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Size dependence of phase transition thermodynamics of nanoparticles: A theoretical and experimental study

Wenjuan Zhang, Yongqiang Xue *, Qingshan Fu, Zixiang Cui, Shuting Wang

Department of Applied Chemistry, Taiyuan University of Technology, Taiyuan 030024, China

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ABSTRACT

The phase transitions of nanoparticles are involved in almost every field, which present amazing difference compared with the corresponding bulk materials. Indeed despite extensive studies into phase transition temperature, little is known about the relationships between the temperature at the maximum rate of phase transition, the phase transition enthalpy, the phase transition entropy and the particle size. Hence, it is urgent to complete the size dependence of phase transition thermodynamics of nanoparticles. In this paper, the general equation of thermodynamic properties of phase transitions for nanoparticles was presented. Then the relations of the thermodynamic properties of crystal transition and the particle size were derived based on a thermodynamics model of crystal transition. The theoretical results indicate that the particle size of nanoparticles can remarkably influence the phase transition thermodynamics: with the decreasing particle size, the phase transition temperature, the temperature at the maximum rate of phase transition, the phase transition enthalpy and the phase transition entropy decrease, which are linearly related to the reciprocal of particle size. In experiment, the phase transitions from tetragonal to cubic of nano-$BaTiO_3$ with different sizes were determined by means of Differential Scanning Calorimetry (DSC); then the regularities of influence of particle size on the phase transition thermodynamics were obtained. The experimental results are consistent with the above relations. The phase transition theory provides a quantitative description of phase behavior of nanoparticles.

1. Introduction

The phase transition plays a central role in a wide variety of chemical processes. Consideration of phase transitions has typically focused on solid –liquid phase transition [1–3], whereas relatively little attention has been paid to the question of size dependence of crystal phase transition. Although there exist experimental data on the phase transition behavior [4,5], little is known about the quantitative relationships between the thermodynamic properties of crystal phase transition of nanoparticles and the particle size. Therefore, study on thermodynamics of crystal phase transition in nanoscale is vital from the theoretical as well as the practical point of view, which can provide theoretical and practical value for the control of the crystalline phase and the further development of new phase transition materials.

Presently, there are some studies devoted to investigating the particle size effects on the crystal transition of nanoparticles. Zhong et al. [6–9] discussed the size-driven phase transition of $BaTiO_3$ and $PbTiO_3$ by using a Landau-type phenomenological theory and the results show that phase transition temperature, heat and latent heat decrease with particle sizes decrease; the phase transition entropy was obtained by $\Delta S = \Delta Q/T_c$. Köferstein et al. [10] studied the phase transition enthalpy from tetragonal to cubic for $CuFe_2O_4$ and the results suggest that the phase transition enthalpy decreases with the decrease of particle size: ranges from 1020 $J \cdot mol^{-1}$ of 36 nm to 1229 $J \cdot mol^{-1}$ of 96 nm. Prabhu et al. [11] studied the phase transition temperature from tetragonal to cubic for $CuFe_2O_4$ (15 nm, 50 nm and bulk) and the results indicate that the phase transition temperature decreases with the decrease of particle size. Jiang et al. [12] studied the phase transition entropy from tetragonal to cubic for nano-$PbTiO_3$ and the results demonstrate that the phase transition entropy decreases with the decrease of particle size.

Nevertheless, the theory of phase transition thermodynamics of nanoparticles and the quantitative regularities of influence of particle size on crystal transition thermodynamic properties have not been reported yet.

In this account, our group presents a general theory of phase transition, developed over the past decade. In this paper, the general equation of phase transition thermodynamics of nanoparticles was derived by defining the surface chemical potential and the relations between thermodynamic properties of crystal transition and particle size were derived based on a thermodynamics model of crystal transition of nanoparticles. Furthermore, the theoretical relationship of temperature at the maximum rate of phase transition and particle size was derived

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* Corresponding author.
E-mail address: xyqlw@126.com (Y. Xue).

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for the first time. In experiment, the crystal transition of nano-BaTiO$_3$ was taken as a system, the regularities of particle size effect on the phase transition thermodynamic quantities were summarized, respectively.

2. The phase transition thermodynamics theory of nanoparticles

The chemical potential of a dispersed phase is composed of that of the bulk phase and the surface phase, it is shown as follows,

$$\mu = \mu^b + \mu^s \tag{1}$$

And the surface chemical potential was defined as [13],

$$\mu^s \equiv \left(\frac{\partial G^s}{\partial n}\right)_{T,p} = \sigma\left(\frac{\partial A}{\partial n}\right)_{T,P} \tag{2}$$

where σ, A and n are the surface tension, the surface area, and the amount of substance of the dispersed phase, respectively.

When dispersed phase α of pure substance turns into dispersed phase β, the change in molar Gibbs energy can be written as,

$$\Delta_\alpha^\beta G_\mathrm{m} = \mu_\beta - \mu_\alpha = \Delta_\alpha^\beta G_\mathrm{m}^\mathrm{b} + \sigma_\beta\left(\frac{\partial A_\beta}{\partial n_\beta}\right)_{T,p} - \sigma_\alpha\left(\frac{\partial A_\alpha}{\partial n_\alpha}\right)_{T,p} \tag{3}$$

where $\Delta_\alpha^\beta G_\mathrm{m}^\mathrm{b}$ is the change in molar Gibbs energy of the phase transitions for the bulk substance from phase α to β, i.e. $\Delta_\alpha^\beta G_\mathrm{m}^\mathrm{b} = \mu_\beta^b - \mu_\alpha^b$.

Applying the Gibbs-Helmholtz equation to phase transition, the Eq. (4) can be obtained,

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta_\alpha^\beta G_\mathrm{m}}{T}\right)\right]_p = -\frac{\Delta_\alpha^\beta H_\mathrm{m}}{T^2} \tag{4}$$

Substituting Eq. (3) into Eq. (4), the general equation of phase transition enthalpy can be obtained,

$$\begin{aligned}\Delta_\alpha^\beta H_\mathrm{m} = \Delta_\alpha^\beta H_\mathrm{m}^\mathrm{b} &+ \left(\frac{\partial A_\beta}{\partial n_\beta}\right)_{T,p}\left[\sigma_\beta - T\left(\frac{\partial \sigma_\beta}{\partial T}\right)_p\right] - T\sigma_\beta\left[\frac{\partial}{\partial T}\left(\frac{\partial A_\beta}{\partial n_\beta}\right)_{T,p}\right]_p \\ &- \left(\frac{\partial A_\alpha}{\partial n_\alpha}\right)_{T,p}\left[\sigma_\alpha - T\left(\frac{\partial \sigma_\alpha}{\partial T}\right)_p\right] + T\sigma_\alpha\left[\frac{\partial}{\partial T}\left(\frac{\partial A_\alpha}{\partial n_\alpha}\right)_{T,p}\right]_p\end{aligned} \tag{5}$$

where $\Delta_\alpha^\beta H_\mathrm{m}^\mathrm{b}$ is the molar enthalpy of the phase transitions of bulk substance.

Taking the partial derivative of thermodynamic basic formula against T, the phase transition entropy can be expressed as,

$$\Delta_\alpha^\beta S = -\left(\frac{\partial \Delta_\alpha^\beta G}{\partial T}\right)_p \tag{6}$$

Substituting Eq. (3) into Eq. (6), the general equation of phase transition entropy can be derived as follow,

$$\begin{aligned}\Delta_\alpha^\beta S_\mathrm{m} = \Delta_\alpha^\beta S_\mathrm{m}^\mathrm{b} &- \left(\frac{\partial A_\beta}{\partial n_\beta}\right)_{T,p}\left(\frac{\partial \sigma_\beta}{\partial T}\right)_p - \sigma_1\left[\frac{\partial}{\partial T}\left(\frac{\partial A_\beta}{\partial n_\beta}\right)_{T,p}\right]_p \\ &+ \left(\frac{\partial A_\alpha}{\partial n_\alpha}\right)_{T,p}\left(\frac{\partial \sigma_\alpha}{\partial T}\right)_p + \sigma_\alpha\left[\frac{\partial}{\partial T}\left(\frac{\partial A_\alpha}{\partial n_\alpha}\right)_{T,p}\right]_p\end{aligned} \tag{7}$$

where $\Delta_\alpha^\beta S_\mathrm{m}^\mathrm{b}$ is the molar entropy of the phase transitions of bulk substance.

When the two phases in the dispersed system are in equilibrium, $\Delta_\alpha^\beta G_\mathrm{m} = 0$, Thus,

$$\Delta_\alpha^\beta G_\mathrm{m}^\mathrm{b} = \sigma_\alpha\left(\frac{\partial A_\alpha}{\partial n_\alpha}\right)_{T,p} - \sigma_\beta\left(\frac{\partial A_\beta}{\partial n_\beta}\right)_{T,p} \tag{8}$$

At the phase transition temperature, the relation of the thermodynamic properties of the phase transition for bulk phase is

$$\Delta_\alpha^\beta G_\mathrm{m} = \Delta_\alpha^\beta H_\mathrm{m} - T\Delta_\alpha^\beta S_\mathrm{m} \tag{9}$$

A general equation of phase transition temperature T_c can be obtained by the simultaneous Eqs. (8) and (9),

$$T_c = \frac{\Delta_\alpha^\beta H_\mathrm{m}^\mathrm{b}}{\Delta_\alpha^\beta S_\mathrm{m}^\mathrm{b}} + \frac{1}{\Delta_\alpha^\beta S_\mathrm{m}^\mathrm{b}}\left[\sigma_\beta\left(\frac{\partial A_\beta}{\partial n_\beta}\right)_{T,p} - \sigma_\alpha\left(\frac{\partial A_\alpha}{\partial n_\alpha}\right)_{T,p}\right] \tag{10}$$

It can be seen from the Eq. (10) that the phase transition temperature of a dispersed system depends on not only the properties of the bulk phase ($\Delta_\alpha^\beta H_\mathrm{m}^\mathrm{b}$ and $\Delta_\alpha^\beta S_\mathrm{m}^\mathrm{b}$) but also the properties of the surface phase (the interfacial tensions and the specific surface areas of the two phases).

Based on the general equation of phase transition of nanoparticles and in combination of a thermodynamics model of crystal transition, the relations of the thermodynamic properties of the crystal transition with the particle size were derived, respectively.

The crystal transition begins on the surface of nanoparticles [14]. Assume that the phase transition shell (β phase) with width t surrounds uniformly the solid core. When the phase transition is in equilibrium, the radii of the solid core and the phase transition shell are r_α and r_β, respectively. The schematic diagram of the crystal transition model is as follows (Fig. 1).

For spherical nanoparticles,

$$\left(\frac{\partial A_\alpha}{\partial n_\alpha}\right)_{T,p} = \frac{2V_\alpha}{r_\alpha} \tag{11}$$

where $\frac{4}{3}\pi r_\alpha^3\rho_\alpha + \frac{4}{3}\pi t^3\rho_\beta = \frac{4}{3}\pi r_\beta^3\rho_\alpha$ is the molar volume of α phase of nanoparticles.

The total mass in the phase transition process is constant, therefore

$$\frac{4}{3}\pi r_\alpha^3\rho_\alpha + \frac{4}{3}\pi\left(r_\beta^3 - r_\alpha^3\right)\rho_\beta = \frac{4}{3}\pi r^3\rho_\alpha \tag{12}$$

where r is the radius of nanoparticle before phase transition, ρ_α and ρ_β are the densities of the solid core and the phase transition shell, respectively.

Since

$$A_\beta = 4\pi {r_\beta}^2 \tag{13}$$

$$n_\beta = \frac{4}{3}\pi\left(r_\beta^3 - r_\alpha^3\right)/V_\beta \tag{14}$$

where V_β is the molar volume of β phase of nanoparticles.

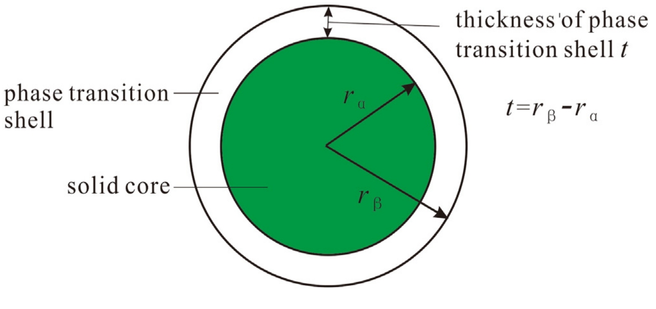

Fig. 1. Phase transition model.