

Statistical Physics

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3 Thermodynamics from statistical mechanics

In thermodynamics we study changes from one equilibrium state to another. We seek relationships between physical quantities of initial and final states only. We do not try to describe the transition between equilibrium states

We consider 2 types of energy transfer here. The first is heat, Q , the disordered energy transfer by random processes. The second is work, W , the ordered energy transfer by an external force. Focusing on a system \mathcal{S} , we will use the sign convention that $Q > 0$ when heat is supplied *to* \mathcal{S} and $W > 0$ when work is done *on* \mathcal{S} .

3.1 Adiabatic processes

An **adiabatic** process is defined by the following conditions

1. $Q = 0$. No heat transfer to or from \mathcal{S} .
2. The process is carried out only by external forces.
3. The process takes place arbitrarily slowly so that each intermediate state can be considered to be an equilibrium state.

Quantum mechanically we can apply **Ehrenfest's principle**, also known as the **adiabatic theorem**, that transitions between quantum states are negligible if the perturbations (changes in V) are slow enough. That is, an adiabatic process is one where we can assume a state which is in $|i\rangle$ will remain in $|i\rangle$ during the next infinitesimal step of the process. (Of course the system will continue to explore the allowed microstates by virtue of being a thermal system. The important point is that the adiabatic process does not force the system into a different state.) In other words, the occupation probabilities ρ_i do not change during an adiabatic process. An adiabatic process is an example of a process which is both **quasistatic**, since it proceeds so slowly that intermediate states are also equilibrium states, and which is **reversible**, since the inverse process can be performed. Reversible processes are quasistatic processes which have no hysteresis effects.

For example, take a gas in an insulated container with a movable piston whose surface area is A (Fig. 4). Applying a force \mathbf{F} , push the piston inward slowly, adiabatically compressing the gas. The work done on the system is

$$\boxed{dW = -\mathbf{F} \cdot d\mathbf{x} = -PA dx = -P dV} \quad (3.1.1)$$

where P is the pressure (force/area) exerted on the piston (assume for simplicity the force is normal to the piston's surface, which we take to be planar). Note that here $dW > 0$ since $dV < 0$. Clearly we can undo this process by pulling the piston instead of pushing it. Therefore, the process is reversible. Note that we use a 'd' to denote an infinitesimal amount of work or heat. Neither dW nor dQ are exact differentials: the amount of work done or heat transferred depends on the specific process undertaken. Since $dV = -dW/P$ is an exact differential, we can consider the pressure to be an integrating factor.

Given that the compression in our example above is slow enough to satisfy the conditions of the adiabatic theorem, then the only microscopic change is due to the

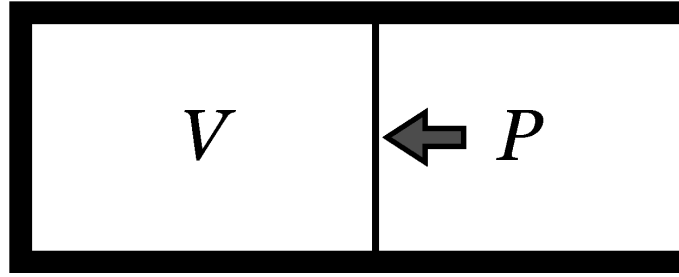


Figure 4: A gas at pressure P occupies volume V inside an insulated container. A piston can be moved to carry out adiabatic changes.

volume dependence of the energies of the microstates. For an infinitesimal step in the process, the change in energy for microstate $|i\rangle$ will be

$$dE_i = \frac{\partial E_i}{\partial V} dV. \quad (3.1.2)$$

Furthermore, the statement of the adiabatic theorem means that the occupation probabilities ρ_i do not change during an adiabatic process, *i.e.* that $d\rho_i = 0$. Changes in the E_i are compensated by a change in the temperature. Thus, the work done on the system changes the total average energy (denoted by E , dropping the $\langle \cdot \rangle$ notation for convenience) is

$$dE = dW \quad \text{by energy conservation} \quad (3.1.3)$$

$$d\left(\sum_i \rho_i E_i\right) = -P dV \quad (3.1.4)$$

$$\sum_i \rho_i \frac{\partial E_i}{\partial V} dV = -P dV \quad (\text{adiabatic} \Rightarrow \frac{\partial \rho_i}{\partial V} = 0) \quad (3.1.5)$$

which implies

$$P = -\sum_i \rho_i \frac{\partial E_i}{\partial V}. \quad (3.1.6)$$

Let us again consider the example of a noninteracting gas in a box with periodic boundary conditions. The single-particle energies are labelled by the wave vector \mathbf{k} (see Eq. 1.2.3) and depend on volume as

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 |\mathbf{k}|^2}{2m} = \frac{4\hbar^2 \pi^2 |\mathbf{n}|^2}{2mL^2} \propto V^{-2/3}. \quad (3.1.7)$$

Therefore the total energy of the many particle state, just the sum of all the single particle states times the number of particles in that state $E_i = \sum_{\mathbf{k}} n_{\mathbf{k}}^{(i)} \varepsilon_{\mathbf{k}}$, has the same volume dependence

$$\frac{\partial E_i}{\partial V} = -\frac{2}{3} \frac{E_i}{V} \quad (3.1.8)$$

and hence the pressure is

$$P = \frac{2}{3V} \sum_i \rho_i E_i = \frac{2}{3V} E = -\frac{\partial E}{\partial V}. \quad (3.1.9)$$

We see that knowing the quantum mechanical Hamiltonian at the particle level allows us to determine the thermodynamic relation between pressure and energy in a macroscopic gas of these particles.

3.2 Entropy

Next we consider processes where heat is transferred. Once we go beyond adiabatic processes, the occupation probabilities for microstates, *i.e.* the statistical distribution, is no longer constant: $d\rho_i \neq 0$. Therefore

$$dE = \sum_i (E_i d\rho_i + \rho_i dE_i) . \quad (3.2.1)$$

Let us define **entropy** in the language of the canonical ensemble (Chapter 2)

$$S = \frac{k}{A} \log W(\{a\}) \quad (3.2.2)$$

where k is Boltzmann's constant,² A is the number of replicas in an ensemble, $\{a\}$ is an enumeration of microstates, and $W(\{a\})$ is the number of arrangements of that enumeration. Inserting the expression for $W(\{a\})$ (2.1.10) we find

$$S = \frac{k}{A} \left(A \log A - \sum_i a_i \log a_i \right) \quad (3.2.3)$$

Since

$$\begin{aligned} \sum_i a_i \log a_i &= \sum_i A \rho_i \log(A \rho_i) \\ &= A \sum_i \rho_i (\log A + \log \rho_i) \\ &= A \log A + A \sum_i \rho_i \log \rho_i . \end{aligned} \quad (3.2.4)$$

In the last step we used the fact that probabilities must sum to 1: $\sum_i \rho_i = 1$. Then we find

$$\boxed{S = -k \sum_i \rho_i \log \rho_i} . \quad (3.2.5)$$

Now consider a quasistatic process which includes transfer of heat. Inserting the Boltzmann distribution

$$\rho_i(V, T) = \frac{1}{Z(V, T)} e^{-\beta E_i(V)} \quad (3.2.6)$$

²Equation (3.2.5) is on Boltzmann's headstone. His work was not widely accepted until after his death. His body was reburied several years after his death, with the new headstone reflecting his contribution to theoretical physics.

we find an infinitesimal step in the process changes the entropy by

$$\begin{aligned}
 dS &= -k \sum_i d\rho_i (\log \rho_i + 1) \\
 &= -k \sum_i d\rho_i (-\beta E_i - \log Z + 1) \\
 &= \frac{1}{T} \sum_i E_i d\rho_i
 \end{aligned} \tag{3.2.7}$$

In the last step, we used the conservation of probability which implies $\sum_i d\rho_i = 0$, the fluctuation in total probability must be zero. Inserting the right hand side of (3.2.7) into (3.2.1) we find

$$\boxed{dE = T dS - P dV.} \tag{3.2.8}$$

Equation (3.2.8) is a useful form of the **first law of thermodynamics**. The general form of the law is

$$dE = dQ + dW. \tag{3.2.9}$$

For reversible processes, where e.g. no energy is lost to friction and no free expansion occurs, then

$$\text{Reversible} \Rightarrow \quad dQ = T dS \quad dW = -P dV \tag{3.2.10}$$

otherwise

$$\text{Irreversible} \Rightarrow \quad dQ < T dS \quad dW > -P dV. \tag{3.2.11}$$

Note also, that for adiabatic processes where $dQ = 0$, that $dS = 0$.

3.3 Thermodynamic potentials

From (3.2.8) we see that the average energy E is naturally a function which treats S and V as the independent variables. The other thermodynamic variables, P and T are then treated as functions of S and V and can be computed if $E(S, V)$ is known

$$T = \left. \frac{\partial E}{\partial S} \right|_V \quad \text{and} \quad P = - \left. \frac{\partial E}{\partial V} \right|_S. \tag{3.3.1}$$

In addition to the average system energy E , we can construct other thermodynamic potentials, which might be useful in various contexts as they naturally depend on different thermodynamic variables.

Note that we can write the entropy as

$$\begin{aligned}
 S &= -k \sum_i \rho_i \log \rho_i \\
 &= -k \sum_i \rho_i (-\beta E_i - \log Z) \\
 &= \frac{E}{T} + k \log Z.
 \end{aligned} \tag{3.3.2}$$

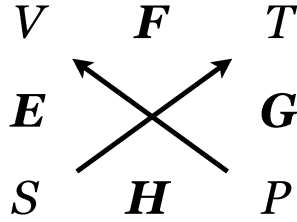


Figure 5: “Very Fine Teachers Enjoy Giving Some Hard Problems.” Mnemonic for remembering the equations (3.2.8), (3.3.4), (3.3.7) and (3.3.9). The thermodynamic potentials are in bold, adjacent to their corresponding independent variables. The arrows connect combinations of variables, the direction of the arrow indicates the sign.

Now let us define the (Helmholtz) free energy³ F by

$$\boxed{F = -kT \log Z = E - TS} \quad (3.3.3)$$

so that

$$dF = dE - TdS - SdT = -SdT - PdV. \quad (3.3.4)$$

In (3.3.3) we have performed a Legendre transform from $E(S, V)$ to $F(T, V)$. The free energy is also useful in statistical mechanics, since the partition function can be written

$$Z = e^{-\beta F}. \quad (3.3.5)$$

There are 2 more potentials we can define. The **Gibbs free energy**⁴ is

$$\boxed{G = E - TS + PV} \quad (3.3.6)$$

which implies

$$dG = -SdT + VdP. \quad (3.3.7)$$

The **enthalpy** is

$$\boxed{H = E + PV} \quad (3.3.8)$$

which implies

$$dH = TdS + VdP. \quad (3.3.9)$$

Aside on Legendre transformations

Recall from classical mechanics the transformation from Lagrangian to Hamiltonian

$$\mathcal{H}(q, p) = p\dot{q} - \mathcal{L}(q, \dot{q}) \quad (3.3.10)$$

³The phrase “the free energy,” one usually refers to this quantity. It is sometimes denoted by A instead of F . Incidentally, some texts use U for the system energy and sometimes refer to it as the internal energy.

⁴Landau & Lifshitz use Φ for the Gibbs free energy

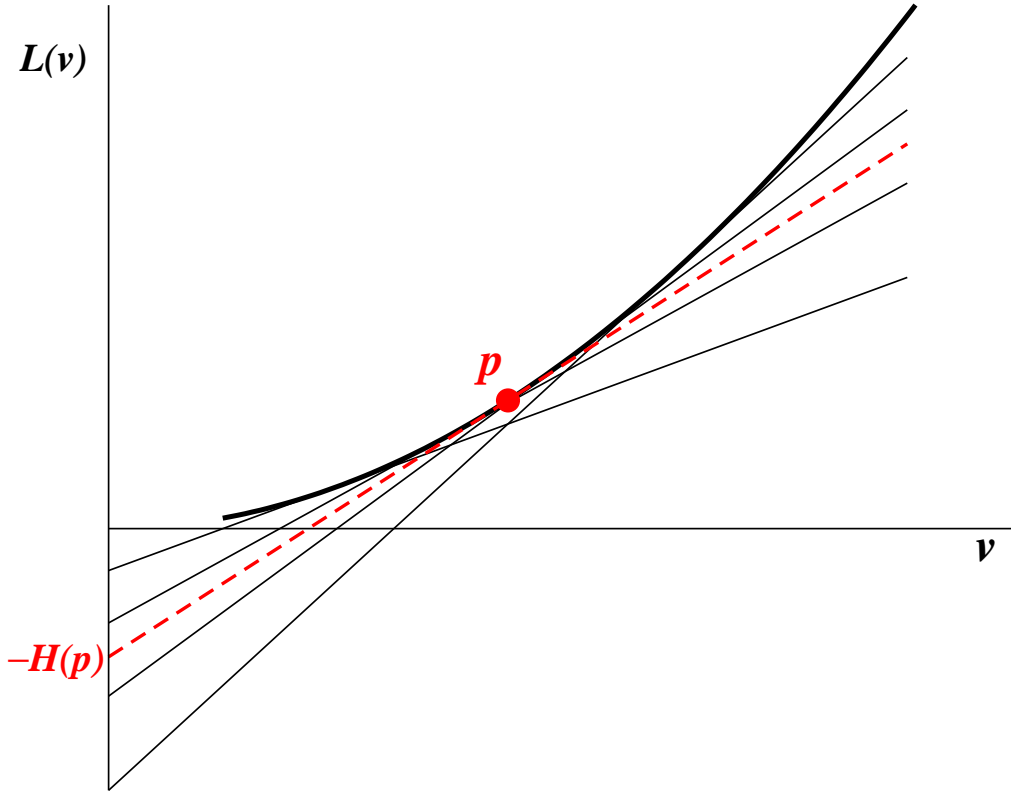


Figure 6: Legendre transform. A curve can be described by the set of points $(v, L(v))$ or by the envelope of a set of slopes and intercepts $(p, -H(p))$.

which exchanges the velocity $v = \dot{q}$ for the momentum p as the independent variable. We can describe the the curve defined by the set of points $(v, \mathcal{L}(v))$. Recall that momentum is the slope of the Lagrangian in the v direction

$$p = \frac{\partial L}{\partial v} \quad (3.3.11)$$

The same curve can be defined by the envelope of a set of tangents, *i.e.* slopes and intercepts $(p, -\mathcal{H}(p))$.

3.4 Extensive and intensive quantities

We introduce some terminology for quantities based on their scaling behaviour. Let us imagine replicating system \mathcal{S}_1 which is in thermodynamic equilibrium, and calling the copy \mathcal{S}_2 . Each have the same P, V, T, N by construction. Now join them together, so that the joint system \mathcal{S}_{12} is a scaled-up version of the original. We consider how thermodynamic quantities differ between the original and scaled systems. Clearly the volume and particle number has doubled ($V_{12} = V_1 + V_2$ and $N_{12} = N_1 + N_2$), while the pressure and temperature remain the same. Quantities that scale with the volume under these types of scale transformations are called **extensive**. Quantities that remain unchanged under scale transformations are called **intensive**.

For a weakly interacting or noninteracting system, joining \mathcal{S}_2 with \mathcal{S}_1 will not change the occupation probabilities: the probability of a particle 1 having E_i in \mathcal{S}_{12} and particle 2 having E_j in \mathcal{S}_{12} is the product of probabilities: of particle 1 having energy E_i in \mathcal{S}_1 and particle 2 having energy E_j in \mathcal{S}_2 . We should assume that V is large enough that doubling the volume does not greatly effect the energy spectrum, *e.g.* we are near the thermodynamic limit. Then,

$$Z_{12} = Z_1 Z_2. \quad (3.4.1)$$

This means that the free energy is extensive:

$$e^{-\beta F_{12}} = e^{-\beta F_1} e^{-\beta F_2} = e^{-\beta(F_1+F_2)}. \quad (3.4.2)$$

Since $-\beta F = \sum_i \rho_i E_i$, the average energy must also be extensive: $E_{12} = E_1 + E_2$. Looking at the definition of free energy (3.3.3), we can see that the entropy is extensive

$$S_{12} - S_1 - S_2 = \frac{1}{T} [E_{12} - F_{12} - (E_1 - F_1) - (E_2 - F_2)] = 0. \quad (3.4.3)$$

All of the four thermodynamic potentials E , F , G , and H have been shown to be extensive. $G(P, T)$ is special. It is the only one which is a function of the 2 intensive variables (see (3.3.6) and (3.3.7)). Therefore, we can factor out from the coefficients of P and T a common factor of N

$$G(P, T) = \mu(P, T) N. \quad (3.4.4)$$

The quantity $\mu(P, T)$ is an intensive function, called the **chemical potential**. We will discuss this more later in Chapter 6.

3.5 Additivity of entropies

The discussion in the previous section relied on scaling a system in thermodynamic equilibrium. The additivity of entropies can be proved without relying on the partition function, which only makes sense in equilibrium.

Let ρ_i be the statistical distribution for system \mathcal{S}_1 and σ_j be the statistical distribution for system \mathcal{S}_2 . The statistical distribution for the joint system \mathcal{S}_{12} is the product $\rho_i \sigma_j$. Therefore, the total entropy can be written as

$$\begin{aligned} S_{12} &= -k \sum_{ij} \rho_i \sigma_j \log(\rho_i \sigma_j) \\ &= -k \sum_{ij} \rho_i \sigma_j (\log \rho_i + \log \sigma_j) \\ &= -k \left[\left(\sum_j \sigma_j \right) \sum_i \rho_i \log \rho_i + \left(\sum_i \rho_i \right) \sum_j \sigma_j \log \sigma_j \right] \\ &= S_1 + S_2. \end{aligned} \quad (3.5.1) \quad (3.5.2)$$

In the last step, we used the fact that the terms in parentheses, sums of probabilities are equal to 1. We see that the entropy of the joint system is just the sum of entropies of the individual systems.

This avoids discussion about equilibrium vs. nonequilibrium states. The entropies are additive even if ρ_i and σ_j are not the ones obtained by maximising W (equivalently, maximising the entropy).

Further reading

1. F Mandl, *Statistical Physics*, (Wiley & Sons, 1988), Chapters 1, 2 & 4.