7 Entropy

Without entropy to complement energy, thermodynamics would have the impact of one hand clapping. The epithaph on Boltzmann's monument shown in Fig. 7.1

$$S = k_B \ln \Omega \,, \tag{7.1}$$

is an equation for entropy of breathtaking generality. Here it is modernized slightly, with k_B as the Boltzmann constant. The nub of the problem is the number Ω, which counts the ways of finding the internal coordinates of a system for thermodynamically-equivalent macroscopic states. Physical questions are, "What do we count for Ω, and how do we count them?"

Sources of entropy are listed in Table 7.1, and some were discussed in Chapter 1. Configurational entropy in the point approximation was used extensively in Chapter 2, and Section 17.4 accounts for magnetic entropy in essentially the same way. This Chapter 7 shows how the configurational entropy of chemical disorder or magnetic disorder can be calculated more accurately with cluster expansion methods. The other major source of entropy is vibrational entropy, and its origin is explained in Section 7.5. Critical temperatures of ordering and unmixing, calculated previously with configurational entropy alone, are then adapted to include effects of vibrational entropy.

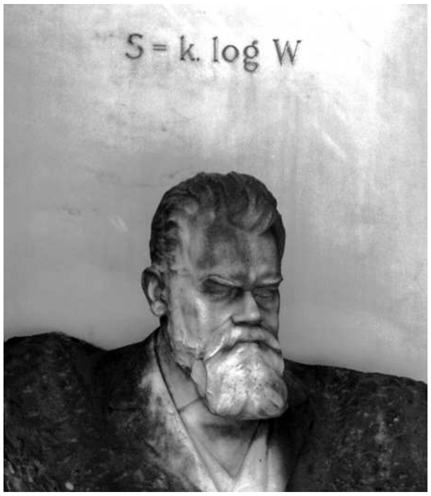

Fig. 7.1 The Boltzmann monument in Vienna. The constant k is related to k_B by the factor 2.3026 if log denotes $\log_{10}$. Our notation uses Ω instead of W.

Table 7.1 Sources of Entropy in Materials

Matter	Structural Configurations
nuclei	sites for the nuclei (the electrons will adapt)
electrons	sites for electrons in mixed-valent compounds
electron spins	orientational disorder (magnetic disorder)
Energy	Dynamics
nuclei	vibrations (phonons)
electrons	excitations across Fermi level (electronic heat capacity)
electron spins	spin waves (magnons)

For metals there is a heat capacity and entropy from thermal excitations of electrons near the Fermi surface, but as discussed in Section 6.2.4 this is often a small effect because not many electrons are available for these excitations. The electronic entropy of a metal increases with temperature, but at high temperatures the electronic excitations may interact with phonons, and phonons interact with other phonons as discussed in Chapter 24.

7.1 Static and Dynamic Sources of Entropy

It is often reasonable to separate the internal coordinates of a material into configurational ones and dynamical ones. As an example, when the number Ω enumerates the ways to arrange atoms on the sites of a crystal, the method to calculate Ω does not depend on temperature. We used this idea extensively in Chapter 2. On the other hand, when the number Ω for dynamical coordinates counts the intervals of volume explored as atoms vibrate, this Ω increases with temperature, as does the vibrational entropy.

Configurational entropies of atoms or spins undergo changes during chemical ordering or magnetic phase transitions, respectively.[1] Configurational entropy was largely understood by Gibbs, who presented some of the combinatoric calculations of entropy that are used today (23). The calculation of Ω is more difficult when there are partial correlations over short distances, but cluster approximation methods have proved powerful and accurate (53)-(55), and are presented in Section 7.2. In essence, new local variables are added to the list of composition and long-range-

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[1] Electronic entropy can also have a configurational component in mixed-valent systems. Nuclear spins undergo ordering transitions at low temperatures, too, although at most temperatures of interest in materials physics the nuclear spins are fully disordered and their entropy does not change with temperature.

order parameter to describe more precisely the atom configurations on lattice sites. Again, although the configurational variables have different equilibrium values at different temperatures, temperature does not alter the combinatorial method for calculating Ω with the configurational variables.

Dynamical entropy grows with temperature as dynamical degrees of freedom of a solid, such as normal modes of vibration, are excited more strongly by thermal energy.[2] With increasing temperature more phonons are created, and the vibrational excursions of atomic nuclei are larger. Fundamentally, the entropy from dynamical sources increases with temperature because with stronger excitations of dynamical degrees of freedom, the system explores a larger volume in the hyperspace[3] spanned by position and momentum coordinates, as discussed in Section 7.5. This volume, normalized by a quantum volume if necessary, is the Ω for Eq. 7.1. For a phase transition, what is important is not the total vibrational entropy so much as the difference in vibrational entropy between the two phases.[4]

7.2 Short-Range Order and the Pair Approximation

Section 2.10 presented a thermodynamic analysis of the order-disorder transition in the point approximation, which assumed that all atoms on a sublattice were distributed randomly. This assumption is best in situations when 1) the temperature is very high, so the atoms are indeed randomly distributed on the sublattice, 2) the temperature is very low, and only a few antisite atoms are present, or 3) a hypothetical case when the coordination number of the lattice goes to infinity. For more interesting temperatures around the critical temperature, for example, it is possible to improve on this assumption of sublattice randomness by systematically allowing for short-range correlations between the positions of atoms.

For example, a deficiency of the point approximation for ordering is illustrated with Fig. 7.2. We see that the numbers of A-atoms and B-atoms on each sublattice are equal, so the LRO parameter $L = (R - W)/(N/2) = 0$. Nevertheless, there is obviously a high degree of order within each of the two domains. It might be tempting to redefine the sublattices within each domain, allowing for a large value of L, but this gets messy when the domains are small. The standard approach to this problem is

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[2] Temperature also drives electronic excitations to unoccupied states, and when many states are available the electronic entropy is large. Spin excitations are another source of entropy, but care must be taken when counting them if the configurations of spin disorder are already counted.

[3] This is frequently called a "phase space," not to be confused with geometric properties of crystallographic phases.

[4] The "Kopp–Neumann rule" from the nineteenth century states that the heat capacity of a compound is the sum of atomic contributions from its elements. By this rule, the vibrational entropy of a solid phase depends only on its chemical composition, and not on its structure. This rule is not helpful for understanding the thermodynamics of phase transitions. Furthermore, the Kopp–Neumann rule has inconsistencies when picking an atomic heat capacity for carbon, for example.