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Hysteresis in the Process of Phase Separation of Nanopowder

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Abstract. The influence of thermodynamic constraints like the size, depletion, surface tension and kinetic constraints like energy barrier for diffusion on nonsteady separation kinetics in binary nanopowder is investigated. Here we present a numeric analysis of size hysteresis and its peculiarities using the standard kinetic equation approach.

1. Introduction

The kinetics of phase transitions in nanofilms or nanoparticles is interesting from theoretical point of view as well as from experimental one. (For example, rapid heating and cooling by laser or needle are used for the preparing of computer disks during which the phase transition appears).

If a nanosystem is quenched into the two-phase region then in addition to size effect the depletion of the surrounding parent phase may occur because of the difference in compositions of the parent phase and 'new born' phase. When one extrapolates this argument to nanomaterials under the different external conditions, one concludes that their thermodynamic and kinetics should differ from the one of bulk material.

In earlier thermodynamic analysis depletion was investigated. It was shown that it results in the existence of critical system volume [1-4]. At the same time the separation kinetics in nanosized systems are not yet well understood. Experimental results on the effect of size on kinetics behaviour of phase transitions in alloys have been obtained in a few works [5].

Recent results on kinetic analysis of first order phase transitions in nanovolumes demonstrate hysteresis phenomena [6]. In present study we will continue to solve this problem. The treated system is a nanopowder of equal size particles. First, we start from the single phase state at high temperature T and let T decrease. Then we stop T at some point, when an alloy is quenched into the two-phase region, and change the direction - increase T with the same rate. The present work is aimed at the study of the kinetic 'decoding' of forth and back transition during the temperature cycling. This analysis is done in the frame of kinetic equation approach. In particular, we study the evolution of the volume fraction of the new phase and illustrate the hysteresis phenomenon in nanopowder related to finite size and depletion effects.

2. Model

According to our simplified model the single spherical nucleus of new intermediate phase will form inside each spherical particle of supersaturated solid solution taken at initial concentration C_0 (Fig. 1) of specie B.

Let us introduce finite rates of temperature changes during the temperature cycling (T will change in time as linear function with constant rate $|dT/dt|$=const for cooling and heating).

First, we decrease the temperature (cooling) starting from high values T at initial single-phase state. Then we stop the temperature at some point when an alloy is quenched into the two-phase region and change the direction - increase the temperature (heating) with the same rate until starting point is reached. Schematically circling (a)→(b), (b)→(a) is presented in Fig 1. The corresponding "kinetic decoding" of these transformations is made for a binary system containing of A and B components. Hereby the new thermodynamically advantageous phase has strong stochiometry (composition in new phase is equal to C_1=0.5, $C_1 \neq C_0$, $C_1 > C_0$). In this case the concentration (and the number N) of component B coincides with the concentration (and the number N) of structure units AB building the new stoichometric phase.

The Gibbs energy per atom for parent and the new phases are taken as follows [6]:

$$\Delta g_o(T,C) = kT\left(C \cdot \ln(C) + (1-C)\cdot \ln(1-C)\right),$$
$$\Delta g_1(T) = \Delta g_1 + \alpha kT\text{ , }(C=C_1). \tag{1}$$

Here α and Δg_1 are parameters determining temperature-dependent behaviour of bulk driving force, k is the Boltzmann constant, T – absolute temperature, $\Delta g_0(T,C)$ is the Gibbs free (mixing) energy of the parent supersaturated phase, $\Delta g_1(T)$ is the Gibbs energy of formation of the new phase 1.

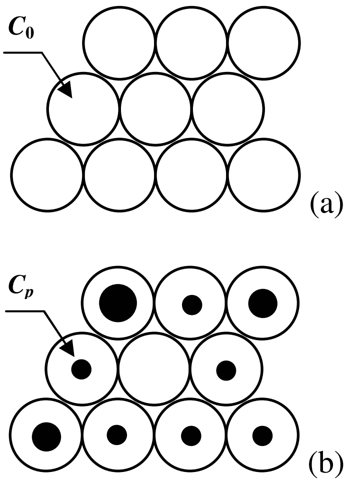

Fig. 1. Schematic representation of separation in nanopowder during the temperature circling: (a) – ensemble of particles of concentration C_0 before transformation, (b) – the same particles after the transformation; C_p – concentration of ambient parent phase after the nucleation.

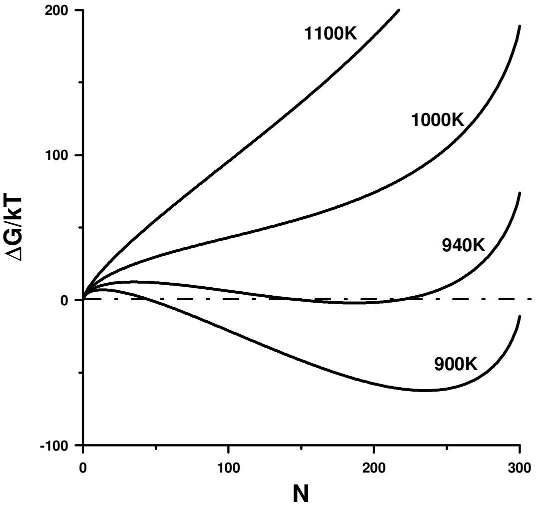

Fig. 2. Gibbs free energy ΔG dependence on the number of structure units N in the nucleus for different temperatures provided other parameters are fixed. Parameters are presented in the text.

The conservation law leads to the depletion of the surrounding parent phase. In two-phase state (case (b) in Fig. 1) the every particle of the nanopowder has the own concentration $C_p \equiv C_p(N)$ in the parent phase:

$$C_p = \frac{C_0 N_0 - N}{N_0 - N/C_1}, \tag{2}$$

where N_0 is the numbers of atoms in the single particle, N is the number of structure units in new phase nucleus.

The change in Gibbs free energy ($\Delta G \equiv \Delta G(N,T) \equiv \Delta G(N)$) of one particle consisting of new phase cluster embedded in the ambient parent phase is defined by:

$$\Delta G(N,T) = \Delta g_1(T)\cdot\frac{N}{C_1} + \Delta g_o\left(T, C_p(N)\right)\cdot\left(N_0 - \frac{N}{C_1}\right) - \Delta g_o(T,C_0)\cdot N_0 + B\left(\frac{N}{C_1}\right)^{2/3}, \tag{3}$$

where $B = 3(4\pi/3)^{1/3}\sigma n^{-2/3}$ is the coefficient of the surface energy contribution taken independent on size N and temperature T, σ is the specific interphase energy on parent phase-nucleus interface. The typical temperature-dependent ΔG curves are presented in Fig. 2 for the given set of parameters: C_0=0.3, C_1=0.5, N_0=1000, $\Delta g_1 = -4.5\cdot 10^{-20}$ J, α=2.3, $B = 3\cdot 10^{-20}$ J.

In the following we shall calculate the size distribution function $f(N,t)$ – the number of droplets of the new phase consisting of N structure units AB at moment t. The evolution of ensemble of clusters formed by nucleation and growth processes may be described by kinetic equation and it reads [2,7]:

$$\frac{\partial f(N,t)}{\partial t} = f(N-1,t)\cdot v_+(N-1) + f(N+1,t)\cdot v_-(N+1) - f(N,t)\cdot\left(v_+(N)+v_-(N)\right). \tag{4}$$

The frequency $v_+(N)$ is the average number of incorporated structure units into a cluster of size N, while $v_-(N)$ indicates similarly the rate of detachment processes. The principle of detailed balancing yields the condition [7]:

$$v_-(N) = v_+(N)\cdot\exp\left(\frac{\Delta G(N)-\Delta G(N-1)}{kT}\right). \tag{5}$$

The value $\Delta G(N)$ is determined by Eq. 3. Further the quantity $v_+(N)$ will be described as $v_+(N) = K\cdot D\cdot C_p\cdot N^{2/3}$ [7]. Hereby the temperature-dependent coefficient of diffusion D of segregating B – specie in the ambient phase in the vicinity of the nucleus of the new phase obeys the Arrhenius law: $D = D_0\cdot\exp(-Q/kT)$ with the activation energy of diffusion $Q\approx 18\,kT_m$ (T_m – melting temperature, T_m=1200 K). So in our next consideration we use new nondimensional variable for time: $\tau = K\cdot D_0\cdot t$.

The conservation of number of particles results in boundary conditions for the cluster size distribution function $f(N,t)$. So one may write:

$$f(N_{\min},\tau) = Z - \sum_{N=N_{\min}+1}^{N_{\max}} f(N,\tau),\quad f(N,\tau=0) = \begin{cases} Z, N = N_{\min} \\ 0, N \neq N_{\min} \end{cases}, \tag{6}$$

where $N_{\min}$ is the minimal number of building units in nuclei, $N_{\max}=N_0C_0$ is the maximal possible number of structure units in each particle, Z is the number of particles in nanopowder. Because of constraint on the number of atoms in the nucleus of new phase 1 the size distribution function on the right boundary $N=N_{\max}$ was taken zero (supply of specie B is absent): $f(N_{\max},\tau)=0$.

The main task of presented kinetic model is to describe the volume fraction ρ of the new phase 1 during the temperature cycling of the isolated nanoparticles ensemble. This value is determined by the formula:

$$\rho = \frac{\sum\limits_{N=N_{\min}}^{N_{\max}} \frac{N}{C_1} f(N,\tau)}{N_0 Z}. \tag{7}$$

Actually, we will show evolution of volume fraction ρ in the process of temperature cycling from high T to low T (see Fig. 2) with fixed constant rate $\upsilon = |dT/d\tau|$, different sizes N_0 of particles, different thermodynamic and kinetic parameters of the system.

When the ensemble of nanosize particles is at equilibrium the probability of fluctuation is given by the theory of thermodynamic fluctuations. The equilibrium distribution function $f_{eq}(N,T)\equiv f_{eq}(N,\tau)$ may be found by Boltzmann dependence [8]. It yields also the equilibrium value of volume fraction ρ_{eq}:

$$f_{eq}(N,T) = \frac{Z}{\sum\limits_{N=N_{\min}}^{N_{\max}} \exp\left(-\frac{\Delta G(N,T)}{kT}\right)}\cdot\exp\left(-\frac{\Delta G(N,T)}{kT}\right),\quad \rho_{eq} = \frac{\sum\limits_{N=N_{\min}}^{N_{\max}} \frac{N}{C_1} f_{eq}(N,\tau)}{N_0 Z}. \tag{8}$$

Here $f_{eq}(N,T)$ coincides with the number of particles in nanopowder in which the new phase nucleus consists of N structure units AB.

3. Effect of Size and Depletion on Hysteresis

Numeric calculations in this paragraph have been realized for next set of parameters: $C_0=0.3$; $C_1=0.5$; $N_{\min}=2$; $Z=10^{10}$; $\Delta g_1=-4.5\cdot10^{-20}$ J; $\alpha=2.3$; $B=3\cdot10^{-20}$ J, $Q=18\,kT_m$, $\upsilon=5\cdot10^{-13}$ K. The number of atoms N_0 in each particle, temperatures T, rates υ, activation energy Q and surface energy coefficient B will be pointed separately in each experiment (if they differ from above mentioned).

Consider the evolution of size distribution function $f(N,\tau)$ and ρ. For finite rate of temperature changes one should observe hysteresis behaviour for ρ presented below. The temperature will change in time with constant rate υ from 1100 K to 800 K and back. Here, at low T, the evolution of $f(N,\tau)$ function becomes very slow process because of the temperature-dependent D (freezing effect).

Let us trace the influence of sizes of the system on hysteresis loop (Fig. 3). The hysteresis shows that the evolution of the size distribution function $f(N,\tau)$ don't keeps pace with respect to the rate of changing of the equilibrium distribution function $f_{eq}(N,\tau)$. Hereby, it is appeared that the greater is the size of a system, the greater is the effective width of the hysteresis loop at the same rate υ. (The less is the size of particles then is the less the effective width of the hysteresis loop.)

For the first time, as far as we know, the tendency to narrowing and disappearing of hysteresis with a decrease of the size of a system (at a given rate of change of external parameters) is observed (Fig. 3).

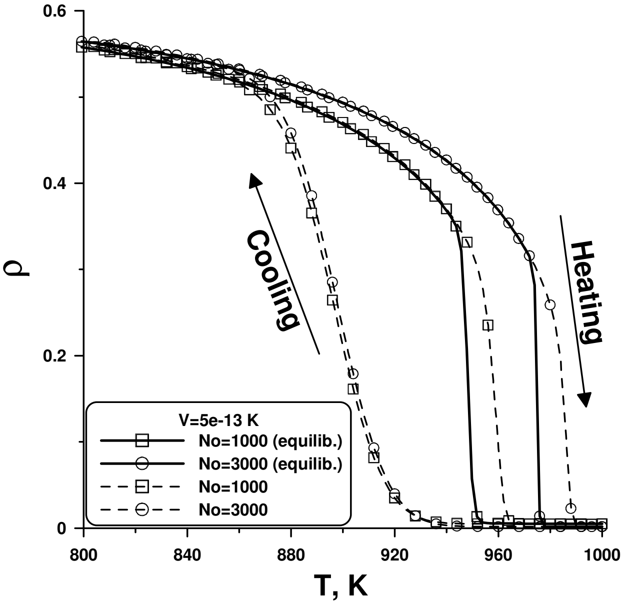

Fig. 3. Effect of size on hysteresis: loops for the fixed rate $\upsilon=5\cdot10^{-13}$ K of temperature cycling between 1100 K and 800 K and different number of atoms in the particles: $N_0=1000$, $N_0=3000$. Solid lines characterize equilibrium statistic values ρ_{eq} which are found by Eq. 8.

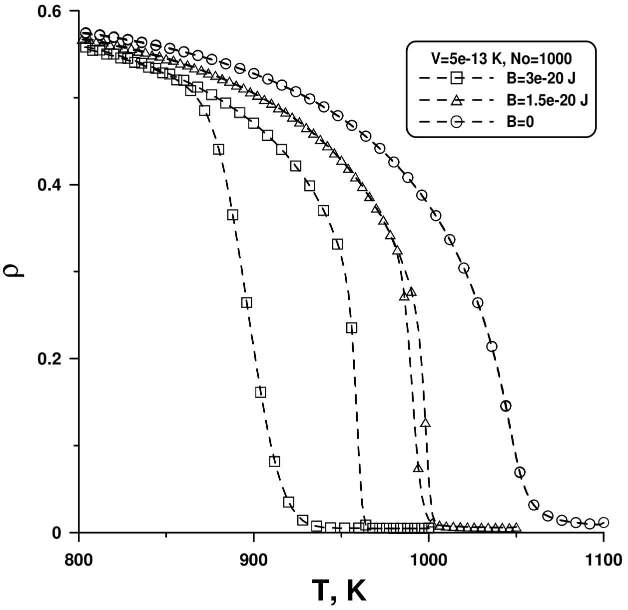

Fig. 4. The demonstration of the influence of thermodynamic factor B (the value of interphase tension) on hysteresis. The simulation is done for the process of temperature cycling at same rate $\upsilon=5\cdot10^{-13}$ K, fixed $N_0=1000$, $Q=18\,kT_m$ and the same other parameters.

In the framework of our model the relaxation processes may be considered as examples of thermodynamic (due to the Gibbs free energy barrier) controlled and kinetic (because of the activation energy Q for the diffusion jump across the parent phase-nucleus interface) controlled processes. The analysis of hysteresis dependence on thermodynamic and kinetic parameters allows one to distinguish the influence of thermodynamics on hysteresis from the influence of kinetics factors on hysteresis. Summarizing we may conclude that, in general, both thermodynamic as well as kinetic factors result in the existence of hysteresis. Here one needs to differentiate two cases: i) case of slow rates υ and ii) case of big rates υ. It is clearly indicated by the results obtained in the present work (Fig. 4 - Fig. 6).

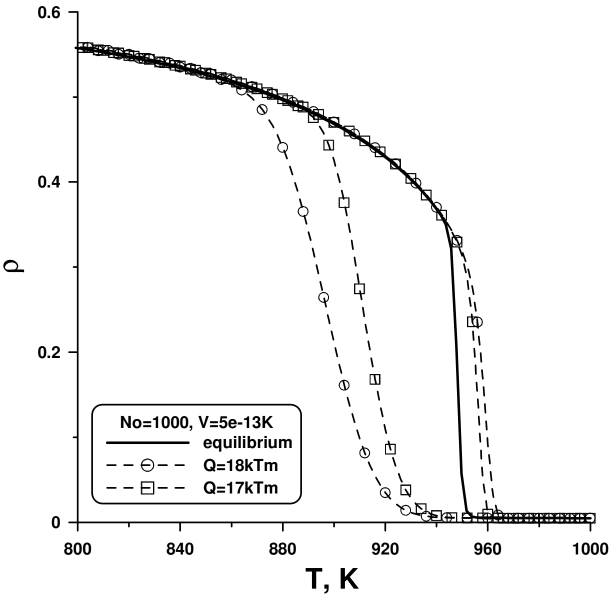

Fig. 5. The influence of the kinetic constraint (activation energy Q) on hysteresis loop at low rate $\upsilon=5\cdot10^{-13}$ K, fixed $N_0=1000$, $B=3\cdot10^{-20}$ J and the same set of other parameters.

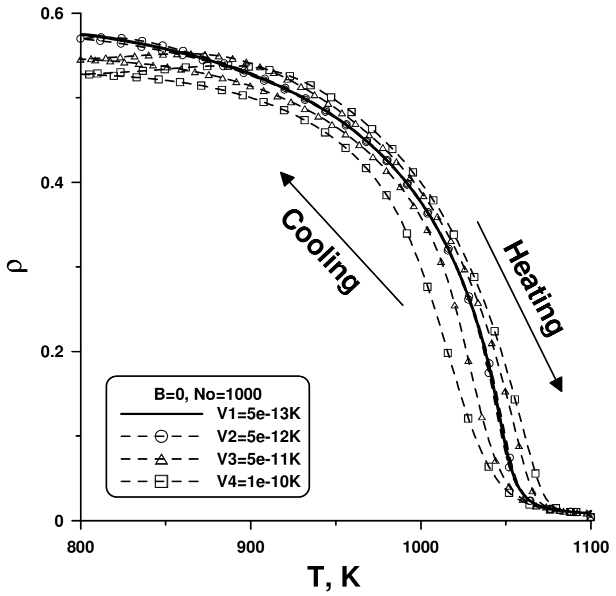

Fig. 6. Freezing effect - the demonstration of the dominating influence of kinetic constraints on hysteresis at low temperatures. The result is presented for different rates υ at $B=0$ ($\sigma=0$), $N_0=1000$ and the same other parameters.

In order to find out the influence of thermodynamic constraints we should establish the different thermodynamic parameters, say, different values of parent phase-nucleus interface tension σ at fixed other ones (Fig. 4). We see that as the value of interphase tension decreases the hysteresis loop narrows. In limit case $\sigma=0$ (and nonzero Q, fixed circling conditions, fixed $N_0=1000$, and fixed other parameters) the hysteresis disappears (Fig. 4) but only for slow rates υ (Fig. 6).

To see the influence of kinetic constraints we should establish the different values of energy barrier Q. Fig. 5 shows the influence of Q on hysteresis loop. Hereby fixed $\upsilon=5\cdot10^{-13}$ K, $N_0=1000$, $B=3\cdot10^{-20}$ J and the same other parameters was used for two different activation energies $Q_1=18\ \mathrm{k}T_m$ and $Q_2=17\ \mathrm{k}T_m$. We see that, the smaller is the Q (the bigger is the D), the less is the width of hysteresis.

If one distinguishes the influence of 'pure' kinetic constraints then one should discuss the case $\sigma=0$. In limit case $\sigma=0$ the nucleation barrier becomes zero (for $B=0$, $\sigma=0$ in Eq. 3). So in the case of slow rate (say, previously chosen $\upsilon=5\cdot10^{-13}$ K), when the evolution of $f(N,\tau)$ function almost coincides with the evolution of equilibrium function $f_{eq}(N,\tau)$, the influence of diffusion hop delay is negligible small. As a consequence of this, the hysteresis in evolution of ρ disappears (Fig. 4). Note that the results in Fig. 4 are presented for the nonzero finite rate ($\upsilon=5\cdot10^{-13}$ K) of change of T; and in the case $\sigma=0$, the evolution path of ρ coincides with the ρ_{eq}. So, for slow rates υ the decrease of Q (leading to increase of D and $\nu_+(N)$) yields the independence of hysteresis loop on kinetic constraints.

At the same time at big rates υ of cycling the existence of hysteresis may take place mainly due to kinetic factor Q. The comparison of situations with big different rates υ and $\sigma=0$ is shown in

Fig. 6. At first, for high T, the diffusion coefficient $D=D_0\cdot\exp(-Q/kT)$ is big. As the temperature decreases the value of D decreases too. That is, at low T the hysteresis curve becomes essentially different from the equilibrium one (‘snake’ or ‘cobra’ shape of hysteresis loop in Fig. 6 for big rates, $\sigma=0$, $N_0=1000$ and the same other parameters) – freezing effect. One can see that the width of hysteresis is different for high T, low T and intermediate ones. In intermediate intervals of T the width (length between the braches) of the hysteresis is thinner. It means that at high temperatures the hysteresis may be related mainly to thermodynamic controlled process but at low temperatures the hysteresis may be related mainly to kinetic controlled process. As one can see from Fig. 6, in the case of slow rate $\upsilon=5\cdot10^{-13}$ K the hysteresis ‘loop’ for ρ coincides with the equilibrium curve ρ_{eq} and shown also in Fig. 4.

4. Summary and Concluding Remarks

The separation kinetics in nanopowder under the temperature cycling is presented. For finite rate of temperature changes one should observe hysteresis behaviour. Such hysteresis is related to the interconnected size and depletion effects and presented in the frame of the kinetic equation approach.

Model shows that the width of hysteresis loop depends on the: i) thermodynamic constraints (like size of a system, number of atoms in the particles, interphase tension) at fixed rate of temperature changes and other parameters; ii) kinetic constraints (energy barrier for diffusion across the parent phase-nucleus interface). In particular, the greater are: i) the size of a system, ii) the interphase tension, iii) the energy barrier for diffusion, iv) the rate of temperature changes, the greater is the width of the hysteresis loop and vice versa. As the mentioned i)-iv) values decrease, the hysteresis loop narrows showing the tendency to disappearing.

The model shows that at high temperatures the hysteresis is related mainly to thermodynamic controlled process and at low temperatures the hysteresis is related mainly to kinetic controlled process.

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