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Abstract
A model, without adjustable parameters, describing the size-dependent phonon frequency of semiconductor nanocrystals is established based on the size-dependent force constant and thus the size-dependent bond length and bond energy of nanocrystals. This model shows frequency shifts as the size of the crystals decreases. Our predictions agree with the results of experiments for the blue shift of TiO_2 nanoparticles, Si and InP quantum dots. The model will be useful for understanding the origins of the phonon behaviour of nanocrystals and the effect of the thermodynamic parameters on the phonon frequency.

Semiconductor nanocrystals, including nanoparticles and quantum dots, have drawn a great deal of attention in the past decade due to their peculiar electronic and optical properties compared to their bulk counterparts [1]. In particular, the phonon behaviour of semiconductor nanocrystals is of great interest to both scientific and technological communities [2–9]. Some experiments have shown phonon frequency shifts with the reduction in the size of crystals by means of Raman spectra [2–6], but the mechanism behind the lattice vibration is less well understood. Related interpretations include surface pressure and the phonon confinement effect. Most of the theoretical study of phonon modes is based on continuum dielectric models [7]. However, these models are limited to small-sized quantum dots of a few nanometres. A microscopic lattice dynamical calculation has already been developed [8, 9]. But a major difficulty of microscopic modelling phonon modes is its computational intensity. A simple and reliable description for phonon behaviour of semiconductor nanocrystals is desirable because it is related to many optical, transport and thermal properties.

In this paper, a quantitative model for the size-dependent phonon frequency of semiconductor nanocrystals is established based on the size-dependent bond length and bond energy. The force constant of nanocrystals is not assumed to be the same as that of the bulk as has been done in the previous theoretical models, but is considered to be size-dependent in our

model. The model's predictions for the blue shift of the phonon frequency of semiconductor nanoparticles and quantum dots correspond well to recent experimental data and calculated results. The model is expressed by an analytic equation with available thermodynamic quantities, which may be useful for understanding the origins of the phonon frequency shift of nanocrystals and the effect of the thermodynamic parameters on the lattice vibration.

It is well known that the atomic vibration frequency ω_b of bulk crystals is proportional to the square root of the force constant β [10], i.e.,

$$\omega_b = c\beta^{1/2}, \tag{1}$$

where c is a constant, the force constant $\beta = c_1\varepsilon/h^2$ is the second-order derivative of the interatomic potential at equilibrium atomic distance, h is the equilibrium atomic distance or bond length, ε is the atomic binding energy or bond energy, and c_1 is a constant. Therefore, $\omega_b = c_2(\varepsilon/h^2)^{1/2}$ with a constant c_2.

Let $\omega(d)$ denote the size-dependent frequency, where d is the diameter of nanoparticles or quantum dots; it is reasonable that we assume that $\omega(d)$ can be similarly determined by the force constant, and thus the bond energy and bond length with size effect, i.e., $\omega(d) = c\beta(d)^{1/2} = c_2[\varepsilon(d)/h(d)^2]^{1/2}$, where $\beta(d)$, $\varepsilon(d)$ and $h(d)$ are the corresponding size-dependent β, ε and h, respectively. Therefore, the ratio $\omega(d)/\omega_b$ can be written as

$$\frac{\omega(d)}{\omega_b} = \frac{h}{h(d)}\sqrt{\frac{\varepsilon(d)}{\varepsilon}}, \tag{2}$$

where the bond length change $h/h(d)$ is related to the lattice strain δ by $h/h(d) = 1/(1+\delta)$, $\delta = [h(d) - h]/h$. According to the Laplace–Young equation [11], the size-dependent strain $\delta = -4\kappa f/(3d)$ for a particle, where κ is the compressibility of the crystal and f is an intrinsic surface stress. Through establishing a relationship between f and the size-dependence of the solid–liquid interface energy [11], the deduction leads to the surface stress $f = \pm[(3\gamma_i d_0)/(8\kappa)]^{1/2}$ with a critical size d_0 and the bulk solid–liquid interface energy γ_i. Since $\gamma_i = 2hS_{vib}H_m(T)/(3V_cR)$ with the vibration entropy S_{vib}, the temperature (T)-dependent melting enthalpy $H_m(T)$, the molar volume of the crystal V_c and ideal gas constant R [11, 12], $\delta = \pm\frac{2}{3d}\sqrt{\kappa d_0 hS_{vib}H_m(T)/(RV_c)}$.

According to the Helmholtz function, $H_m(T) = g_m(T) - T\,\mathrm{d}g_m(T)/\mathrm{d}T$, where $g_m(T)$ is the volume Gibbs free energy difference between the crystal and the liquid. For semiconductors, $g_m(T) = H_m(T_m - T)T/T_m^2$ in terms of the difference of specific heat between the crystal and the liquid, $H_m(T) = H_m(T/T_m)^2$, where H_m is the melting enthalpy at melting point T_m [13]. Finally,

$$\frac{h}{h(d)} = \frac{1}{1 \pm \frac{2}{3d}\sqrt{\kappa d_0 hS_{vib}H_m T^2/(RV_cT_m^2)}}, \tag{3}$$

where the negative sign is taken for lattice contraction [11]. The critical diameter d_0 of a crystal is defined as the size at which almost all atoms are located on the crystal's surface. Given that the definition of d_0, $hA/V = h\pi d_0^2/(\pi d_0^3/6) = 1$ for a spherical particle with surface area A and volume V, $d_0 = 6h$. The vibration entropy S_{vib} denotes the vibrational part of melting entropy S_m; for semiconductors, $S_{vib} \approx 0.4S_m$ because of the larger contribution of electronic entropy to S_m [14]. T is taken as room temperature considering corresponding experimental conditions [2–6]. The compressibility $\kappa = 1/B$ with bulk modulus B. The molar volume $V_c = M/\rho$ with molar mass M and density ρ of the crystal.

For the change of bond energy $\varepsilon(d)/\varepsilon$ in equation (2), let the coordination number of an atom in the bulk crystal be n, and the corresponding cohesion energy of one molar crystal $E = nN_a\varepsilon/2$, with Avogadro constant N_a, $\varepsilon = 2E/(nN_a)$. When the surface effect is not negligible, as is the case of nanocrystals with large surface-to-volume ratio and severe
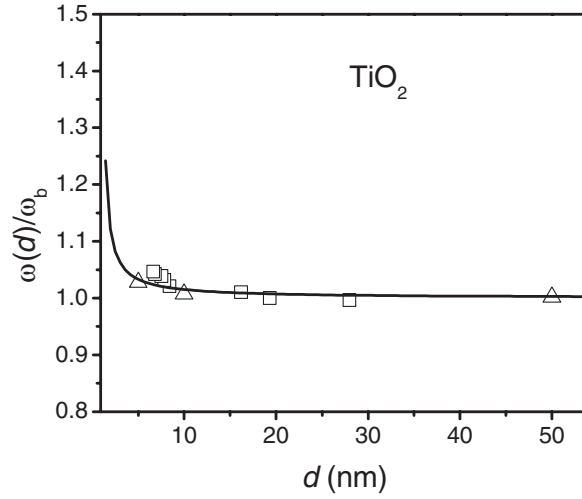
Figure 1. $\omega(d)/\omega$ as a function of the diameter of TiO_2 nanoparticles, where the solid curve shows the prediction of equation (2) combined with equations (3) and (4), and the triangles and the squares are the experimental results from [4] and [5], respectively. $B = 15.02$ GPa [16]. $h = a/\sqrt{2}$ and $a = 0.458$ nm [17]. $S_m = 10.45$ J g-atom^{-1} K^{-1} [17]. $M = 79.88$ g mol^{-1} and $\rho = 3.84$ g cm^{-3} [17]. $N_s = 3/2$. $n_s = 7$ and $n = 14$. Other parameters are given in table 1.

surface breaking bonds, $E(d) = [(n - n_s)y + n(1 - y)]N_a\varepsilon(d)/2 = (n - n_s y)N_a\varepsilon(d)/2$ or $\varepsilon(d) = 2E(d)/[(n - n_s y)N_a]$, where $y = d_0/d$ is the ratio of the number of surface atoms to the total number of atoms, and n_s denotes the decrease of surface atomic coordination number compared with n. Therefore, $\varepsilon(d)/\varepsilon = [E(d)/E]/[1 - n_s y/n]$. Taking $E - E(d) \approx \gamma_s A_f$ as a first order approximation, where γ_s is surface energy of the crystal and $A_f = 6V_c/d$ is a surface-volume transforming factor [15], we have

$$\frac{\varepsilon(d)}{\varepsilon} = \frac{1 - \frac{6\gamma_s V_c}{Ed}}{1 - \frac{n_s}{n}\frac{d_0}{d}}, \tag{4}$$

where n_s and n are both determined by considering the nearest-neighbour and next-nearest-neighbour of the corresponding structure. The surface energy γ_s can be approximately calculated by the change of internal energy per unit area of the (100) face, i.e., $\gamma_s \approx N_s n_s(\varepsilon/2)/a^2 = N_s n_s E/(n N_a a^2)$ with the number of atoms per unit area of (100) face N_s, and the lattice constant a. Through substituting equations (3) and (4) into (2), $\omega(d)/\omega_b$ could be determined.

Figures 1–3 show a comparison between the model's predictions and recent experimental measurements and calculated results of the size-dependent phonon frequency of TiO_2 nanoparticles [4, 5], Si and InP quantum dots [6, 9]. It can be found that the model prediction is in agreement with the experimental evidence and calculation data. The phonon frequency increases as the size of crystals decreases, i.e., blue shift occurs. And the frequency shift is about 1%–5% in the range of 2–50 nm. When $d \rightarrow d_0$, blue shift becomes notable, which may be due to the special structure with almost all atoms on the surface. It is interesting that although equation (1) is based on the Einstein model, the model can predict the frequency shift of general phonon modes, including the optical modes with the lower frequency as the experiments show [4–6, 9]. This may be because what the model emphasizes is a relative change of nanocrystals compared to the bulk.
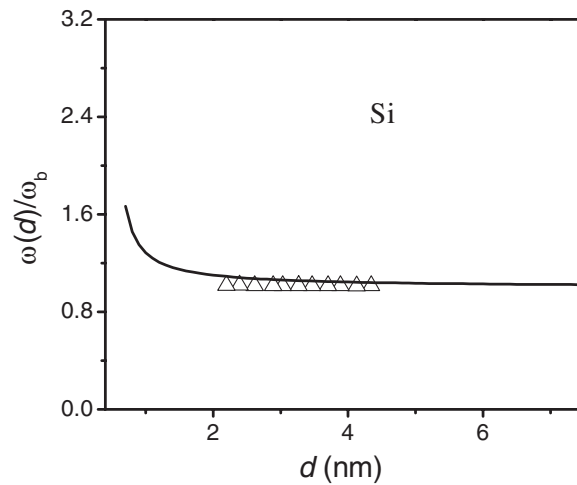
Figure 2. $\omega(d)/\omega$ as a function of the diameter of Si quantum dots, where the solid curve shows the prediction of equation (2) combined with equations (3) and (4), and the symbols are the calculated results of the transverse optical mode at *x* point [9]. $n_s = 6$ and $n = 16$. Other parameters are given in table 1.
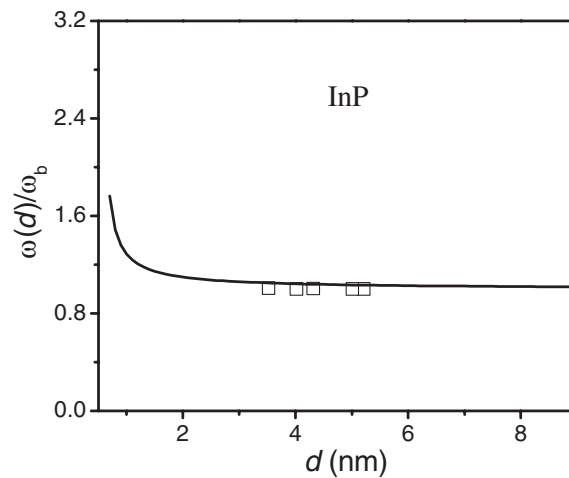

Figure 3. $\omega(d)/\omega$ as a function of the diameter of InP quantum dots, where the solid curve shows the prediction of equation (2) combined with equations (3) and (4), and the symbols are experimental results of the transverse optical mode [6]. $h = \sqrt{3}a/4$ and $a = 0.587$ nm [17]. $S_m = 23.83$ J g-atom^{-1} K^{-1} [14]. $M = 145.79$ g mol^{-1} and $\rho = 4.787$ g cm^{-3} [17]. $N_s = 1$. $n_s = 6$ and $n = 16$. Other parameters are given in table 1.

It is clear that when the bond length contracts and the bond energy increases with decreasing crystal size, the phonon frequency is enhanced in terms of equation (2). The model indicates that the phonon blue shift originates from several contributing factors: one is intrinsic surface tension stress and the concomitant lattice contraction of nanocrystals determined by equation (3), which has already been confirmed by experiments [11] and causes a lattice vibration change compared with the corresponding bulk. At the same time, the increase of the atomic binding energy based on equation (4) also contributes to the phonon behaviour

Table 1. The related parameters used in figures 1–3.

	TiO$_2$	Si	InP
κ (10^{-10} Pa^{-1})	0.670	0.306 [17]	0.735 [17]
h (nm)	0.3239	0.2352 [18]	0.2542
d_0 (nm)	1.9434	1.4112	1.5252
S_{vib} (J g-atom^{-1} K^{-1})	4.18	6.72 [14]	9.53
H_m (10^3 J mol^{-1})	66.88 [17]	50.55 [19]	50.16 [14]
V_c (cm^3 mol^{-1})	20.802	12.100 [19]	30.455
T_m (K)	2128 [17]	1685 [19]	1330 [17]
γ_s (J m^2)	3.994	1.568 [20]	0.358
E (10^3 J mol^{-1})	672.4 [17]	446.0 [21]	197.9 [17]
n_s/n	1/2	3/8	3/8

change of nanocrystals, which results from the large numbers of surface breaking bonds and the intrinsic small size effect. In addition, the changes of bond length and bond energy are both relative to the large surface-to-volume ratio d_0/d of nanocrystals. Consequently, the phonon frequency is roughly proportional to $1/d^2$ in our model, which is different from the previously predicted linear relation of $1/d$ [3].

To some extent, the physics of our model conforms to the discussion on surface bond contraction and bond strengthening and thus phonon frequency increase [10, 22]. Note that the model is different from the surface pressure interpretation [23], which is related to external influence. The relation of $1/d^2$ in our model implies not only intrinsic surface effects but also internal contributions, such as quantum confinement and electron–phonon interaction; all have an influence on phonon vibration. The quantum and surface effects become dominant with decreasing crystal size; phonon frequency shifts obviously at the size of d_0; then the lattice may be degenerate. Because d_0 of TiO$_2$ is larger, the frequency increase of TiO$_2$ nanoparticles is more obvious than that of Si and InP quantum dots at the range of $d < 10$ nm, as shown in figures 1–3.

Note that our prediction is based on the isotropic assumption. In fact, phonon behaviour will exhibit diversity in different orientations; for example, red shifts can be observed [23], which may be due to bond length expansion and bond energy decrease. In that case, the surface stress and average lattice strain state, surface atomic coordinate number and internal energy will be different, which may also be due to a special interface condition such as the matrix interacting with the nanoparticles; how they interact has to be studied further. The effect of the matrix is indeed in dispute [24]. Although the phonon distribution is not always with a single size-dependent frequency, the model will be helpful to understand the phonon behaviour change of nanocrystals compared to that of the bulk.

The model is expressed by some available thermodynamic quantities such as vibration entropy S_{vib}, which may reflect the inherent correlation between the thermodynamic properties and phonon vibration. Consequently, as a mesoscopic bridge between a micro-mechanism and a macro-phenomenon, the model provides a simple feasible method to derive a detailed description of the phonon frequency of nanocrystals.

In conclusion, a model, without adjustable parameters, for the size-dependent phonon frequency of semiconductor nanocrystals is developed based on the size-dependent bond length and bond energy. The model prediction is consistent with experimental results on semiconductor nanoparticles and quantum dots. The model demonstrates that the blue shift may originate from the intrinsic surface stress and lattice strain, the surface bond state and the inherent small size effect.

Acknowledgment

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