

Size-Dependent Enthalpy of Condensation

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Received: June 6, 2006; In Final Form: July 13, 2006

A thermodynamic model for the size dependence of enthalpy of condensation, ΔH_{con} , is discussed. The model is valid over a range of radii where the arrangement of surface layer and surface tension remain invariable; it provides a way of calculating enthalpy and entropy changes and equilibrium vapor pressures. The difference between ΔH_{con} for two liquid bodies of the same chemical nature is equal to the variation of the autoadsorption energies on their surfaces.

Introduction

An abundance of scientific data is now available to make useful comparisons between nanosize materials and their counterpart microscale or bulk materials. The fundamental physical and biological properties of materials are remarkably altered as the size of their constituent grains decreases to a nanometer scale. These novel materials offer unique and entirely different electrical, optical, mechanical, magnetic, and catalytic properties compared with conventional micro- or millimeter-size materials.^{1–3}

Experimental facts show that the reduction of body sizes leads to the change of thermodynamic properties. For example, it is becoming commonplace to observe unusual phases when “ordinary” materials are fabricated in a nanocrystalline form.^{4–8} One particular phenomenon—particle-size-dependent melting point—occurs when the particle size is of the order of nanometers.^{9,10} Computational simulation work and experimental studies have shown a cluster-dependent depression of the latent heat of fusion^{10,11} and cohesive energy.¹² The size-dependence of the chemical potential of metal atom particles has been observed.¹³ Physical models for the size-dependent heat of fusion and formation enthalpy have been established on the basis of the thermodynamic approach, which seems to be consistent with the experimental results on nanocrystals.^{14–16} The phenomenological models predict either the existence of a quasi-liquid layer covering the surface of the particle below its equilibrium melting temperature or the nucleation and growth of a liquid layer at a surface.^{17–22} However, as pointed out by Lia et al.,¹⁰ it is not reasonable to think that studies restricted to the melting point could lead to a comprehensive understanding of the thermodynamics of nanosized systems. The crystal structure and specific surface properties of solids make the interpretation of experimental data more complicated, and a keen insight into the thermodynamics on the nanoscale could be more readily gained by the consideration of nanodroplets.

In recently published articles,^{23,24} a hypothesis was put forward that the energetic effect of translation of a molecule from an adsorption site on a liquid surface to the bulk volume is independent of body geometry. The hypothesis forms a basis of the thermodynamic theory of the size dependence of enthalpy of condensation, ΔH_{con} . The physical reasoning leads to the conclusion that the difference between ΔH_{con} for two liquid bodies, ΔH_{db} , of the same chemical nature is equal to the variation of the autoadsorption energies, $\Delta\epsilon_{\text{bd}}^*$, on their surfaces:

$$\Delta H_{\text{db}} \equiv \Delta H_{\text{con(b)}} - \Delta H_{\text{con(d)}} \cong -\Delta\epsilon_{\text{db}}^* \equiv \Delta\epsilon_{\text{bd}}^* \quad (1)$$

Here the subscripts b and d denote a bulk liquid and droplets, respectively, and the subscript db refers to the difference of parameters related to the bulk liquid and droplets. Here $\Delta\epsilon_{\text{db}}^* \equiv \epsilon_{\text{b}}^* - \epsilon_{\text{d}}^*$ is the difference of energies of autoadsorption. The term “autoadsorption” refers to adsorption of vapor on the surface of its own condensed phase. For a bulk liquid, the energy of autoadsorption on its surface ϵ_{b}^* is equal in magnitude to the total surface energy usually labeled as E_{s} , but the droplet curvature causes the energy to be reduced so that the difference between ϵ_{b}^* and ϵ_{d}^* is equal to

$$\Delta\epsilon_{\text{db}}^* = E_{\text{s}} - E_{\text{s}} \frac{\epsilon_{\text{sp}}^*}{\epsilon_{\text{slab}}^*} \equiv E_{\text{s}} \lambda \quad (2)$$

where λ is the geometrical factor:

$$\lambda = 1 - \frac{\epsilon_{\text{sp}}^*}{\epsilon_{\text{slab}}^*} \quad (3)$$

Here ϵ_{sp}^* and ϵ_{slab}^* are the Lennard-Jones contributions to the energy of autoadsorption on the spherical droplet surface and to that on the planar surface simulated by a semi-infinite slab. The value of ϵ_{sp}^* , being the function of radii, determines the effect of radii on ΔH_{db} . Substituting ΔH_{db} in the Clausius–Clapeyron equation gives the equilibrium pressures over droplets, p ,

$$RT \ln \frac{p}{p_{\text{s}}} = E_{\text{s}} \lambda \quad (4)$$

where p_{s} is the saturation pressure of the bulk liquid.

Although the basic idea that the energetic effect of a molecular translation from a surface adsorption site to the bulk volume is independent of the body geometry is the starting point for the development of the quantitative theory, it has not been proved. The purposes of this work are the following: (1) to prove the underlying hypothesis; (2) to outline the region of validity of the theory and compare it with the Kelvin equation.

Condensation Heat

Consider condensation of vapor on droplets and bulk liquids. Our objective is to calculate the difference between enthalpy of condensation on the surface of a bulk liquid, on one hand, and ΔH_{con} on the surface of the droplet of the same chemical nature, on the other hand. These values will be compared at

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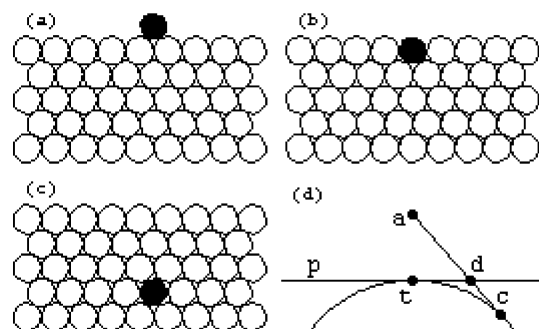


Figure 1. Steps of condensation and the effect of geometry on autoadsorption: (a) molecule (black disk) from the gas phase adsorbs on the liquid surface; (b) adsorbate penetrates in the surface layer; (c) molecule from the surface layer penetrates in the bulk liquid; (d) comparison of the autoadsorption energies when the molecule located on the point *a* is adsorbed either on a planar surface represented by the line *p* or on a convex droplet surface depicted by the circular arc. The separations *ac* between adsorbate *a* and points of a convex surface *c* are greater than the distances *ad* from the planar surface *p*, except for the tangential point *t*; as a consequence, the energy of adsorption on the planar surface exceeds that on the convex droplet surface.

the same temperatures. Because of this, the molecular kinetic energies of both bodies are equal to one another, and, hence, it is enough to examine the changes of potential energies on condensation. We start with calculating the internal energy, *U*.

Since *U* is the state function,²⁵ one can choose any convenient way between initial and final states for calculating the variation of the internal energy on condensation, ΔU_{con} .

In particular, imagine that condensation consists of three stages: in the first stage, each of the molecules adsorbs on the surface of the droplet (Figure 1a) and then, in the second and third stages, the adsorbate penetrates into the surface layer (Figure 1b) and, finally, into the interior of the droplet (Figure 1c). The first stage is autoadsorption. This term denotes adsorption of vapor on a surface of its own condensed phase (for example, water vapors on surfaces of either ice or liquid water) when molecules only touch the surface without entering the surface layer. The energy of autoadsorption ϵ^* is calculated in the absence of lateral neighbors when a molecule interacts only with species located below it. In the parlance of the adsorption theory, ϵ^* is the adsorption energy in the Henry limit;²⁶ it is expressed as the sum of the interactions of adsorbate with all molecules of the droplet. Figure 1d illustrates that ϵ^* varies with the sample geometry: separations *ac* between adsorbate *a* and points of a convex surface represented by a circular arc are greater than the distances *ad* from the planar tangent surface *p*, except for the tangential point *t*; as a consequence, the energy of adsorption on the planar surface exceeds that on the convex droplet surface. Hence, ϵ^* is a size-dependent property.

As the adsorption layer is filled by adsorbate, it evolves into a surface layer (Figure 1b) where each of the molecules interacts also with lateral molecules. The energy of lateral interactions, ϵ_{lat}^* , contributes to ΔU_{con} . The energetic effect of the third stage when a molecule moves from the surface layer to the bulk liquid (Figure 1c) is equal in magnitude but opposite in sign to the total (excess) surface energy E_s . The total surface energy is defined as the energy gained by a molecule on being transferred from the bulk liquid to its surface;^{27–31} it is the excess energy of the molecules in the surface layer with respect to their energy in the volume. This value is in the close association with the free surface energy (the surface tension), γ :

$$E_s = \gamma - T \frac{d\gamma}{dT} \quad (5)$$

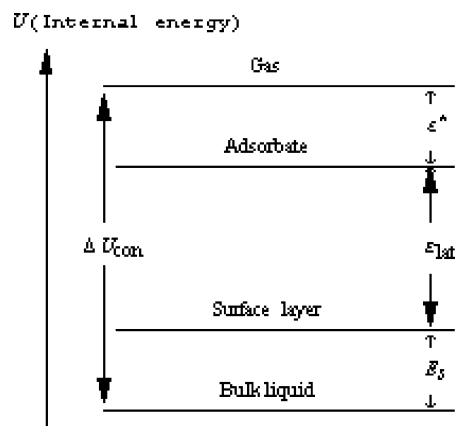


Figure 2. Schematic diagram of energy changes on condensation. ΔU_{con} , ϵ^* , and ϵ_{lat} are the energies of condensation, autoadsorption, and lateral interactions, respectively; E_s is the excess surface energy.

Here $(-d\gamma/dT)$ is the excess surface entropy and $T(-d\gamma/dT)$ is the quantity of latent heat absorbed in the reversible isothermal change of the surface area.³¹ E_s is nearly temperature independent in the wide range not too close to the critical temperature but eventually drops to zero at T_c .²⁷ Note that E_s in this study will be given in units of J mol^{-1} , that is, energy/area occupied by 1 mol in the surface layer.

Figure 2 presents a schematic diagram of energy changes. Adsorption parameters referring to equilibrium separations, as is customary, are indicated by the asterisk (*). By convention, adsorption energies are positive, whereas changes of potential energies on condensation are negative. It is evident from Figure 2 that

$$\Delta U_{\text{con}} = -(\epsilon^* + E_s + \epsilon_{\text{lat}}^*) \quad (6)$$

Let us now consider the term $\epsilon_{\text{lat}}^* + E_s$. Accordingly to Israelsvili,³² the surface energy remains invariable even for a cluster of a few molecules. The thermodynamic theory of Tolman³³ suggests that the surface tension of liquids $\gamma(r)$ changes with radii *r* as

$$\frac{\gamma(r)}{\gamma_b} = \frac{1}{1 + 2\delta/r} \quad (7)$$

where γ_b is the bulk surface tension and $\delta \approx 0.1$ nm. The size dependence of γ has been discussed recently in a number of publications. Lu and Jiang³⁴ come to the conclusion that the surface tension of water droplets becomes constant for $r > 1$ nm, whereas for liquid aluminum and sodium it approaches a constant value at $\gg 3$ –4 nm. Similar results were reported by Ouyang and co-workers³⁵ for the chemical constituents of the interface energy for bilayered metal films. For metal nuclei with $r < 1$ nm, the surface tension is a function of radii.³⁶ Lu and Jiang³⁴ consider that the size dependence strongly depends on the bond strength; a decrease of the strength leads to the diffusion of the liquid–vapor interface due to weakening the energetic difference between molecules on the liquid surface and that in the gas phase. Thus, the liquid–vapor interface transition zone becomes narrow. It is clear that the constancy of the surface energy means that the arrangement of the surface layers at the molecular level is independent of sizes. But the surface layer determines both E_s and the energy of lateral interactions ϵ_{lat} , which, hence, is also independent of the curvature. One may see that the autoadsorption energy is the only term in eq 2 that is a function of radii. Hence, the difference between ΔU_{con} for two liquid bodies of the same chemical nature, which

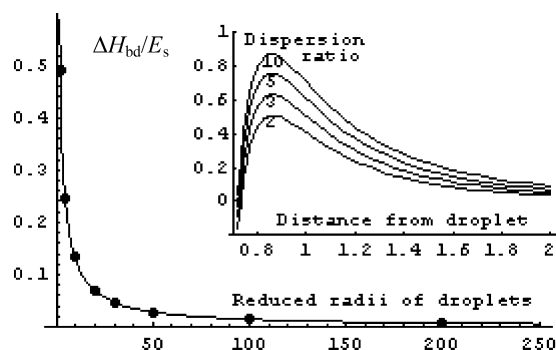


Figure 3. Effect of radii on $\Delta H_{bd}/E_s$. The results are obtained by the numerical solution of eq 9 (solid line) and approximate eq 11 (points). Insert: Dispersion ratio ($\epsilon_{sp}^*/\epsilon_{slab}^*$) for droplets with R of 2, 3, 5, and 10 as a function of reduced distance (z) between droplets and adsorbate.

differ from one another only with respect to their geometry, is equal to the variation of ϵ^* . In particular, for droplets and the bulk liquid $\Delta U_{db} \equiv \Delta U_{con(b)} - \Delta U_{con(d)}$ is given as

$$\Delta U_{db} = -\Delta \epsilon_{db}^* \equiv \Delta \epsilon_{bd}^* \quad (8)$$

As for condensed phases, U and enthalpy H are practically equivalent; thus, one obtains the desired eq 1.

One may see that the derivation is valid for the liquid objects for which the arrangement of surface layers and, hence, γ and E_s are independent of the object's geometry. Proceeding from data on the size dependence of γ , it may be suggested that the model is applicable for water droplets with $r > 1$ nm; for liquid metal droplets the low limit probably increases by several nanometers.

Effect of Radii on Thermodynamic Properties

To take advantage of eqs 1–4, one needs to know the total surface energy and the dispersion ratio $\epsilon_{sp}^*/\epsilon_{slab}^*$ for a sphere and semi-infinite slab. The latter is known from the adsorption theory.²⁴ Note that all lengths in the expressions for energies are given in the reduced form taking the Lennard-Jones diameter, σ_{aa} , as a scale parameter. For the interaction between a molecule at the reduced distance z and a sphere of reduced radius R , the dispersion ratio is given as follows:²⁹

$$\frac{\epsilon_{sp}(R,z)}{\epsilon_{slab}^*} = \frac{24R^3}{\sqrt{10}} \left\{ \frac{1}{((R+z)^2 - R^2)^3} - \frac{15(R+z)^6 + 63(R+z)^4 R^2 + 45(R+z)^2 R^4 + 5R^6}{15[(R+z)^2 - R^2]^9} \right\} \quad (9)$$

Here, $\epsilon_{sp}(R,z)$ is a function of R and z but ϵ_{slab}^* is a constant value that is equal to the energy of dispersion interactions between the molecule and the bulk liquid at the equilibrium separation. The insert in Figure 3 shows the effect of z on the dispersion ratio for spheres (droplets) of different radii.

For the given R , the maximum, $\epsilon_{sp}^*(R,z^*)$, is searched by the numerical method with respect to z ; it usually occurs at $z^* \approx 0.858$. When radii spheres increase, $\epsilon_{sp}^*(R,z^*)$ grows, approaching the energy of interactions with the bulk liquid ϵ_{slab}^* . The expression for the difference of enthalpies ΔH_{bd} comes from eqs 1 and 2:

$$\Delta H_{bd} = E_s \lambda \quad (10)$$

After $\epsilon_{sp}^*/\epsilon_{slab}^*$ has been found, the values of $\lambda \equiv (1 - \epsilon_{sp}^*/\epsilon_{slab}^*)$ and $\Delta H_{bd}/E_s$ become known. $\Delta H_{bd}/E_s$ may be presented with a very high precision by the approximate expression

$$\frac{\Delta H_{bd}}{E_s} = \frac{1.4428}{R} - \frac{1.1514}{R^2} + \frac{0.4687}{R^3} \quad (11)$$

Figure 3 illustrates correlations among $\epsilon_{sp}^*/\epsilon_{slab}^*$, $\Delta H_{bd}/E_s$, and eq 11. For instance, for a droplet with $R = 5$, the maxima of dispersion ratio $\epsilon_{sp}^*/\epsilon_{slab}^* \approx 0.754$ (see insert) and $\Delta H_{bd}/E_s = 0.246$ (solid line in Figure 3); practically the same value gives eq 11 (points in Figure 3). In particular, for liquid silver²⁷ E_s is 45.63 kJ·mol⁻¹ and $\Delta H_{bd} = 0.246E_s$ comes out to 11.22 kJ·mol⁻¹. Equation 11 shows that for large radii ΔH_{bd} decays as the inverse power of radii. Because reduced lengths are used, the geometrical radius r is linked with R as $r = \sigma_{aa}R$.

Several points in treating the experimental data are worthy of notice. One should take into account that that polar and nonspherical molecules are not described by the LJ one-centered potential; for such molecules the LJ diameters σ_{aa} are just the empirical constants obtained mainly from viscosity data, which are useful for purposes of calculation.^{37,38} The parameters give an account of the effect of intermolecular distances on interactions, while the values obtained by the integration over the body volume provide accounting the body geometry. For complex molecules, the empirical LJ diameters may be approximately calculated from the empirical equation

$$\sigma_{aa} = 1.18V_b^{1/3} \quad (12)$$

where V_b is the Le Bas value obtained from atomic volumes.³⁷ The basic challenge in the treatment is estimating a surface area occupied by 1 mol in the surface layer, a_m , required for a conversion of the surface energy given in units of energy/m² to the energy/mol. A usual practice is to treat molecules as spheres.^{27–30} Then

$$a_m = \chi L_0^{1/3} V_m^{2/3} \quad (13)$$

where L is the Avogadro number and χ is the steric factor that is close to unity, and

$$E_s (\text{J} \cdot \text{mol}^{-1}) = E_s (\text{J} \cdot \text{m}^{-2}) \times a_m \quad (14)$$

It is clear that such an approach is valid for simple spherical molecules, but it may introduce a significant error in the cases of complex, nonspherical molecules with specific orientations on liquid surfaces. Consider, for example, aromatic compounds. It has been shown that the area occupied by the aromatic molecule of toluidine on the liquid surface is practically independent of the support liquid: for a toluidine–water solution and for a toluidine on hexane–water and benzene–water interfaces the area falls in the range 0.254–0.262 nm²/molecule.³⁹ According to the approach developed by Harkins,⁴⁰ the amino group of toluidine must be turned toward the water, and the aromatic ring should be turned toward the vapor. The detail study of vapor–liquid interface of pure aromatic compounds⁴¹ shows that the orientation of aromatic rings of these compounds at the vapor–liquid interfaces is tilted relative to the surface plane, the plane of the aromatic ring does not lie in the interfacial plane, and the substituent groups favor the liquid side of the interface. One may see that the orientation of molecules of toluidine on different interfaces resembles the orientation of benzene and toluene on vapor–liquid interfaces, and we can take as a first approximation that the molecular area of benzene and toluene, ω , is also about 0.25 nm²/molecule. For comparison, when these molecules lie flat on the active carbon surface ω is 0.40 and 0.54 nm² for benzene and toluene,

TABLE 1: Parameters of Liquids

substances	T (K)	γ (mJ·m ⁻²)	dy/dT (mJ K ⁻¹ m ⁻²)	E_s (J·mol ⁻¹)	σ_{aa} (nm)
water	298	72.14	-0.16	7450	0.2649 ^a
mercury	393	448	-0.162	31900	0.2898 ^a
benzene	293	28.88	-0.13	10080 ^c	0.527 ^a
toluene	293	28.52	-0.12	9580 ^c	0.579 ^b

^a Reference 37. ^b Equation 12. ^c Equation 15.

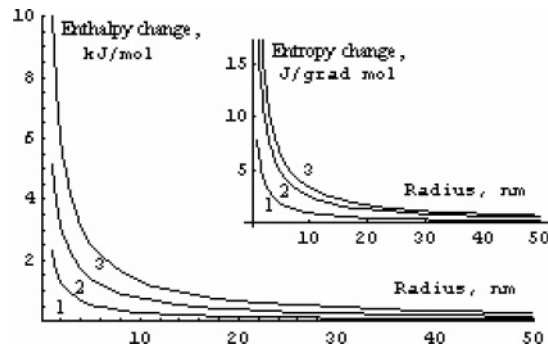


Figure 4. Variation of thermodynamic properties with droplet radii. Curves 1–3 refer to water, benzene, and mercury, respectively.

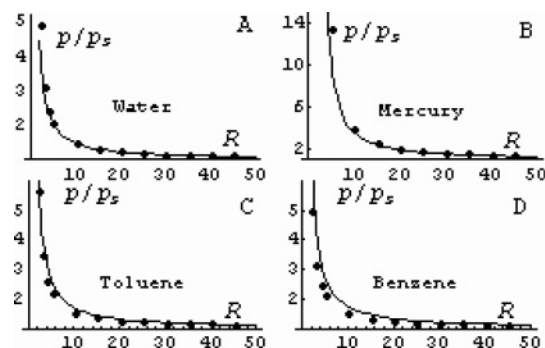


Figure 5. Effects of reduced radii R on relative pressures p/p_s over droplets of water, mercury, benzene, and toluene. Solid lines are for eq 4, and points are for the Kelvin equation.

respectively.⁴² If ω is known, then the requested value of E_s (J·mol⁻¹) is found as

$$E_s = \omega L(\gamma - dy/dT) \quad (15)$$

where γ is given in usual units of energy/m². Parameters of equations for several liquids are presented in Table 1. The recommended values of E_s for mercury and water are taken from the literature.^{27,30}

The changes of enthalpy of droplets with respect to the bulk liquids are shown in Figure 4. Since a variation of radii is due to either condensation or evaporation, this process, as well as any phase transition, is associated with changing the droplet entropy $\Delta S_{bd} = \Delta H_{bd}/T$ (insert in Figure 4). Variation of thermodynamic properties becomes significant for the nanoscale; it practically disappears for microparticles.

According to the classical theory, the equilibrium pressure of droplets obeys the Kelvin equation:^{27–30}

$$RT \ln \frac{p}{p_s} = \frac{2\gamma V_m}{r} \quad (16)$$

where $r = \sigma_{aa}R$ is the droplet radius. A comparison of equilibrium pressures calculated by eq 4 (solid lines) and by the Kelvin equation points is shown in Figure 5, which demonstrates that the approaches are in close agreement.

Conclusions

A thermodynamic model for the size-dependent enthalpy of condensation is discussed. The physical reasoning leads to the conclusion that the difference between these values for two liquid bodies of the same chemical nature is equal to the variation of the autoadsorption energies on their surfaces. The model is valid over a range of radii where the arrangement of the liquid surface layer and its surface tension remain invariable; it provides a way of calculating enthalpy and entropy changes and equilibrium pressures.

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