanow introduced a theoretical concept for both the fulfilment and the exceptions of Ostwalds' rule when applied to problems of phase formation [25]. In such a way, the competition in the formation of critical clusters of different modifications, possible under the given thermodynamic conditions, the maximal nucleation rate determines the dominant appearance of the corresponding structure. As a consequence of this kinetic rule the maximal value of the nucleation barrier is considered as being responsible for the competition of different phases to be formed. Thus, in the framework of the classical theory of nucleation, the nucleation probability, p, depends on the kinetic description and is qualitatively proportional to: $p \sim \exp\{-\Delta G^*/kT\}$ [26–28]. Here ΔG^* is the nucleation barrier. Obviously, in our case the following question appears: Which mode is kinetically possible? Or what kinetic mechanism gives the priority to one mode with respect to the other one? But it must be recalled that in this article, the kinetic aspect is not considered. The corresponding analysis is now in progress and will be presented elsewhere.

It is worth noting that under the thermodynamic approach there must be fulfilment of the ergodic hypothesis. It means that under the infinite time of an observation all mentioned modes should be realized eventually. Thus, only the kinetic factors (coefficients) can restrict the more or less simultaneous appearance of all mentioned modes. If such a kinetic effect takes place then one can say that the whole class of situations of our problem may be separated into two (or more) subclasses of relatively independent situations. Let us estimate the conditions of such possibility for our problem due to the kinetic limitations. If α-Fe transforms directly to γ-Fe by homogeneous configurations (1 in Figure 2a) then the incubation time τ_1 for such transition is proportional to the corresponding energy barrier in the following way: $\tau_1 \sim \exp\{\Delta G_{hm}(N_\gamma, T)/kT\}$. The similar reasons for configuration 1 in Figure 2b yields the incubation time τ_2 of direct heterogeneous formation: $\tau_2 \sim \exp\{\Delta G_{ht}(N_\gamma, T)/kT\}$. We must also calculate the possibility of new redistributions of the number of particles appeared from already formed homogeneous or heterogeneous configurations $\tau_3 \sim \exp\{[\Delta G_{hm}(N_\gamma, T) - \Delta G_{ht}(N_\gamma, T)]/kT\}$ and $\tau_4 \sim \exp\{[\Delta G_{ht}(N_\gamma, T) - \Delta G_{hm}(N_\gamma, T)]/kT\}$. Under the kinetic restriction the division on independent subclasses (modes) occurs when: $\tau_3 > \tau_1$, $\tau_3 > \tau_2$ and $\tau_4 > \tau_1$, $\tau_4 > \tau_2$.

Let us consider the transformation in more detail and assume at first that each of the mentioned modes (Figure 2) can exist independently and then investigate the case of competitive phase formation by both modes (Figure 3).

Mode 2a: Homogeneous nucleation at 'forth' and 'back' phase transitions (Figure 2a). More precisely, now we deal with homogeneous nucleation of γ-Fe inside the α-Fe particle during the 'forth' phase transition and homogeneous formation of α-Fe inside the γ-Fe particles during the 'back' phase transition. The change in the volume fraction of new born γ-Fe at different fixed temperatures as obtained by the thermodynamic method Equation (7) is presented in Figure 4. It clearly exhibits a new result, a size-induced thermodynamic hysteresis of the α-Fe $\rightarrow$ γ-Fe $\rightarrow$ α-Fe transformation. Figure 4a shows the different hysteresis loops in the volume fraction – temperature diagram.

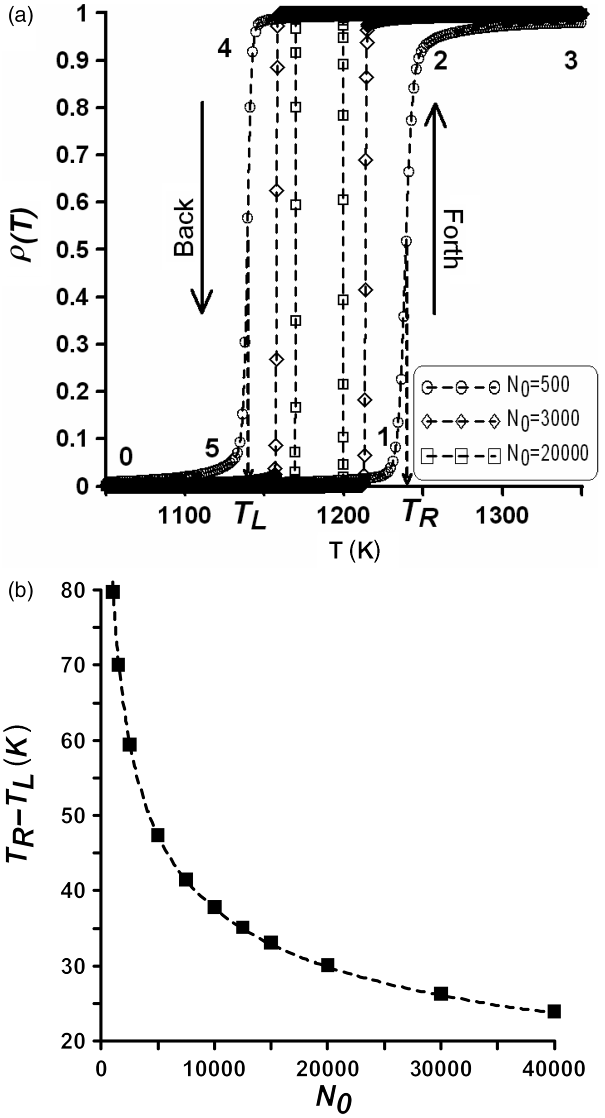

Figure 4. (a) Effect of temperatures between 950 and 1350 K on hysteresis loops in mode 2a for the different number of atoms in the Fe-particles: o – $N_0 = 500$, ◇ – $N_0 = 3000$, □ – $N_0 = 20{,}000$. All points represent the equilibrium values $\rho(T)$ for each fixed temperature. (b) Effect of size on the width of hysteresis: the dash line is the approximation formula for points (■): $T_R - T_L = 1183 \cdot 0.685 \cdot N_0^{-1/3}$.

Our thermodynamic model shows that the width and shapes of hysteresis loops depend on sizes N_0. In particular, we traced the influence of the system's size N_0 on the hysteresis loop.

In this model the existence of the hysteresis becomes clear if one considers the value of the volume fraction $\rho(T)$ and compare the corresponding results for the 'forth' and 'back' paths. For this mode at the 'forth' transformation we have $\rho(T)$ which is equal to the $\rho_{hm}(T)$ found from Equation (7a) whereas at the 'back' transition $\rho(T)$ is characterized by the $\rho_{ht}(T)$ from (7b). Thus, at every fixed temperature T the values $\rho_{hm}(T)$ and $\rho_{ht}(T)$ are different.

In more detail, one can see that the step-by-step temperature change in a Fe-nanopowder, $950\,\mathrm{K} \rightarrow 1350\,\mathrm{K} \rightarrow 950\,\mathrm{K}$, leads to a loop-like $\rho(T)$ curve – the path 0123450 in Figure 4a. Hereby, one may distinguish between the following stages: 01 – supersaturated single-phase states (parent α-Fe phase) of the nanopowder (see also Figures 1 and 2b); 12 – phase transition from the point 1 of single-phase states to two-phase states (parent α-Fe phase + new γ-Fe phase) at point 2 (this event indicates nucleation) due to two-phase α-Fe + γ-Fe phase states; 23 – change in two-phase states of a nanopowder in the vicinity of point 2 into single γ-Fe phase states at point 3; 34 – cooled γ-Fe-phase states; 45 – back transition from γ-Fe phase states at point 4 to α-Fe + γ-Fe states at point 5 and then to α-Fe phase states at point 0.

It is worth noting that we have no rates of temperature change, and all the results are found by calculations of formulae (6, 7) for the equilibrium states. For the first time, as far as we know, the thermal thermodynamic hysteresis is shown.

Let us introduce the phase transition criterion in the thermodynamics of considered transformation. For this we assume that a phase transition does proceed when half of the volume is transformed, that is when $\rho(T) = 0.5$ is reached. This criterion determines the value of the transition temperature T_L at the left branch of the hysteresis loop and similarly, T_R, at the right branch of it. The difference $T_\mathrm{R} - T_\mathrm{L}$ is the width of hysteresis loop, which is a function of size (Figure 4b). It is turned out that the greater the size of a system, the smaller the effective width of the hysteresis loop. For the first time, as far as we know, the tendency of narrowing and disappearing of hysteresis loop with an increase in the size of a system is observed here in the thermodynamics of a structural transformation. Also, we see that the greater the sizes of a system, the sharper the branches and jumps of $\rho(T)$ curves and, hence, the more exact the values of the transition temperatures.

In the usual meaning, the hysteresis is assumed as the kinetic phenomena and it is related to the rate of system's state parameters change under the external parameters changing with time. It is argued here that there exists the hysteresis related to the choice of multiple optimal states of a nanosystem at fixed external parameters. The thermodynamic hysteresis arose from the nonsymmetry of the transforming path of a system with respect to the initial conditions that is due to the dependence of the phase transformation on the mechanisms of nucleation of a new phase which are crucial for nanosystems. We see that it is required to differentiate the kinetic hysteresis and thermodynamic hysteresis and, also, usual language of the phase transition theory becomes restricted in this case. One can say that small size of a system helps us to see this peculiarity and visualizes the understanding of first order phase transformations with respect to those for bulk materials.

Mode 2b: Heterogeneous nucleation at 'forth' phase transition and homogeneous formation at 'back' phase transition (Figure 2b). Let us look at the case of heterogeneous nucleation of γ-Fe at the wall of the α-Fe particle during the 'forth' phase transformation and homogeneous formation of α-Fe inside the γ-Fe particle during the 'back' phase transformation. By doing so we will find that there is no hysteresis loop, the $\rho(T)$ curves in both the directions coincide. This is due to the symmetry of both paths with respect to the initial α-Fe state: the value $\rho(T)$ in both the directions are equal to the $\rho_{ht}(T)$ and found by the same distributions (6b, 7b).

If one extrapolates arguments concerning the phase transition criterion onto equilibrium volume fraction of the new phase, $\rho = 0.5$, for mode 2b, then one obtains the temperature of this transition, T_{tr}, related to the equilibrium distribution equations (6b, 7b). Generally speaking T_{tr} is defined from the thermodynamically averaged value $\rho(T)$ and due to this fact it represents the averaged transition temperature and also depends on the size of the particles in nanopowder (Figure 5). The approximation of corresponding points in Figure 5 by one curve gives the fit function:

$$T_{tr} = 1183(1 - 0.31/N_0^{-1/3}) \text{ or } T_{tr} = T_\infty(1 - 4.27 \times 10^{-11}/R),$$

where R is the radius of the nanoparticles.

Mode 3: All nucleation possibilities at 'forth' and 'back' phase transitions (Figure 3). Under the chosen conditions, it is assumed that the transformation takes place simultaneously due to both mentioned modes.The probability factors are:

$$Z_{hm}(N_\gamma, T) \equiv \frac{\exp(-\Delta G_{hm}(N_\gamma, T)/kT)}{\sum_{N\gamma=N_{\min}}^{N_{\max}} \{\exp(-\Delta G_{ht}(N_\gamma, T)/kT) + \exp(-\Delta G_{hm}(N_\gamma, T)/kT)\}} \tag{8}$$

for the homogeneous configurations (Figure 3) and

$$Z_{ht}(N_\gamma, T) \equiv \frac{\exp(- \Delta G_{ht}(N_\gamma, T)/kT)}{\sum_{N\gamma=N_{\min}}^{N_{\max}} \{\exp(- \Delta G_{ht}(N_\gamma, T)/kT) + \exp(- \Delta G_{hm}(N_\gamma, T)/kT)\}} \tag{9}$$

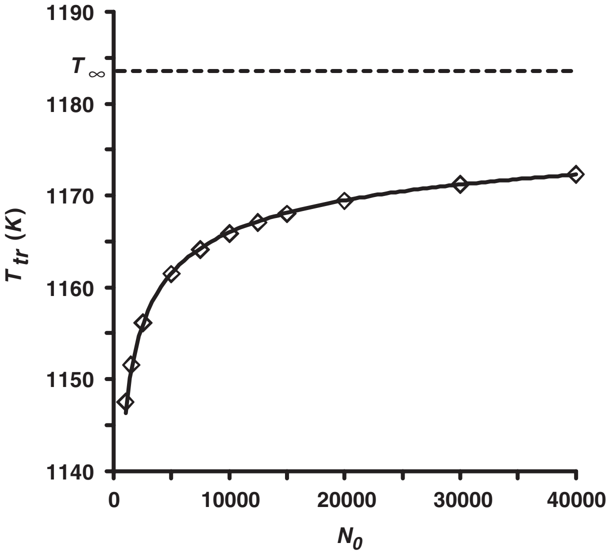

Figure 5. Size-induced temperature dependences of the phase transition in Fe-nanopowder found by transition criterion: points (◇) define values T_{tr} from number of atoms N_0 in each particle of the nanopowder, the dash line denotes the phase transition temperature $T_\infty = 1183$ K in bulk material. The solid line is the extrapolation formula: $T_{tr} = 1183(1 - 0.31/N_0^{-1/3})$.

for heterogeneous configurations. Here $Z_{hm}(N_\gamma,T)$ and $Z_{ht}(N_\gamma,T)$ are the probabilities to transform due to homogeneous and heterogeneous mechanism, respectively.

We divide the initial powder into 2 groups proportionally to Z ($Z = Z_{hm} + Z_{ht}$). The value Z_{hm} indicates the number of the particles undergoing homogeneous nucleation whereas Z_{ht} characterizes the number of the particles undergoing the heterogeneous nucleation:

$$Z_{hm} = Z \cdot \sum_{N\gamma = N_{\min}}^{N_{\max}} \{Z_{hm}(N_\gamma, T)\}, \quad Z_{ht} = Z \cdot \sum_{N\gamma = N_{\min}}^{N_{\max}} \{Z_{ht}(N_\gamma, T)\}.$$

Again, calculating the new phase volume fractions $\rho(T)$ in both the directions, we obtain that these values are equal due to the condition that at fixed T each particle has two possibilities for the nucleation: homogeneous formation inside the particle and heterogeneous formation on the walls. In other words, in this mode:

$$\rho(T) = \rho_{hm}(T) + \rho_{ht}(T) = \frac{\sum_{N_\gamma = N_{\min}}^{N_{\max}} N_\gamma \cdot Z_{hm}(N_\gamma, T)}{N_0 Z} + \frac{\sum_{N_\gamma = N_{\min}}^{N_{\max}} N_\gamma \cdot Z_{ht}(N_\gamma, T)}{N_0 Z}. \qquad (10)$$

Hereby, in the thermodynamic limit of infinite time there is no restriction on the new redistributions of the number of particles Z_{hm} and Z_{ht} for each different fixed temperature T. Thus, when both homogeneous and heterogeneous modes coexist and there are no kinetic constraints, the thermodynamic hysteresis becomes absent.

One can investigate which mechanism (homogeneous or heterogeneous one) dominates during the α-Fe to γ-Fe phase transformations by comparing the volume fractions: for homogeneous case – $\rho_{\mathrm{hm}}(T)$, for heterogeneous case – $\rho_{\mathrm{ht}}(T)$. The results shown in Figure 6 characterize the 'forth' transformation in Fe-nanopowder. We see that the thermodynamic limitations are related to the high probability of heterogeneous nucleation

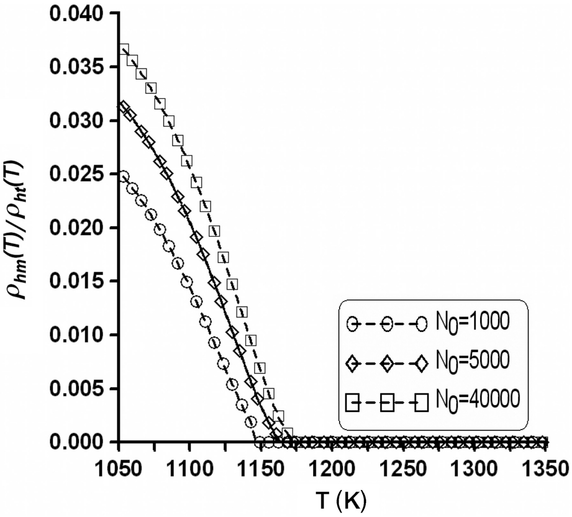

Figure 6. Size-induced temperature dependences of mechanisms of new phase formation in Fe-nanosystem.

of the new γ-Fe phase. Again, the greater the size the more the influence of homogeneous mechanism of phase formation.

5. Discussion and concluding remarks

We presented a thermodynamic analysis and model describing the existence of a size-induced thermal hysteresis for the volume fraction of the new phase. One must differentiate the kinetic hysteresis and thermodynamic hysteresis in the first order phase transition. The width of the thermodynamic hysteresis loop depends on the size of a given system. In particular, the greater the size of a system, the smaller the width of the thermodynamic hysteresis loop showing the tendency to disappear.

The results depend on the symmetry, the possible evolution paths and kinetic constraints on the transition modes. In the symmetrical case and also when both homogeneous and heterogeneous modes coexist the ‘thermodynamic’ hysteresis may be absent. The computations show a size-induced change in critical temperatures of phase transitions in small isolated nanoparticles.

These findings help to understand the kinetic analysis in the CdSe nanostructured system mentioned in the introduction. These experiments turn out to be almost independent of nanocrystal size whereas our previous kinetic model predicts a considerable increase in the width of the hysteresis loop with the increasing particle size [13,14]. It is worth noting that there is a difference between the mentioned problems. We treat the size-induced temperature hysteresis whereas the group of Alivisatos et al. performed size-induced pressure hysteresis experiments. Second, as we showed here, the thermodynamic hysteresis may lead to the decrease in the width of the hysteresis with the increase in the system’s size. In our opinion, in the case of semiconductor CdSe nanocrystals Alivisatos et al. dealt with, the evolution paths for ‘forth’ and ‘back’ transitions may be quite different and it leads to the averaged picture as shown by us in Figure 4a. Our last kinetic calculations (when the external temperature is changed in time) show that kinetic characteristics lay upon thermodynamic ones and it may give the average size-independent results for kinetic hysteresis phenomena. The results depend on the rate of change in external parameters with respect to the rate of change in system’s state parameters. The corresponding analysis will be done in the following article.

Another explanation is based on the opinion that the pressure change leads to the redistribution of grain sizes and the boundaries between grains. In particular, as soon as the mean grain size is above a few nanometres, the melting temperature falls with decrease in grain size and as the mean grain size becomes smaller than a few nanometres, the melting temperatures keep almost constant. The corresponding explanation is based on the ideas that (i) a nanocrystal can be viewed as a composite of a grain boundary phase and embedded grain phase, (ii) with mean grain size decreasing to a certain degree, the grain boundary phase becomes dominant in melting [29]. A similar situation may be the reason for the peculiarities of the CdSe nanosystem.

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