1

ATOMIC BONDING

Throughout this book, we try to understand the behavior of interfaces from an atomistic viewpoint. In particular, we look at many phenomena from the point of view of nearest-neighbor bonding among atoms. This approach is satisfying because it is simple and physical. However, it is sometimes too simple to be even qualitatively correct. Nonetheless, the positives far outweigh the negatives, and we use the approach often.

We begin by exploring some basic properties of bonding among atoms and their relation to physical properties of materials. In this chapter and throughout the book, we give as many examples as possible using the face centered cubic (f.c.c.) crystal structure, because it is typical of many metallic alloys. It is important to remember two things as one works through this book. First, calculations performed using nearest-neighbor bonding are only approximate, maybe accurate to within 10% to 20%. Second, this book is only concerned with the equilibrium properties of interfaces. It does not consider nonequilibrium phenomena.

1.1. INTERATOMIC POTENTIAL AND BINDING ENERGY

The following discussion is based on that of Tu et al. [1]. The binding energy is defined as the energy needed to transform one mole of solid or liquid into a gas at zero temperature and pressure. It is approximately the same magnitude as the energy of sublimation ΔH_s when transforming a solid to a gas or the energy of vaporization ΔH_v when transforming a liquid to a gas, except that these are usually measured at 1 atm pressure. These quantities are often obtained at finite temperatures such as 298 K or at the boiling point T_b, but this does not alter the binding energy or bond enthalpy, which is assumed to be independent of temperature. These energies are related to a fundamental energy in materials, the interatomic potential energy between atoms.

A schematic curve of the interatomic potential energy ϕ as a function of distance r is shown in Figure 1.1a. The minimum potential energy $\phi = -\epsilon_b$ corresponds to the equilibrium interatomic separation r_e. In solids, r_e can readily be measured by X-ray diffraction. The depth of the well is clearly proportional to the strength of the interatomic bond.

An atom in a solid that is displaced from its equilibrium position experiences a restoring force

$$F = -d\phi/dr. \tag{1.1}$$

A schematic curve of this force as a function of distance is illustrated in Figure 1.1b. For small displacements on the order of 0.1% of the interatomic spacing, the curve is approximately linear and the displacement is proportional to the force. In solids, this linear displacement is the origin of Hooke's law, where the strain is directly proportional to the stress, as we shall see shortly. The direction of the force is indicated in Figure 1.1c. The force is defined as positive or negative depending on whether it increases or decreases the interatomic distance from its equilibrium value. If the atoms are displaced toward one another, a repulsive force acts to increase the interatomic distance. This repulsive force is positive. The opposite occurs when the atoms are stretched apart.

The shape of the interatomic potential energy curve controls many of the physical properties of materials, such as the bulk modulus and thermal expansion. For now, though, we are mostly concerned with whether the potential is short- or long-range, because an understanding of this issue is important, for example, in using nearest-neighbor models to evaluate the surface energy of a material.

In some cases, the potential energy can be represented by the so-called Lennard-Jones (6–12) potential, given as

$$\phi(r) = \epsilon_b\,[(r_e/r)^{12} - 2(r_e/r)^6], \tag{1.2}$$

where ϵ_b is the bond energy between two atoms and the attractive interaction has an r^{-6} dependence and the repulsive interaction scales as r^{-12}. The inverse sixth-power attractive force arises from weak dipole-induced van der Waals forces between atoms. The inverse twelfth-power repulsive force arises from the repulsion of the partially screened positively charged nuclei and the interpenetrating negatively charged electron clouds (the Pauli exclusion principle) as the atoms approach one another [2,3]. Clearly the repulsive interaction is very short-range, whereas the attractive interaction is somewhat longer. This strong repulsive interaction makes it often realistic to represent atoms as "hard spheres." Although the Lennard-Jones (LJ) potential is an empirical potential, it is quite accurate for f.c.c. inert gas solids such as argon and is reasonable for some more relevant engineering metals such as f.c.c. copper, in which the atoms behave as hard spheres. We use the LJ potential throughout this book.

At the equilibrium position, $r = r_e$, the potential energy is at its minimum, that is $d\phi/dr = 0$ in Figure 1.1b, and $\phi(r_e) = -\epsilon_b$. This energy is often referred to as the pair

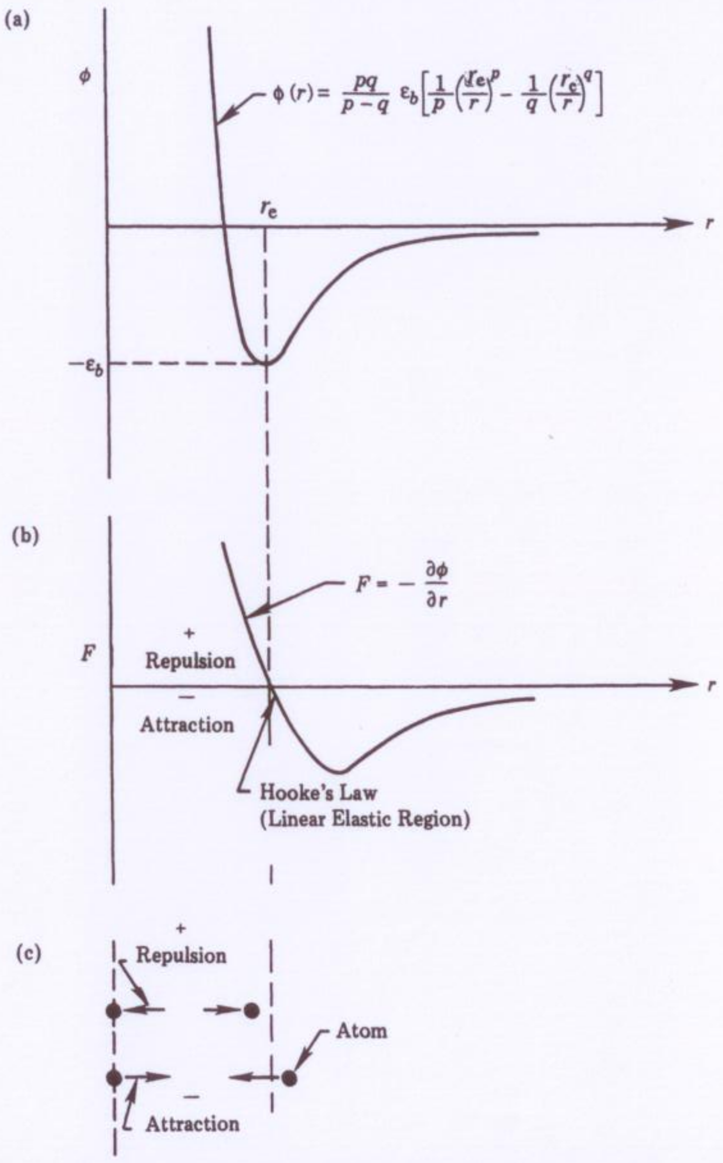

Figure 1.1. (a) Interatomic potential function ϕ plotted versus interatomic distance r. The attractive potential is short-range. (b) Interatomic force F plotted versus r. (c) The direction and sign of the force. The LJ (6–12) potential is a special form of the Mie potential $\phi(r)$ given by the equation in (a), where p and q are integers. Reprinted from [1] by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

the interaction energy beyond the nearest neighbors and approximate the binding energy by considering only the nearest-neighbor bonds. A physical interpretation of this process is offered as follows.

In metals, the binding energy (or cohesive energy) is due to the interaction of the regularly arranged positive ion cores with the surrounding electron cloud, where the electrons move about freely. When the positive ion cores are surrounded by the free electrons, electrical neutrality is achieved locally about each atom and the attractive interaction between atoms is short-range with an r^{-6} dependence. Hence, the nearest-neighbor approximation works well for estimating the binding energy (as shown in the next chapter) for metals.

In other materials, such as ionic solids, the attraction between the positive and negative ions is coulombic and much longer in range. The attractive coulombic potential is proportional to r^{-1}, which decays slowly with increasing r when compared to the atomic dimensions. The repulsive potential may display an r^{-12} dependence, as with metals, so the resulting profile looks like that shown in Figure 1.2, although it is often more accurate to use an exponential function to represent the repulsive potential in ionic crystals. In either case, it is possible to accurately estimate the binding energy by considering the interaction energies among the positive and negative ions and using a quantity known as the Madelung constant to sum over all of the ions. The reader is referred to books such as Borg and Dienes [2] and Kittel [4] for a thorough discussion of this topic.

In covalent solids, such as semiconductors and organic materials where electrons are shared between neighboring positive ions, the screening effect of the positively charged nuclei by the core electrons again leads to short-range attractive interaction and the previous interatomic or LJ ionic or metallic bond description is useful, although the directionality of the bonds is critical in these cases.

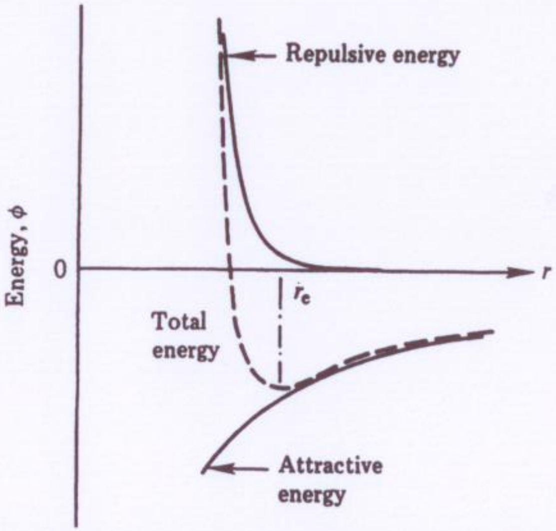

Figure 1.2. The broken curve shows the interatomic potential energy when the attractive interaction is long-range with an r^{-1} dependence. Reprinted from [1] by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

1.2. CORRELATION OF BINDING ENERGY AND INTERATOMIC POTENTIAL WITH PHYSICAL PROPERTIES

In this section, we examine how the binding energy correlates with various physical properties of a material, such as its heat of sublimation, and also how other properties such as the vibrational frequency of a solid and its response to a stress can be explained using the interaction potentials developed in Section 1.1. We are interested in determining the binding energy of atoms so we can use broken-bond models to estimate surface and interfacial energies.

1.2.1. Interatomic Potential, Binding Energy and Enthalpy of Sublimation

If we define z as the coordination number (the number of nearest neighbors) of an atom in a solid or liquid, then the binding energy of 1 mole of atoms is given by

$$E_b = \tfrac{1}{2} z N_A \epsilon_b, \tag{1.3}$$

where N_A is Avogadro's number and the factor of ½ arises because we have counted each bond twice in the produce zN_A. The maximum coordination for close-packed f.c.c. and hexagonal (h.c.p.) structures is 12. For more open covalently bonded structures such as diamond cubic (d.c.) silicon, $z = 4$, and for body centered cubic (b.c.c.) structures such as α-iron, $z = 8$. Note that the binding energy is also referred to as the cohesive energy, which is the heat of vaporization at 0 K. It is also sometimes called the dissociation energy or formation energy.

Using the nearest-neighbor approximation, we can estimate the interatomic potential energy or binding energy per pair of atoms ϵ_b from thermodynamic data such as the heat (enthalpy) of sublimation, vaporization or melting. We want to be able to estimate the binding energy ϵ_b, or more generally, the interaction energy between atoms pairs, because as we shall see throughout this book, knowledge of this parameter allows us to calculate such quantities as the surface energies and interfacial energies of solids. For example, if one assumes that the binding energy per mole of solid is equal to the enthalpy of sublimation ΔH_s per mole at low pressure, then

$$\epsilon_b = 2\Delta H_s / zN_A. \tag{1.4}$$

In crystalline solids, the coordination number z can be substituted directly into Eq. (1.4), for example 12 in the case of an f.c.c. metal. In the molten state, metal atoms typically have 10 or 11 nearest neighbors, so if heats of vaporization or melting are used to estimate ϵ_b, it is reasonable to use a coordination number of 11 instead of 12. In general, the values for the heats of vaporization of f.c.c. metals are approximately 10% lower than the values of the heats of sublimation because there are approximately 10% fewer bonds to break in going from the liquid state to the vapor.

To illustrate these points, we calculate the interatomic potential energy ϵ_b for copper, silver, and gold from values of their heats of sublimation ΔH_s at 0 K and 1 atm pressure (see Appendix B) using Eq. (1.4) and compare these with values obtained from the heats of vaporization ΔH_v (also in Appendix B) using Eq. (1.4) with $z = 11$. The results are shown in Table 1.1. Note the generally good agreement considering that this is an approximate calculation. Also, note that the heats of sublimation and vaporization scale with the melting temperatures of these elements (i.e., 1084°C for copper, 961°C for silver and 1063°C for gold, as they should, because all of these quantities are related to the fundamental quantity, the interatomic potential energy or binding energy ϵ_b. We discuss melting points in greater detail in Parts II and III.

1.2.2. Interatomic Potential and Theoretical Strength

A piece of a solid is under stress when its atoms are displaced from their equilibrium positions by a force. The displacement is governed by the interatomic potential described previously with respect to Figure 1.1. If we apply an external tensile force to a solid, the external force is defined as

$$F_{ex} = +d\phi/dr, \tag{1.5}$$

where a positive sign is used to reflect the fact that an external tensile force (or stress) tends to lengthen the solid and increase the interatomic distance. On the basis of the sign convention established in Figure 1.1c, the force that increases the interatomic distance is positive and hence the tensile force (or stress) is positive. An external compressive force (or stress) which tends to shorten the solid is negative. The relationship among the interatomic potential, the external force and the sign of the force, are shown schematically in Figure 1.3.

Note that Figure 1.3b is an inverted diagram of Figure 1.1b. We can define a point F_{max} as the maximum force that corresponds to the dissociative distance r_d of the material. F_{max} is thus the maximum tensile force needed to pull the solid apart because the force needed to increase the interatomic distance beyond r_d is less than F_{max}. We can regard F_{max} as the theoretical strength of the solid. To calculate F_{max}, we require that $\partial^2\phi/\partial r^2 = 0$ at $r = r_d$. If we assume that the solid obeys the Lennard–Jones potential and that the function ϕ is given by Eq. (1.2), we obtain its second derivative with respect to r as

$$\frac{\partial^2\phi}{\partial r^2} = \left(\frac{12\epsilon_b}{r_e^2}\right)\left(\frac{r_e}{r}\right)^8\left[13\left(\frac{r_e}{r}\right)^6 - 7\right] = 0, \quad \text{at } r = r_d, \tag{1.6}$$

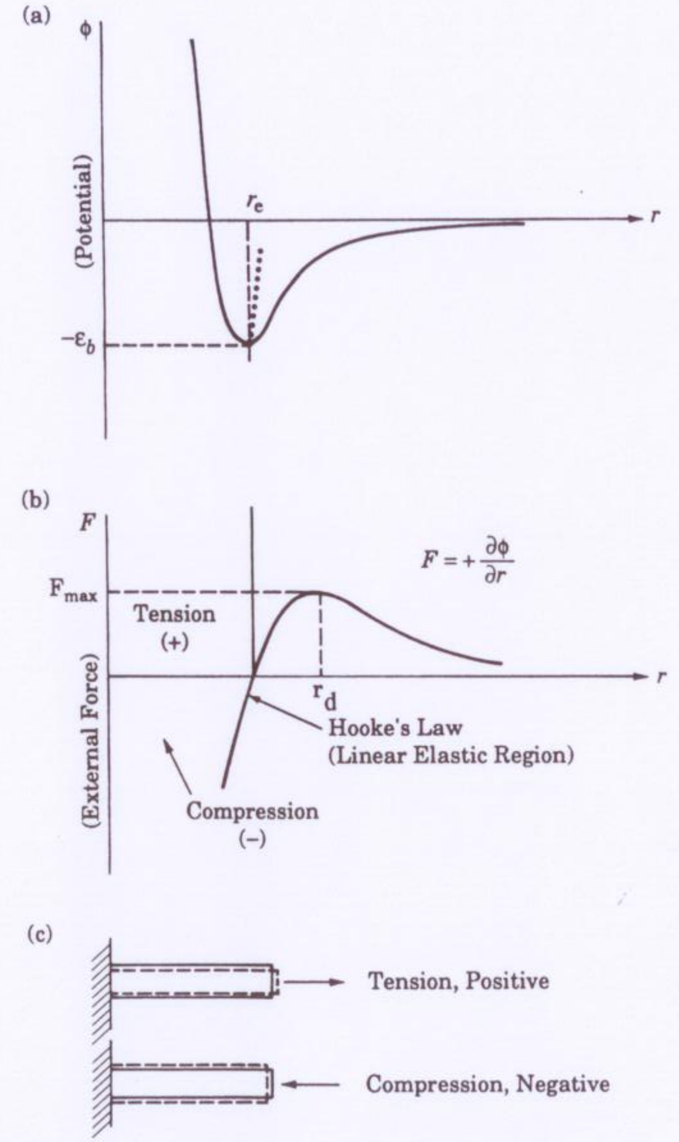

Figure 1.3. (a) Interatomic potential function plotted versus interatomic distance. (b) Applied force plotted versus atomic displacement. (c) The direction and sign of the applied force according to the established convention. Reprinted from [1] by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

where r_e is the equilibrium interatomic distance. The solution of Eq. (1.6) shows that

$$r_d = 1.11 r_e.$$

Theoretically, the solid can be strained approximately 11% before it breaks. Furthermore, if stretched just below that strain, it would return to its original condition. We know that experimentally these conditions are not found. Most polycrystalline metals, whether they obey the Lennard–Jones potential or not, have an elastic limit of only 0.2%. After that, plastic deformation sets in.

It is interesting to estimate the magnitude of the energy involved in elastic strain. Consider the case at the limit. The elastic energy is given by

$$E_{el} = \int \sigma \, de = \tfrac{1}{2} Y e^2, \tag{1.7}$$

where σ is the stress, e is the strain and Y is Young's modulus. To estimate the elastic energy, let's select one of the stiffest materials, steel, with $Y = 2.0\times10^{11}$ Pa and use 8.4×10^{22} atoms/cm^3 to convert to electron volts per atom. If we take $e = 0.2\%$, then

$$E_{el} = \tfrac{1}{2} Y e^2 = 4\times10^5 \text{ Pa} \cong 3\times10^{-5} \text{ eV/atom}.$$

This value of the elastic energy per atom is several orders of magnitude smaller than the binding energy of a metal or compound, which is on the order of 3.5 eV/atom, as in Table 1.1. Therefore, the effects of elastic stress on the enthalpy of compound formation are often negligible. The potential energy corresponding to a strain of 0.2% is still very close to the binding energy.

Although small, the strain energy can be important in cases where solids are near equilibrium. At equilibrium, the forces are balanced, so any small additional force can drive a reaction one way or another. Thus, the effects of stress are important in coarsening reactions in solids that are near equilibrium, and the strain energy is also important in stabilizing metastable phases during precipitation processes in solids and in thin films.

Table 1.1. Comparison of the interatomic potential energies of copper, silver and gold calculated from the heats of sublimation and vaporization using Eq. (1.4)

Element	ΔH_s (kJ/mol)	ϵ_b (eV/atom pair)	ΔH_v* (kJ/mol)	ϵ_b (eV/atom pair)
Cu	336	0.58	300.5	0.57
Ag	284	0.49	250.6	0.47
Au	368	0.64	324.4	0.61

*Heats of vaporization are usually specified at the boiling point, not at 0 K.

1.2.3. Interatomic Potential and Vibrational Frequency

Now we examine one last fundamental parameter of a solid, the vibration frequency of atoms, again based on the interatomic potential. Figure 1.4a shows a sketch of a single surface atom that is bonded to a solid by a potential ϕ as in our previous discussion. We assume that the atom undergoes harmonic motion. It is a simplified model, but it yields a vibrational frequency that is of the same order of magnitude as that of atoms in a solid. We approximate the bottom portion of ϕ around r_e by a parabolic potential and move the point $(-\epsilon_b, r_e)$ to the origin of the coordinates, as shown in Figure 1.4b. This approximation is reasonable for small amplitudes of vibration and we write

$$\phi = \tfrac{1}{2}\mathfrak{C} r^2. \tag{1.8}$$

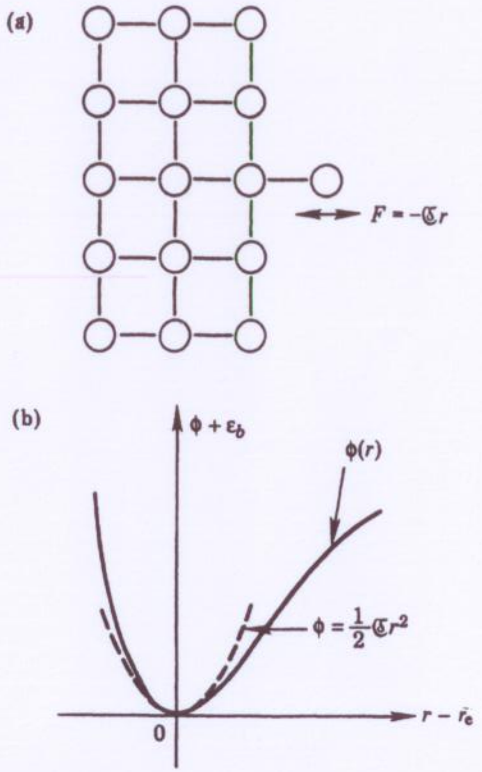

Figure 1.4. (a) A surface atom undergoes simple harmonic vibration. (b) The interatomic potential $\phi(r)$ of the surface atoms is plotted on the coordinates of $r - r_e$ and $\phi(r) + \epsilon_b$. Near the origin, $\phi(r)$ can be approximated by $\phi = \mathfrak{C}r^2/2$. Reprinted from [1] by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

Thus,

$$F = -\partial\phi/\partial r = -\mathfrak{C}r, \qquad (1.9)$$

where $\mathfrak{C}$ is the force (or spring) constant. It describes a simple harmonic motion; the equation of motion is

$$m\,\mathrm{d}^2r/\mathrm{d}t^2 = -\mathfrak{C}r, \qquad (1.10)$$

where m is the mass of the atom. Equation (1.10) has a simple solution of the form

$$r = \cos \nu t,$$

where $\nu = (\mathfrak{C}/m)^{1/2}$ is the oscillation frequency. Because we know that the cosine function has a period of 2π, the time needed to complete a period of motion is

$$\nu t = 2\pi \quad \text{or} \quad t = 2\pi/\nu.$$

Hence, the frequency of vibration is

$$\nu_0 = 1/t = \nu/2\pi = (1/2\pi)(\mathfrak{C}/m)^{1/2}. \qquad (1.11)$$

We can calculate ν_0 if we know $\mathfrak{C}$ and m. The latter is found from the atomic weight of the solid and Avogadro's number. To determine $\mathfrak{C}$, we take the second derivative of ϕ in Eq. (1.8) and obtain

$$\partial^2\phi/\partial r^2 = +\mathfrak{C}. \qquad (1.12)$$

Equating this to Eq. (1.6) shows that

$$\mathfrak{C} = 72\epsilon_b/r_e^2, \quad \text{at } r = r_e. \qquad (1.13)$$

Substituting $\mathfrak{C}$ into Eq. (1.11) gives

$$\nu_0 = (3/\pi)(2\epsilon_b/mr_e^2)^{1/2}. \qquad (1.14)$$

If we consider the atoms in Figure 1.4 to be gold, then $m = 32.8\times10^{-23}$ g/atom, $r_e/\sqrt{2} = 0.288$ nm, $\epsilon_b = 0.64$ eV/atom pair from Table 1.1 and we obtain

$$\nu_0 = 2.62\times10^{12}\ \mathrm{sec}^{-1}.$$

If this simple calculation is extended to an atom with an f.c.c. lattice where it has twelve nearest neighbors, the force constant has to be multiplied by a factor of six for vibration along a close-packed direction. The factor of six comes about because we use the principle of superposition and sum the projections ($\cos\theta$) of the interatomic force of all twelve atoms. In turn, we have to multiply ν_0 by $\sqrt{6}$ and we have

$$\nu_E = (6/\pi)(3\epsilon_b/mr_e^2)^{1/2}. \qquad (1.15)$$

This is called the Einstein frequency. It represents a maximum characteristic frequency of vibration for a solid and it depends on the strength of the interatomic potential (spring constant) in the solid. It does not depend on thermal (kinetic) energy. For a gold atom with an f.c.c. lattice, we then have $\nu_E = 6.42\times10^{12}\ \mathrm{sec}^{-1}$.

The formal treatment of elastic vibrations (phonons) in a finite solid has been given by Debye and is covered in solid-state textbooks [2–4]. The Debye frequency

$$\nu_D = k_B T_\theta/h, \qquad (1.16)$$

where h is Planck's constant, T_θ is the Debye temperature at which all the $3N$ modes of elastic waves are operative, N is the number of atoms and the factor three arises because the problem is three dimensional. Again, for gold with $T_\theta = 165$ K,

$$\nu_D = 3.42\times10^{12}\ \mathrm{sec}^{-1},$$

which is not very different from the frequency we just calculated. Since the Debye temperatures of metals only vary by a factor of two or three (e.g., $T_\theta = 428$ K for aluminum), the atomic vibrational frequency of metals is typically taken as $10^{13}\ \mathrm{sec}^{-1}$.

1.3. EMBEDDED ATOM, MONTE CARLO AND MOLECULAR DYNAMICS CALCULATIONS

The LJ (6–12) interatomic potential discussed in Section 1.1 is a two-body potential. It is simple and quite useful for determining the structure and behavior of many molecular solids and metals, where the atoms can be approximated as hard spheres with only nearest-neighbor interactions. In many materials, particularly metals, the electronic interactions can be long range, and we need to solve a more complex, many-body problem. Ideally, we would like to be able to predict phase transitions and defect structures of metals and alloys from first principles, that is, by simply plugging in the atomic numbers of the atoms into some calculation, which then proceeds to tell us the free energies of the different states and how the atoms evolve into these states. This is an extremely formidable task, although enormous progress has been made in this direction, particularly with the increase in computational power that has occurred over the past decade. Three particular techniques have become popular for solving these types of problems: the embedded atom method (EAM), Monte Carlo (MC) calculations, and molecular dynamics (MD) calculations. Because this book often refers to the results from such calculations and compares the output of EAM calculations with the results from the simpler pair-potential calculations, the remainder of this section provides a brief explanation of the procedures involved in these calculations.

In the EAM, the energy of each atom is computed from the energy needed to embed the atom in the local electron density provided by all the other atoms in the metal [5–7]. This electron density is approximated by linear superposition of the individual atomic electron densities. Thus, the electron density in the vicinity of each atom can be expressed as a sum of the density contributed by the atom in question plus the electron density from all the surrounding atoms. This latter contribution is a slowly varying function of position. If we make the simplification that the background electron density is a constant, the energy of the atom in question is the energy associated with the electron density of the atom plus the constant background density. In addition, there is an electrostatic repulsion energy contribution due to core–core overlap. In equation form, the total energy of the ensemble of atoms is given by

$$E_{\text{tot}} = \sum_i F_i(\rho_{h,i}) + \tfrac{1}{2} \sum_i \sum_{j(\neq i)} \phi_{ij}(r_{ij}). \qquad (1.17a)$$

In this expression, $\rho_{h,i}$ is the host electron density at atom i due to the remaining atoms of the system, $F_i(\rho)$ is the energy to embed atom i into the background electron density, and $\phi_{ij}(r_{ij})$ is the core–core repulsion between atoms i and j separated by the distance r_{ij}. As mentioned above, the electron density is approximated by the superposition of atomic densities

$$\rho_{h,i} = \sum_{j(\neq i)} \rho_{e,j}(r_{ij}), \qquad (1.17b)$$

where $\rho_{e,j}(r)$ is the electron density contributed by atom j.

To apply this method, the embedding functions, pair repulsions and atomic densities must be known. The atomic densities $\rho_{e,j}(r)$ can be represented by the spherically averaged free-atom densities calculated with the Hartree–Fock theory [8]. The pair interaction term $\phi_{ij}(r_{ij})$ in the EAM is physically analogous to the LJ interaction described in Eq. (1.2), although it has a slightly different form. It is assumed to be Coulombic in origin and decrease monotonically with increasing separation. The pair interaction between different atoms is approximated by the geometric mean of the pair interaction for the individual species. A functional form for the embedding energies $F_i(\rho)$ is obtained empirically by adjusting parameters to fit known bulk properties of the elements such as the sublimation energy, lattice constants, elastic constants and vacancy formation energy. Once the parametric fit has been accomplished, these quantities can be substituted into Eq. (1.17a) to find the total energy of an arbitrary arrangement of atoms including defects. This energy is minimized by adjusting the lattice constants or atomic coordinates to find the configuration that yields the lowest possible energy. In the case of defects, the calculations are usually performed using a computational cell of 500 atoms or more with periodic boundary conditions. The relative stabilities of various phases are determined by varying the atomic configurations and lattice constants and comparing the total energies [E_{tot} in Eq. (1.17a)] of the phases. In the case of defects, the defect energy is minimized with respect to the atomic coordinates of all of the atoms in the computational cell and with respect to the dimensions of the periodic cell. Using this procedure, it is possible to calculate other (unknown) properties of the elements or alloys, such as the migration energies of the atoms, the surface energies, heats of segregation and heats of solution. These calculations are usually performed at 0 K and do not include entropic contributions.

In the Monte Carlo method [9], an initial configuration of atoms with known interatomic potentials (for example an LJ or EAM potential) is placed in a finite box with periodic boundary conditions at fixed temperature T. Random numbers are then used to select and move individual atoms. If the potential energy change $\Delta\phi$ resulting from a move is less than zero, then the new configuration is accepted. If $\Delta\phi$ is greater than zero, then it is accepted only with a probability $\exp(-\Delta\phi/k_BT)$. This procedure is repeated until the system converges to a stage of local equilibrium at which values of the total energy and pressure can be obtained. In terms of surfaces and interfaces, the Monte Carlo technique is useful for finding the most favorable arrangement of atoms at equilibrium, particularly in alloys, where impurities may segregate to specific sites on a surface or at an interface. This technique has been combined with the EAM to study surfaces and interfaces in metals [10]. The time required for these calculations places a limit on the number of atoms that can be used (typically a few thousand). This can prevent phase transitions from occurring at the equilibrium point so that they have not been used extensively to map phase boundaries. Monte Carlo calculations cannot be used to gain insight into kinetic aspects of a phenomenon.

In molecular dynamics calculations, Newton's equations of motion are solved for a few hundred (or maybe a few thousand) particles in a box at a particular temperature T [11]. The energy and pressure of the system can be calculated as the system evolves over time, and a plot of the atomic trajectories provides a visual snapshot of the detailed dynamical processes of the system. Ultimately, the system converges to local thermodynamic equilibrium. The temperature can be varied and the nature of phenomena such as grain boundary melting or surface melting can be examined. Again, because of the finite size of the computational cell and the accuracy of the atomic interactions, there is often the same difficulty in accurately locating phase boundaries as in the Monte Carlo method so that the temperatures at which the transitions occur are only approximate. The time scale that can be simulated is short (i.e., simulations generally run only hundreds of picoseconds) because atomic vibrations occur on the order of 10^{13} sec^{-1}. Thus it is not possible to directly study comparatively slow processes such as diffusion.

PROBLEMS

1.1. Plot the Lennard-Jones potential (Eq. 1.2) from $r = 0.1r_e$ to $r = r_e$ for gold where $\epsilon_b = 0.64$ eV/atom.

1.2. Starting with Eq. (1.2), derive Eq. (1.6), and use it to show that $r_d = 1.11r_e$.

1.3. Based on the values in Table 1.1 and below, calculate the Einstein frequency and the Debye frequency for copper, silver and gold and compare these values.

Element	n (10^{22}/cm^3)	Atomic Weight	T_θ (K)
Cu	8.45	63.5	343
Ag	5.85	107.9	225
Au	5.9	197	165

1.4. Using the Lennard–Jones potential with $n = 8\times10^{22}$ atoms/cm^3, $\epsilon_b = 0.6$ eV/atom and $r_e = (1/n)^{1/3}$:

(a) Calculate the maximum force $F_{\max}$.

(b) Assume the solid is in the linear elastic region and calculate Young's modulus Y.

(c) What is the elastic energy E_{el} at $F_{\max}$?

1.5. (a) For the Lennard-Jones potential, discuss the influence of increasing the attractive interaction while keeping the repulsive interaction fixed. How will this effect the equilibrium separation r_e and the pair potential ϵ_b?

(b) Repeat this process but decrease the repulsive interaction and do this while keeping the attractive interaction constant.

1.6. Suppose an atomic cluster of only 12 atoms forms. Assuming that the atoms can be described by the Lennard–Jones potential, would you expect the interatomic spacing and elastic modulus of the cluster to be greater or less than that of a corresponding bulk crystal? Explain.

1.7. Estimate the bond energies ϵ_b of copper, silver and gold from the heats of melting of the elements, assuming that there are 11 nearest neighbors in the liquid. How do your results compare with the values in Table 1.1?

2

REGULAR SOLUTION (QUASI-CHEMICAL) MODEL

Certain properties of binary solutions are used frequently in this book to explain phenomena such as segregation to interfaces and chemical gradients at interfaces. Thus, it is important that the reader be familiar with properties of binary solutions. This chapter summarizes some of the most important of these properties, including the regular solution model and the effect of temperature on solid solubility and also includes a brief review of some thermodynamics which lead up to the regular solution model. Our treatment is based on that of Porter and Easterling [12] and the reader may refer to this and other books on thermodynamics [2,13,14] for additional background.

2.1. THE GIBBS FREE ENERGY OF BINARY SOLUTIONS

In alloys, the Gibbs free energy is a function of composition, temperature and pressure. In this book, the pressure is usually assumed to be 1 atm and the reaction is carried out at constant temperature, so that these variables are fixed. In this case, the relative stability of a system is determined by its Gibbs free energy, which is defined as

$$G = H - TS, \tag{2.1}$$

where H is the enthalpy, T is the absolute temperature and S is the entropy of the system. The quantity G is usually expressed in joules per mole. Enthalpy is a measure of the heat content of the system and is given by

$$H = E + PV, \tag{2.2}$$