

Theo yêu cầu của khách hàng, trong một năm qua, chúng tôi đã dịch qua 16 môn học, 34 cuốn sách, 43 bài báo, 5 sổ tay (chưa tính các tài liệu từ năm 2010 trở về trước) Xem ở đây

**DỊCH VỤ
DỊCH
TIẾNG
ANH
CHUYÊN
NGÀNH
NHANH
NHẤT VÀ
CHÍNH
XÁC
NHẤT**

Chỉ sau một lần liên lạc, việc dịch được tiến hành

Giá cả: có thể giảm đến 10 nghìn/1 trang

Chất lượng: Tao dựng niềm tin cho khách hàng bằng công nghệ 1. Bạn thấy được toàn bộ bản dịch; 2. Bạn đánh giá chất lượng. 3. Bạn quyết định thanh toán.

Tài liệu này được dịch sang tiếng việt bởi:

www.mientayvn.com

Từ bản gốc:

<https://drive.google.com/folderview?id=0B4rAPqlxIMRDcGpnN2JzSG1CZDO&usp=sharing>

Liên hệ để mua:

thanhlam1910_2006@yahoo.com hoặc frbwrthes@gmail.com hoặc số 0168 8557 403 (gặp Lâm)

Giá tiền: 1 nghìn /trang đơn (trang không chia cột); 500 VND/trang song ngữ

Dịch tài liệu của bạn: http://www.mientayvn.com/dich_tiang_anh_chuyen_nganh.html

A thermodynamic model for the melting of supported metal nanoparticles 9 h 13 15/7

Abstract

We construct a simple thermodynamic model to describe the melting of a supported metal nanoparticle with a spherically curved free surface both with and without surface melting. We use the model to investigate the results of recent molecular dynamics simulations, which suggest the melting temperature of a supported metal particle is the same as that of a free spherical particle with the same surface curvature. Our model shows that this is only the case when the contact angles of the supported solid and liquid particles are similar. This is also the case for the temperature at which surface melting begins.

1. Introduction

Despite decades of study, the melting of nanoparticles continues to generate interest [1-4]. In general, the melting temperature of spherical nanoparticles has been found to decrease in proportion to the surface area to volume ratio of the particle [5], as the surface free energy of a molten droplet is less than that of the corresponding solid particle. Although free nanoparticle calorimetry has advanced considerably in recent years [6, 7], most experimental determinations of the melting points of nanoparticles are conducted with supported particles (gold [8], lead [9] and tin [10], for example). The melting of supported nanoparticles is also important in carbon nanotube growth and other catalytic processes [11,12],

Mô hình nhiệt động lực học cho quá trình nóng chảy của các hạt nano kim loại phủ

Tóm tắt

Chúng tôi xây dựng mô hình nhiệt động lực học đơn giản để mô tả quá trình nóng chảy của một hạt nano kim loại phủ với bề mặt tự do hình cầu khi có và không có hiện tượng nóng chảy bề mặt. Chúng tôi sử dụng mô hình để đánh giá kết quả của các mô phỏng động học phân tử gần đây, các mô phỏng này cho rằng nhiệt độ nóng chảy của hạt kim loại phủ bằng nhiệt độ nóng chảy của một hạt hình cầu tự do có cùng độ cong bề mặt. Mô hình của chúng tôi chứng tỏ rằng điều này chỉ đúng khi các góc tiếp xúc của các hạt phủ rắn và lỏng bằng nhau. Điều này cũng đúng ở nhiệt độ bắt đầu quá trình nóng chảy bề mặt.

1. Giới thiệu

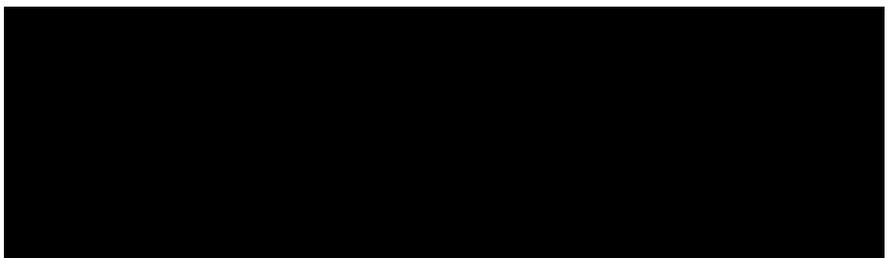
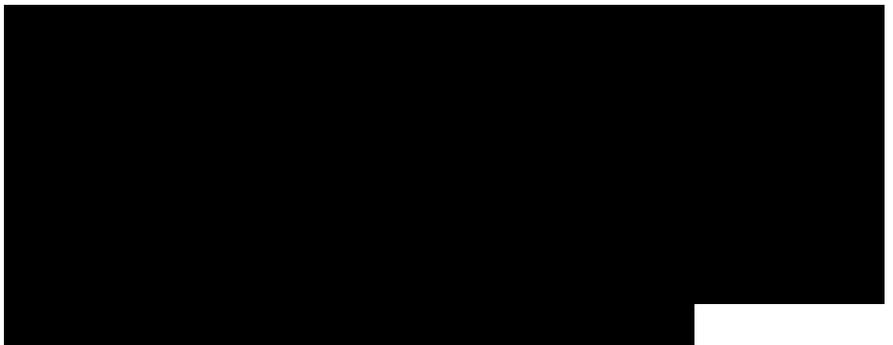
Dù trải qua nhiều thập kỉ nghiên cứu, quá trình nóng chảy của các hạt nano vẫn được tập trung nghiên cứu ngày càng nhiều [1-4]. Nói chung, người ta thấy nhiệt độ nóng chảy của các hạt nano cầu giảm theo tỷ số diện tích bề mặt-thể tích của hạt [5], vì năng lượng tự do bề mặt của một giọt nóng chảy nhỏ hơn hạt rắn tương ứng. Mặc dù phép đo nhiệt lượng hạt nano tự do đã đạt được những bước tiến đáng kể trong những năm gần đây [6, 7], nhưng trong thực nghiệm người ta thường xác định nhiệt độ nóng chảy của hạt nano bằng các hạt phủ (chẳng hạn vàng [8], chì [9] và thiếc [10]). Quá trình nóng chảy của các hạt nano phủ cũng rất quan trọng trong quá trình hình thành ống nano carbon và các quá trình xúc tác khác [11,12], và cho sự ổn định của các thiết bị cấu thành từ các hạt nano [13, 14]. Do đó, chúng ta cần phải nghiên cứu ảnh hưởng của đế đến nhiệt độ nóng chảy của một hạt nano phủ.

Substrate: đế, nền

and for the stability of devices assembled from nanoparticles [13, 14]. Thus, it is of interest to study the effect of the substrate on the melting point of a supported nanoparticle.

Recent molecular dynamics simulations [15] of supported iron nanoparticles with a strongly interacting substrate found that the melting point of the particles was reduced in inverse proportion to the equilibrium surface curvature that results as they relax to wet the substrate. This statement also holds in the free particle limit because the curvature of a free spherical particle of radius a is proportional to its surface to volume ratio, $3/a$. Interestingly, the simulations in [15] found that the constant of proportionality between the decrease in melting point and the surface curvature did not depend on whether the particle was supported or free. In other words, the melting temperature of a supported particle that has a free surface with radius of curvature a , was found to be the same as that of a free spherical particle with the same surface curvature. The simulated nanoparticles in [15] also exhibited surface melting prior to complete melting. Surface melting is a phenomenon thought to occur both on certain bulk metal surfaces [16] and in certain metal nanoparticles [17, 18].

In this paper we use a simple thermodynamic model to investigate the role of the substrate in both melting and surface melting of metal nanoparticles. Our model suggests



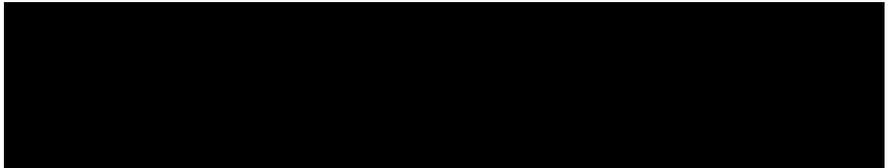
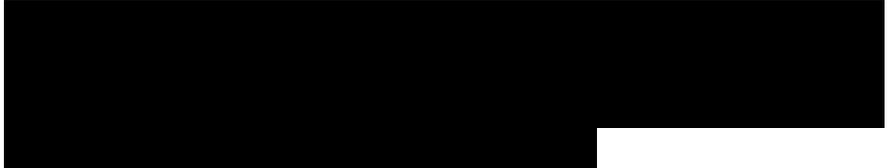
that the result in [15], that the relative decrease in melting point is proportional to the solid particle surface curvature, only holds when the contact angles of the supported solid and liquid particles with the substrate are similar. We also show that supported clusters will exhibit surface melting under certain circumstances, and that the surface melting temperature in free and supported particles in clusters with the same surface curvature is the same only when the contact angles of the supported solid and liquid phases coincide.

2. Geometry of supported particles

We start by considering a solid nanoparticle, initially spherical with radius a , that is placed on a flat substrate. We neglect the effect of faceting, curvature dependent surface energies and internal strains due to epitaxial mismatch with the substrate.

Figure 1. The model for the geometry of a supported nanoparticle in equilibrium. We assume that the particle is a spherical cap of height H and radius of curvature R (left—the dashed lines simply illustrate the radius of curvature). At the onset of surface melting, we assume that the geometry is close to that of the solid particle in its equilibrium geometry and that the solid particle (radius of curvature r and height h) is initially wet by a molten layer of uniform thickness $\delta = R - r = H - h$ (right).

Furthermore, we will assume that the particle has relaxed to its equilibrium geometry i.e. that the nanoparticle



has relaxed to ‘wet’ the substrate. Provided the nanoparticle is heated sufficiently slowly, the particle should relax to this geometry prior to melting. With these simplifying assumptions, the geometry of the relaxed particle can be approximated by a spherical cap, as shown in figure 1, with dimensions parameterized by either the cap height H , or radius of curvature of the free surface R , which minimizes the surface energy of the nanoparticle and substrate.

The surface energy T of the system can be written as:

$$T = 2\pi RH\gamma_s + \pi H(2R - H)(\gamma_{sb} - \gamma_b) + \Gamma_b \quad (1)$$

where γ_s is the surface energy density of the free particle surface, γ_b is the surface energy density of the substrate, γ_{sb} is the particle-substrate interfacial energy density and Γ_b is the total energy of the bare substrate. We will assume that the density of the particle ρ_s does not depend on the contact angle so that the volume of the supported particle remains the same as that of the free particle.

Writing the volume of the particle as a function of H and R , it is then straightforward to show that T is minimized if $H = -(\gamma_{sb}/\gamma_s)R$ where $\gamma_{sb} = \gamma_b - \gamma_s$. We note that γ_{sb} is often called the spreading parameter in the context of wetting phenomena: if $\gamma_{sb} > 0$ then the particle will relax to fully wet the substrate. Here we are interested in the case where the particle does not fully wet the substrate (contact angles greater than zero) i.e. when $\gamma_{sb} < 0$ and $H/R =$

$$\Gamma = 2\pi RH\gamma_s + \pi H(2R - H)(\gamma_{sb} - \gamma_b) + \Gamma_b \quad (1)$$

$$\Gamma^* = 2\pi\gamma_s \left(\frac{a}{R_s^*}\right) a^2 + \Gamma_b, \quad (2)$$

— $\Delta\gamma_{sb}/\gamma_s > 0$ at equilibrium. In fact this minimum value of T can be written as

where R^* is the corresponding radius of curvature of the supported solid nanoparticle, given by

$$R_s^* = \left(\frac{2\gamma_s}{\Delta\gamma_{sb}} \right)^{2/3} \frac{a}{(3 + \Delta\gamma_{sb}/\gamma_s)^{1/3}}. \quad (3)$$

Thus, T^* and R^* are the equilibrium surface energy and radius of curvature of the particle respectively. Note that the contact angle of the particle can range from 0° to 180° depending on the value of the spreading parameter $\Delta\gamma_{sb}$.

3. Melting and surface melting

In what follows we will assume that the density of the solid and liquid phases are identical i.e. $\rho_s = \rho_l = \rho$. We first consider the situation in which there is no surface melting. In this case, melting will occur at a temperature when the free energy of the solid particle wetting the substrate is equal to that of the corresponding liquid droplet wetting the substrate. If γ_l is the surface energy density of the free liquid droplet and R_l^* is the corresponding equilibrium radius of curvature, then the difference in free energy between the solid and liquid is

$$\Delta F = \frac{4}{3}\pi a^3 \rho \left(f_s - f_l + 3 \left(\frac{\gamma_s}{R_s^*} - \frac{\gamma_l}{R_l^*} \right) \right) \quad (4)$$

where f_s (f_l) is the bulk free energy density of the solid (liquid). Now, using $f_l - f_s = \rho L(1 - T/T_c)$, where L is the latent heat of melting and T_c is the bulk melting temperature, we find that the melting temperature T_m of the supported particle is given by:

$$\begin{aligned} T_m &= T_c \left(1 - \frac{3}{\rho L} \left(\frac{\gamma_s}{R_s^*} - \frac{\gamma_l}{R_l^*} \right) \right) \\ &= T_m^{\text{free}}(R_s^*) + \frac{3\gamma_l}{\rho R_s^* L} \left(1 - \frac{R_s^*}{R_l^*} \right) T_c. \end{aligned} \quad (5)$$

Thus, if $R_s^* = R_l^* = R^*$ then we recover the result of [15], namely

that $T_m = T_{m\text{free}}(R^*)$. In other words, if the contact angles of the solid and liquid droplets are equal, the melting temperature of the supported particle is the same as that of a free particle with an identical surface curvature, $a = R^*$. However, if the curvature of the supported liquid particle is different from that of the supported solid particle, it can be seen that the melting temperature will deviate from that found in [15].

Now we consider surface melting as illustrated in figure 1 which is thought to occur in many metals prior to melting [16]. We are interested in determining the onset of melting, when the solid particle is wet by a thin layer of melt (thickness δ) at the solid-vapour interface. We will assume that this melt forms a layer of uniform thickness with a geometry like that represented in figure 1 with $\delta = R - r = H - h$. The total free energy of the surface melted particle is then a function of δ : $F(\delta) = \gamma_s(\delta)(\gamma_s - \gamma) + V_{fl} + T(\delta)$ where $V_s(l)$ is the volume

Figure 2. The melting temperature T_m and critical liquid film thickness for supported Pb clusters as a function of the radius of curvature R_s of the relaxed solid particle for $\gamma = 0.05, 0.10, 0.15 \text{ J m}^{-2}$ and in the case where $\cos \theta_s = \cos \theta$ ($\gamma_{lv} \sim 0.13 \text{ J m}^{-2}$). Also shown is the melting temperature of a free particle with radius R_s . Other surface energies used are $\gamma_{sv} = 0.61, \gamma_{v} = 0.48, \gamma_{sl} = 0.05, \gamma_b = 0.25$ and $\gamma_{sb} = 0.1 \text{ J m}^{-2}$ giving a contact angle of 75.8° for the solid supported cluster, and contact angles for the liquid droplets ranging from 78.0° to 65.4°

respectively. Other parameters used were $\xi = 0.63$ nm, $\rho = 10\,950$ kg m⁻³, $L = 22\,930$ J kg⁻¹ and $T_c = 600.65$ K [9].

of the solid (liquid) and T is the thickness dependent surface energy.

In particular

$$T = n(2RH\gamma_l + r(2r - h)\gamma_{sb} + S(2R - S)\gamma_b + 2rh\gamma_{sl}(\delta))$$

where $\gamma_{sl}(S) = \gamma_{sl} + A_{ysl}\exp(-S/\xi)$ and ξ is a correlation length that describes the thickness dependence of the interfacial energy in thin metallic liquid films [16] (in Pb, for example, ξ has been measured to be ~ 0.6 nm [19]). As the surface melting proceeds, the curvature of the particle will relax to minimize the free energy i.e. $R^* = R^*(S)$ where R^* minimizes the free energy F for a given S .

In an isolated spherical nanoparticle of radius a , by minimizing the free energy $F(S)$ with respect to S and setting $S = 0$, one can show that surface melting begins at a temperature, $T_s(a)$ given by

$A_{ysl} > 0$ and $a > \xi(\gamma_s - \gamma_l)/A_{ysl}$ (if a is less than this, full melting will precede surface melting i.e. $T_{sfree} > T_{mree}$ [17], and equation (5) will hold).

For surface melting to occur in a supported solid nanoparticle with equilibrium curvature R_s , a minimum in the free energy $F(S)$ must appear at $S = 0$. It is straightforward to show that a minimum in F at $S = 0$ occurs at the temperature T_s :

.....

where Q_s and Q are the contact

$$\Gamma = \pi(2RH\gamma_l + r(2r - h)\gamma_{sb} + \delta(2R - \delta)\gamma_{lb} + 2rh\gamma_{sl}(\delta))$$

$$T_s^{free}(a) = T_c \left(1 - \frac{\Delta\gamma_{sl}}{\rho\xi L} + 2 \frac{(\gamma_s - \gamma_l)}{\rho a L} \right) \quad (6)$$

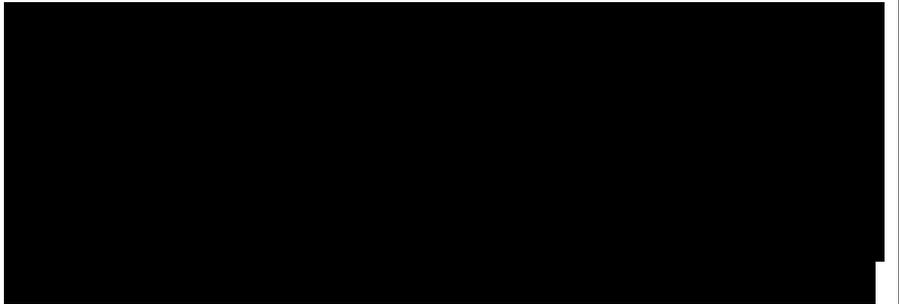
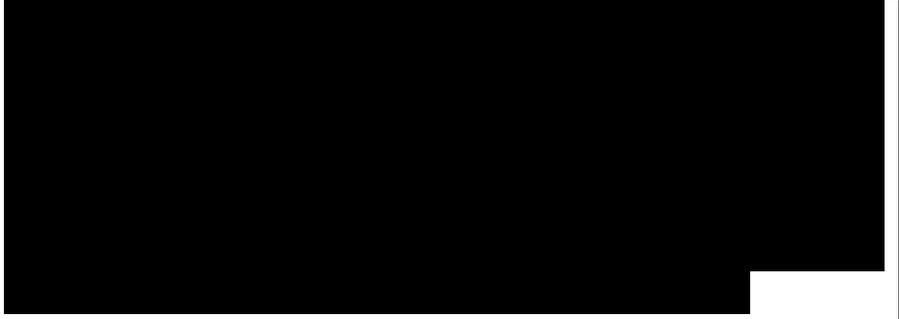
$$\begin{aligned} T_s(R_s) &= T_s^{free}(R_s) + \frac{T_c}{\rho R_s L} \left(\frac{\gamma_s \Delta\gamma_{lb} - \gamma_l \Delta\gamma_{sb}}{\Delta\gamma_{sb}} \right) \\ &= T_s^{free}(R_s) + \frac{\gamma_l T_c}{\rho R_s L} \left(\frac{\cos\theta_s - \cos\theta_l}{1 - \cos\theta_s} \right) \end{aligned} \quad (7)$$

angles for the solid particle and liquid particle respectively (defined via Young's relation $Y_s(l) \cos Q_s(l) = Y_b - Y_s(i)b$). Once again, if the contact angles of the solid and liquid droplets are equal, then the temperature at which surface melting occurs is identical to that of a free particle with the same surface curvature, R_s i.e. $T_s = T_{sfree}(R_s)$. Furthermore, if $\cos Q_s > \cos Q_l$, so that the substrate favours contact with the solid over that with the liquid, the corresponding T_s increases and vice versa.

Complete melting will occur once the free energy of the surface melted particle, $F(S)$, equals that of the corresponding liquid droplet, F_x , i.e. at the temperature T_m and liquid film thickness S_m which satisfy $F(S_m) = F_x$. It is not possible to obtain an analytic expression for S_m or T_m , but numerical solutions to the resulting equations are shown in figure 2 as a function of R_s for Pb particles. The figures clearly show the strong dependence of the melting temperature on the liquid droplet contact angle: a difference of $\sim 10^\circ$ in the molten particle contact angle can shift the melting point by ~ 100 K. Note that the melting point of a free particle with radius R_s no longer coincides with that of a supported particle with radius of curvature R_s when $\cos Q_s = \cos Q_l$, as in general the radius of curvature of the critical surface melted droplet will not be that of the solid particle (although the curves lie close to each other).

4. Conclusion

We conclude that the melting temperature (and surface melting



temperature, if the particle exhibits surface melting) of supported nanoparticles depends on the radius of curvature (or the contact angle) of both the supported solid and liquid particles. In general, we do not expect these curvatures to be the same: on a non-ideal solid substrate for example, epitaxial effects may favour one phase over the other. It is likely that the ideal substrate used in [15] resulted in very similar solid and liquid particle contact angles. We have shown that it is only in this 'ideal' case that the melting temperature of free and supported particles with the same curvature is coincident, whether they exhibit surface melting or otherwise. Thus, results from free particle melting, where the curvature of the solid and liquid particles remain substantially the same, have only limited applicability to supported particle melting.

