

Topics in Physical Chemistry and Biophysics

1 Review of probability

1.1 Rules of probability

18.04.23 lec 1

Definition 1.1

Probability. If N is the total number of outcomes, and n_A fall in category A , then

$$p_A = \frac{n_A}{N} = \frac{\text{outcomes cat. } A}{\text{all outcomes}}.$$

Rules of composite events:

1. Mutually exclusive: outcomes (A_1, A_2, \dots) are *mutually exclusive* if one outcome precludes another outcomes. (Event A_1 prevents even A_2 from happening simultaneously.)
2. Collectively exhaustive: if all known outcomes are also all possible outcomes. $\sum p_i = 1$.
3. Independence: outcomes do not depend on each other.
4. Multiplicity: total number of ways in which outcomes occur.

Rules of calculation:

1. Let there be 3 outcomes A, B, C with probability p_A, p_B, p_C . What is the probability that either one occurs (A or B or C)?

$$p(A \cup B \cup C) = p_A + p_B + p_C.$$

That's the addition rule.

2. Probability that all outcomes occur? (Assuming independence)

$$p(A \cap B \cap C) = p_A p_B p_C.$$

3. Probability that an event A is not happening? $p = 1 - p_A$.

Example. We roll a die twice. What is the probability of rolling a 1 first **or** a 4 second?

Split the problem to parts. Note that the events are not mutually exclusive. Condition applies if:

- 1 first and not a 4 second: $\frac{1}{6} \cdot \frac{5}{6}$
- not a 1 first and a 4 second: $\frac{5}{6} \cdot \frac{1}{6}$
- 1 first and 4 second: $\frac{1}{6} \cdot \frac{1}{6}$

Now sum up all of the options to get result.

Definition 1.2

Correlated events. $p(B|A)$ is the probability that B occurs given A has occurred.

Joint probability. $p(AB)$ that both A and B occur.

Definition 1.3

General multiplication rule.

$$p(AB) = p(B|A) p(A) .$$

$P(A)$ is called the a priori probability and $p(B|A)$ is called the a posteriori probability

Theorem 1.4

Bayes theorem.

$$p(B|A) p(A) = p(A|B) p(B) .$$

Example. 1% of population has breast cancer. We use mammography to detect cancer.

Event A : breast cancer. $p(A) = 0.01$. $p(\bar{A}) = 1 - p(A) = 0.99$.

Event B : diagnosis. $p(B|A) = 0.8$. $p(B|\bar{A}) = 0.096$. (i.e. false positive)

What is the chance that a doctor has diagnosed someone with cancer? i.e. $p(A|B)$

$$p(A|B) = \frac{p(B|A) p(A)}{p(B)} .$$

$p(B)$ is the diagnosis of breast cancer irrespective whether it's there or not there.

$$p(B) = p(BA) + p(B\bar{A}) = p(B|A) p(A) + p(B|\bar{A}) p(\bar{A}) = 0.8 \cdot 0.01 + 0.096 \cdot 0.99 = 0.103,$$

$$p(A|B) = \frac{0.8 \cdot 0.01}{0.103} = 0.078 = 7.8\% .$$

The reason that $p(A|B)$ is so small is that the rate of false positive is really low and the rate of having breast cancer is really low.

1.2 Combinatorics and probability distributions

Combinatorics. Concerned with composition of events, and not with their order.

Example. How many combinations there are of N amino acids?

$$W = N! = N (N - 1) (N - 2) \dots$$

Example. Distinguish or not Distinguish: What are the possible number of ways to arrange N amino acids? Divide all permutations (assuming objects are distinguishable) by the number of permutations of objects that are indistinguishable.

$$W = \frac{N!}{N_A} .$$

In general, for N objects consisting of t categories in which the objects are indistinguishable:

$$W = \frac{N!}{(n_1!) (n_2!) \cdots (n_t!)}.$$

So, if $t=2$, (e.g. possible number of ways to arrange three acids A,A,H)

$$W = \frac{N!}{n_1! \cdot n_2!} = \frac{N!}{n_1! (N - n_1)!} = \binom{N}{n}.$$

Definition 1.5

Distribution functions. Describe collections of probabilities. Relevant for continuous variables.

$$\sum_i p_i \rightarrow \int_a^b p(x) dx.$$

Popular distributions:

1. *Binomial Distribution.* Relevant when there are only two outcomes.

Example. What is the probability that a series of N trials has n_H heads and n_T tails in any order?

p_H, p_T are mutually exclusive, so the probability of one sequence is

$$p_H^{n_H} \cdot p_T^{n_T} = p_H^{n_H} (1 - p_H)^{N - n_H}; \quad N = n_H + n_T.$$

and the number of ways to arrange the coins is

$$W = \frac{N!}{n_H! (N - n_H)!}.$$

Therefore, the possibility for the outcome (getting n_H and n_T) in any order is

$$p(n_H, N) = \binom{N}{n_H} p_H^{n_H} (1 - p_H)^{N - n_H}.$$

That's the binomial distribution.

Example. Given the molecule $C_{27}H_{44}O$ such that 1.1% is ^{13}C and the rest are ^{12}C , the fraction of molecules without a single ^{13}C is given by the binomial distribution.

2. *Multinomial distribution.* Basically the extension of the binomial distribution.

$$p(n_1, n_2, \dots, n_t, N) = \left(\frac{N!}{n_1! n_2! \cdots n_t!} \right) p_1^{n_1} p_2^{n_2} \cdots p_t^{n_t}.$$

Definition 1.6

Moments of distributions. Averages and Variances of distribution functions.

Given $p(i)$ s.t. $\sum_i p(i) = 1$, the **Average** is defined as

$$\langle i \rangle = \sum_i i p(i) \rightarrow \langle x \rangle = \int x p(x) dx.$$

Given $f(x)$,

$$\langle f(x) \rangle = \int f(x) p(x) dx.$$

Given $a \in \mathbb{R}$

$$\langle af(x) \rangle = \int af(x) p(x) dx = a \langle f(x) \rangle.$$

Given 2 functions $f(x), g(x)$,

$$\langle f(x) + g(x) \rangle = \langle f(x) \rangle + \langle g(x) \rangle,$$

$$\langle f(x) \cdot g(x) \rangle \neq \langle f(x) \rangle \langle g(x) \rangle.$$

The 2nd and 3rd **Moments** of the distributions $p(x)$ are

$$\langle x^2 \rangle = \int x^2 p(x) dx,$$

$$\langle x^3 \rangle = \int x^3 p(x) dx.$$

The **Variance** of the distribution, σ^2 is defined as

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = \langle (x - \langle x \rangle)^2 \rangle.$$

2 Entropy

2.1 Definition and Stirling's approximation

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Carved on the tombstone of Ludwig Boltzmann in the central cemetery in Vienna is the definition of *entropy*.

Definition 2.1

Entropy.

$$S = k \ln W.$$

- $k = 1.3806 \times 10^{-23} \text{ J K}^{-1}$ is Boltzmann's constant.
- W is the multiplicity; the microscopic degrees of freedom of a system.

Entropy can help describe the state of a system in equilibrium, as systems tend toward their states of maximum multiplicity W (and minimum energy).

Note. Entropy is an *extensive* (thus additive) quantity. Consider a thermodynamic system having two subsystems, A and B , with multiplicities W_A and W_B , respectively. The multiplicity of the total system is $W_{\text{total}} = W_A W_B$. Following def. 2.1, $S_{\text{total}} = S_A + S_B = k \ln W_A + k \ln W_B$. This is why incorporating the multiplicity in a logarithm makes sense.

Why does def. 2.1 assume this particular mathematical form? The multiplicity could be maximized as $W^2, 15W^3$ etc. We first show that expressing the entropy in terms of a *set of probabilities* p_i ,

$$\frac{S}{k} = - \sum_{i=1}^t p_i \ln p_i. \quad (2.1)$$

is equivalent to def. 2.1. Roll a t -sided die N times. The multiplicity of outcomes is given by

$$W = \frac{N!}{n_1! n_2! \cdots n_t!},$$

where n_i is the number of times that side i appears face up. Use Stirling's approximation,

Definition 2.2

Stirling's approximation. For $n \gg 1$ (at least 1000),

$$\ln n! \approx n \ln n - n.$$

$$n! \approx \left(\frac{n}{e}\right)^n.$$

and define the probabilities $p_i = n_i/N$, to get

$$W = \frac{(N/e)^N}{(n_1/e)^{n_1} (n_2/e)^{n_2} \cdots (n_t/e)^{n_t}} = \frac{N^N}{n_1^{n_1} n_2^{n_2} \cdots n_t^{n_t}} = \frac{1}{p_1^{n_1} p_2^{n_2} \cdots p_t^{n_t}}.$$

Take the logarithm of both sides and divide by N to get

$$\ln W = - \sum_{i=1}^t n_i \ln p_i \quad \Rightarrow \quad \frac{1}{N} \ln W = - \sum_{i=1}^t p_i \ln p_i = \frac{S_N}{Nk} = \frac{S}{k},$$

where S_N is the total entropy for N trials, so the entropy per trial is $S = S_N/N$.

Note. def. 2.1 is reformulated from eq. (2.1) if the microstates whose permutations sum up to multiplicity W are *degenerate*, or equivalently, if $p_i = 1/W$.

Note. Boltzmann's constant k puts entropy into units that inter-convert with energy for thermodynamics. Basically, k is the entropy per particle.

Sometimes, it is more convenient to express the entropy per mole of particles,

$$S = R \ln W.$$

where $R = \mathcal{N}k$ is the *gas constant* and \mathcal{N} is Avogadro's number—the number of molecules per mole.

2.2 Lattice models

Example. Entropy of mixing calculation for *lattice models*.

Two solutions, A and B , are allowed to mix. Calculate the change in entropy of the system due to mixing.

Method. Describe the solution (space) as a lattice, or grid, which has N lattice sites, which are filled by n particles.

W is the number of ways to arrange particles in the available sites.

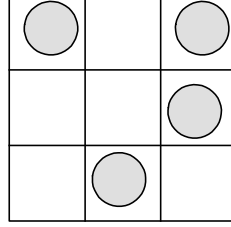


Figure 2.1. Each particle may occupy a lattice site.

Each site can either be occupied or vacant, so W behaves according to the binomial distribution.

$$W_A = \frac{N!}{n! (N-n)!}.$$

Using def. 2.2,

$$W_A \approx \frac{N^N}{n^n (N-n)^{N-n}}.$$

Similarly, for the second solution,

$$W_B \approx \frac{M^M}{m^m (M-m)^{M-m}}.$$

As entropy is extensive,

$$S = S_A + S_B = k \ln (W_A W_B).$$

After mixing there are $M + N$ lattice sites and $m + n$ particles. Note that $W_{AB} = W_A W_B$ is the combined multiplicity without mixing. The multiplicity after mixing, W_{AB}^* behaves according to the multinomial distribution.

$$W_{AB}^* = \frac{(N+M)!}{n! m! (N+M-m-n)!} \approx \frac{(N+M)^{N+M}}{n^n m^m (N+M-m-n)^{N+m-m-n}}.$$

For simplification, assume $N = M$ and $n = m$.

$$W_{AB}^* = \frac{(2N)^{2N}}{n^{2n} (2N-2n)^{2N-2n}}.$$

In this case, the combined multiplicity prior to mixing is

$$W_{AB} = \frac{N^{2N}}{n^{2n} (N-n)^{2(N-n)}}.$$

What is the change in entropy due to mixing?

$$\Delta S = S_{AB}^* - S_{AB} = k \ln \frac{W_{AB}^*}{W_{AB}} = \dots = k \ln (2^{2n}) = 2n k \ln 2.$$

Obviously, mixing increased the total entropy of the system.

2.3 Predicting distributions by maximizing entropy

In an isolated environment (no exchange of energy or matter), entropy maximization predicts the distribution of states of the system.

From eq. (2.1) it is clear that S is a *function* of the possible states: $S = f(p_1, \dots, p_t)$. a function $f(x)$ is maximized when $df/dx = 0$ and $d^2f/dx^2 < 0$.

Additionally, if we know the value of $f(x)$ at some point $x = a$, we can use *Taylor series expansion* to compute $f(x)$ near that point:

$$\Delta f = f(x) - f(a) = \left(\frac{df}{dx} \right)_{x=a} \Delta x + \frac{1}{2} \left(\frac{d^2f}{dx^2} \right)_{x=a} \Delta x^2 + \frac{1}{6} \left(\frac{d^3f}{dx^3} \right)_{x=a} \Delta x^3 + \dots$$

For very small changes, $\Delta x = (x - a) \rightarrow dx$, non-linear terms in the series expansions are negligible, and thus $df \approx \left(\frac{df}{dx} \right)_{x=a} dx$.

In the case of a bivariate function, $f(x, y)$,

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy.$$

We can generalize to multivariate functions, and define

$$df = \sum_{i=1}^t \left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} dx_i.$$

The extrema of multivariate functions occur where the partial derivatives are zero. The *global* extremum occurs where *all* partial derivatives are zero: $\left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} = 0$ for $i = 1, 2, \dots, t$.

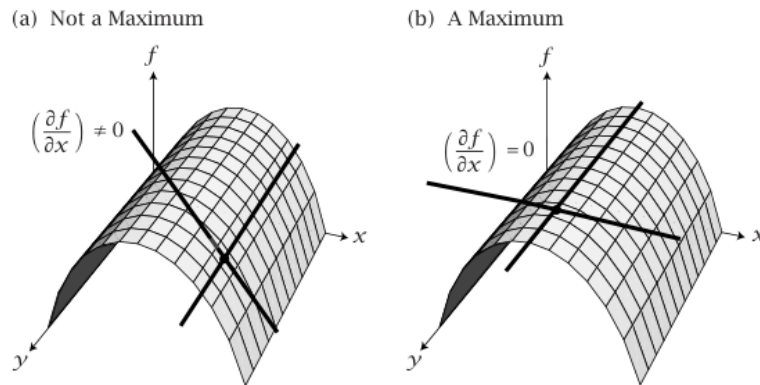


Figure 2.2. To identify the maximum of this function, both $(\partial f / \partial x)$ and $(\partial f / \partial y)$ must equal zero, as they do in (b), but not in (a).

Note that when calculating entropy we are constrained by $\sum p_i = 1$. How do we find the extrema of a function that is subject to a constraint? We must find a set of values that satisfy *both* the extremum equation

$$df = \sum_{i=1}^t \left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} dx_i = 0,$$

and the constraint equation, $\sum p_i = 1$.

Note. A constraint equation has the form $g(x_1, x_2, \dots, x_t) = \text{constant}$. For example, if we require $x = y$, the constraint function $g(x, y)$ would be:

$$g(x, y) = x - y = 0.$$

Because x and y are related through the equation $g(x, y) = \text{constant}$, they are **not** independent variables. To satisfy both the extremum equation and the constraint equation, put the constraint equation into differential form and combine it with the extremum equation.

$$dg = \left(\frac{\partial g}{\partial x} \right)_y dx + \left(\frac{\partial g}{\partial y} \right)_x dy = 0.$$

In this example,

$$dg = 1 \cdot dx - 1 \cdot dy = 0 \rightarrow dx = dy.$$

If the extremum equation is

$$df = 0 = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy,$$

then if we replace dy by dx in the extremum equation, we get:

$$df = 0 = \left[\left(\frac{\partial f}{\partial x} \right)_y + \left(\frac{\partial f}{\partial y} \right)_x \right] dx = 0,$$

which gives

$$\left(\frac{\partial f}{\partial x} \right)_y = - \left(\frac{\partial f}{\partial y} \right)_x.$$

Solving this equation identifies the point that is both an extremum of f and also satisfies $g(x, y) = \text{constant}$.

2.3.1 Extrema with constraints: Method of Lagrange Multipliers

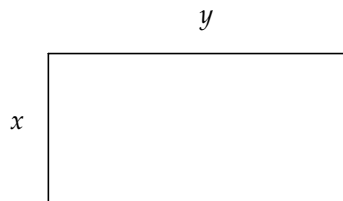
Suppose you want to find the extremum of $f(x, y)$ subject to the constraint $g(x, y) = \text{constant}$.

It can be shown that the derivatives of f and g need only be the same to within an arbitrary constant λ , called the *Lagrange multiplier*:

$$\left(\frac{\partial f}{\partial x} \right)_y = \lambda \left(\frac{\partial g}{\partial x} \right)_y \quad \text{and} \quad \left(\frac{\partial f}{\partial y} \right)_x = \lambda \left(\frac{\partial g}{\partial y} \right)_x. \quad (2.2)$$

The values $x = x^*$ and $y = y^*$ that satisfy (2.2) are at the extremum of f and satisfy the constraint.

Example. Suppose you want to find a rectangle of the largest possible area that is 40 cm in circumference.



Mathematically, find the extremum of

$$f(x, y) = xy,$$

with the constraint equation

$$g(x, y) = 2x + 2y = 40.$$

Use Lagrange multipliers to maximize f subject to g :

$$\left(\frac{\partial f}{\partial x}\right) = y, \quad \left(\frac{\partial g}{\partial x}\right) = 2 \Rightarrow y^* = 2\lambda,$$

$$\left(\frac{\partial f}{\partial y}\right) = x, \quad \left(\frac{\partial g}{\partial y}\right) = 2 \Rightarrow x^* = 2\lambda.$$

Substituting these into the constraint equation and solving for λ gives $\lambda = 5$ and $x^* = y^* = 10$.

Note. For the extremum of $f(x_1, x_2, \dots, x_t)$ subject to more than one constraint, $g(x_1, \dots, x_t) = c_1$ and $h(x_1, \dots, x_t) = c_2$, etc., where the c_i are constants, the Lagrange multiplier method gives the solutions

$$\begin{aligned} \left(\frac{\partial f}{\partial x_1}\right) - \lambda \left(\frac{\partial g}{\partial x_1}\right) - \beta \left(\frac{\partial h}{\partial x_1}\right) - \dots &= 0, \\ \left(\frac{\partial f}{\partial x_2}\right) - \lambda \left(\frac{\partial g}{\partial x_2}\right) - \beta \left(\frac{\partial h}{\partial x_2}\right) - \dots &= 0, \\ &\vdots \\ \left(\frac{\partial f}{\partial x_t}\right) - \lambda \left(\frac{\partial g}{\partial x_t}\right) - \beta \left(\frac{\partial h}{\partial x_t}\right) - \dots &= 0, \end{aligned}$$

where λ, β, \dots are the Lagrange multipliers for each constraint. Each multiplier is found from its appropriate constraint equation.

An alternative representation:

$$d(f - \lambda g - \beta h) = \sum_{i=1}^t \left[\left(\frac{\partial f}{\partial x_i}\right) - \lambda \left(\frac{\partial g}{\partial x_i}\right) - \beta \left(\frac{\partial h}{\partial x_i}\right) \right] dx_i = 0. \quad (2.3)$$

2.3.2 Maximizing entropy of an isolated system

Back to entropy, we had

$$\frac{S}{k} = -\sum_i p_i \ln p_i.$$

This function can only have a maximum.

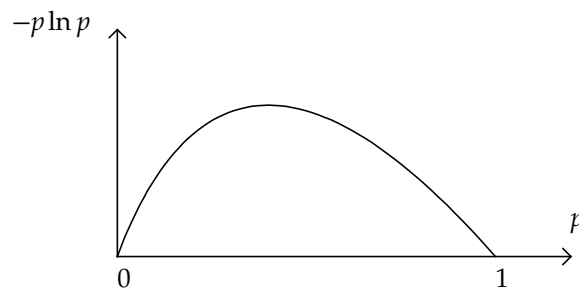


Figure 2.3. $-p \ln p$ versus p has a maximum.

The only (trivial) constraint is normalization: $g = \sum_{i=1}^t p_i = 1$. For a simple case of $t = 2$ states,

$$S = -k (p_1 \ln p_1 + p_2 \ln p_2).$$

$$g = p_1 + p_2 = 1.$$

Calculate partial derivatives:

$$\frac{1}{k} \left(\frac{\partial S}{\partial p_1} \right)_{p_2} = - \left(\ln p_1 + p_1 \frac{1}{p_1} \right) = -\ln p_1 - 1, \quad \left(\frac{\partial g}{\partial p_1} \right)_{p_2} = 1,$$

$$\frac{1}{k} \left(\frac{\partial S}{\partial p_2} \right) = -\ln p_2 - 1, \quad \left(\frac{\partial g}{\partial p_2} \right)_{p_1} = 1.$$

Via eq. (2.2),

$$\begin{cases} -1 - \ln p_1 - \lambda = 0 \\ -1 - \ln p_2 - \lambda = 0 \end{cases} \Rightarrow p_1^* = p_2^* = e^{-1-\lambda}.$$

Plug these to the constraint equation to get

$$g = 2e^{-1-\lambda} = 1 \Rightarrow e^{-1-\lambda} = \frac{1}{2} \Rightarrow p_1 = p_2 = \frac{1}{2}.$$

Conclusion. Maximum entropy predicts a *flat* distribution of states. All states are equally likely.

In non-isolated systems, there may be additional constraints such as conservation of energy, conservation of mass, etc.

2.3.3 Maximizing entropy with an energy constraint

Roll a dice having t sides, with faces numbered $i = 1, 2, 3, \dots, t$. You don't know the distribution of outcomes of each face, but you know the total score after N rolls. You want to predict the distribution function.

First, let's generalize our dice problem. instead of having the numbers $i = 1, 2, \dots, 6$ painted on its six sides, the die has a more general set of numbers painted on its t sides. When side i appears face up, the score is ε_i . The total score after N rolls will be $E = \sum_{i=1}^t \varepsilon_i n_i$, where n_i is the number of times that you observe face i .

Let $p_i = n_i / N$ represent the fraction of the N rolls on which you observe face i . The average score per roll, $\langle \varepsilon \rangle$ is:

$$\langle \varepsilon \rangle = \frac{E}{N} = \sum_{i=1}^t p_i \varepsilon_i.$$

What is the distribution of outcomes $(p_1^*, p_2^*, \dots, p_t^*)$ consistent with the average score $\langle \varepsilon \rangle$? We seek the distribution that maximizes the entropy, subject to two constraints: (1) that all probabilities sum to one, and (2) that the average score agrees with the observed value $\langle \varepsilon \rangle$.

$$g(p_1, p_2, \dots, p_t) = \sum_{i=1}^t p_i = 1 \Rightarrow \sum_{i=1}^t dp_i = 0,$$

$$h(p_1, p_2, \dots, p_t) = \langle \varepsilon \rangle = \sum_{i=1}^t p_i \varepsilon_i \Rightarrow \sum_{i=1}^t \varepsilon_i dp_i = 0.$$

Solve via method of Lagrange multipliers.

$$\left(\frac{\partial S}{\partial p_i}\right) - \alpha \left(\frac{\partial g}{\partial p_i}\right) - \beta \left(\frac{\partial h}{\partial p_i}\right) = 0 \quad \text{for } i = 1, 2, \dots, t.$$

The partial derivatives are evaluated for each p_i :

$$\left(\frac{\partial S}{\partial p_i}\right) = -1 - \ln p_i, \quad \left(\frac{\partial g}{\partial p_i}\right) = 1, \quad \left(\frac{\partial h}{\partial p_i}\right) = \varepsilon_i.$$

Substitute into the above equation to get t equations of the form

$$-1 - \ln p_i^* - \alpha - \beta \varepsilon_i = 0.$$

Solve for each p_i^* to get

$$p_i^* = e^{-1-\alpha-\beta\varepsilon_i}.$$

To eliminate α , use the normalization constraint to divide both sides by one. The result is an *exponential distribution law*:

$$p_i^* = \frac{p_i^*}{\sum_{i=1}^t p_i^*} = \frac{e^{(-1-\alpha)} e^{-\beta\varepsilon_i}}{\sum_{i=1}^t e^{(-1-\alpha)} e^{-\beta\varepsilon_i}} = \frac{e^{-\beta\varepsilon_i}}{\sum_{i=1}^t e^{-\beta\varepsilon_i}}. \quad (2.4)$$

In Statistical Mechanics, the average score is translated to *average energy* of the system, and eq. (2.4) is called the *Boltzmann distribution law*. The quantity in the denominator is called the *partition function*, q :

$$q \equiv \sum_{i=1}^t e^{-\beta\varepsilon_i} \quad (2.5)$$

Using the score constraint and the above, we get

$$\langle \varepsilon \rangle = \sum_{i=1}^t \varepsilon_i p_i^* = \frac{1}{q} \sum_{i=1}^t \varepsilon_i e^{-\beta\varepsilon_i}. \quad (2.6)$$

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3 Toward the Fundamental Thermodynamic Equations

3.1 Definitions and conventions

Definition 3.1

Energy.

Energy is system property, and describes the capacity of a system to perform work. Energy is **conserved** and can flow, so that capacity to perform work can be moved from one place to another.

Energy is ubiquitous, and can take any form, e.g. mechanical, potential, or electrical.

Definition 3.2

The First Law of Thermodynamics. (JR Von Mayer, 1842.)

The internal energy ΔU of a system changes when it takes up or gives off heat q or work w :

$$\Delta U = q + w. \quad (3.1)$$

The internal energy is conserved; if ΔU increases in the system, the energy decreases in the surroundings.

General conventions:

- If heat goes **into** the system, $q > 0$, and vice versa.
- If work is done **on** the system, $w > 0$, and vice versa.

3.2 Energy is quantized

Quantum theory debuted in the 20th century showed that energies of atoms and molecules are quantized. Each particle has discrete amounts of energy associated with each of its allowed degrees of freedom, some of which are translations rotations, vibrations, and electronic excitations.

The allowed energies for a given system are indicated in *energy-level diagrams*, and they predict thermodynamic properties.

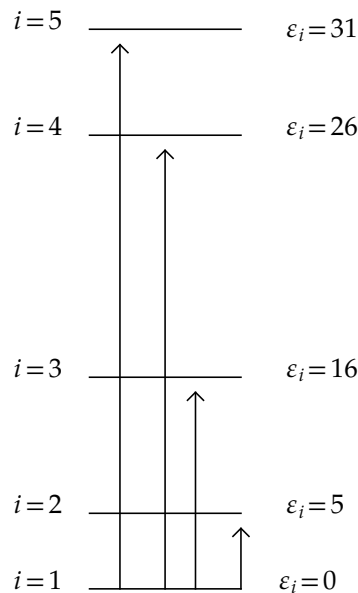


Figure 3.1. An exemplary 5-level energy diagram. Each state has its corresponding energy, and particles may occupy the different states.

For simple systems of independent, non-interacting particles, such as ideal gases, we can express the total *internal energy* of a thermodynamic system as the sum of the particle energies:

$$U = \sum_i N_i \epsilon_i, \quad (3.2)$$

where ε_i is the energy of any particle at level i and N_i is the number of particles at energy level i . When the total internal energy of a system is increased by heating it, the energy levels **do not** change, but the populations $\{N_i\}$ change.

3.3 Flow of heat

What drives molecules or materials to exchange energy? Why does heat flow? The First Law of Thermodynamics cannot explain this phenomenon. Heat flow is a consequence of the tendency toward maximum multiplicity, which is the *Second Law of Thermodynamics*.

Previously, we've seen that lattice models predict that:

- Gases expand because the multiplicity W increases with volume V .
 - The dependence of W on V defines the force called *pressure*.
- Particles mix because the multiplicity W increases as the particle segregation decreases.
 - The tendency to mix defines the *chemical potential*.

These are both manifestations of the Second Law of Thermodynamics.

As a system absorbs heat, the internal energy increases, and the possible distributions of particles within the energy states (that sum up to the total internal energy) increases.

Why, then, does heat flow from hot objects to cold ones?

Consider two systems, A and B , both having two possible energy states: $\varepsilon_1=0, \varepsilon_2=1$. Each system has 10 particles. Suppose that system A starts with energy $U_A=2$ and system B starts with energy $U_B=4$.

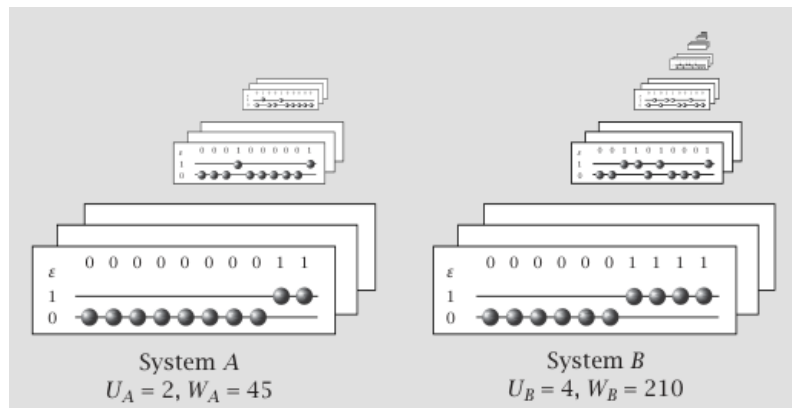


Figure 3.2. Energy-level diagrams for two different systems with 10 particles each. System B has a higher internal energy, and thus a greater multiplicity of states.

What would happen if we let the systems exchange energy? The multiplicities $W(U)$ of the isolated systems are given by binomial distribution.

$$W_A = \frac{10!}{2!8!} = 45, \quad W_B = \frac{10!}{4!6!} = 210.$$

The combined multiplicity of the isolated systems is $W_{AB} = W_A W_B = 9450$. When the systems exchange energy, their total internal energy must be conserved— $U_A + U_B = \text{const.}$

One possibility of heat flow is $U_A = 3, U_B = 3$. The total multiplicity would be

$$W_{AB} = \frac{10!}{3!7!} \frac{10!}{3!7!} = 14,400.$$

As the multiplicity increased, we can infer that heat flows from B to A , in this case to equalize energies. Consider an alternative outcome of heat flow: $U_A = 1, U_B = 5$. The total multiplicity in this case is

$$W_{AB} = \frac{10!}{1!9!} \frac{10!}{5!5!} = 2520.$$

The principle of maximal multiplicity predicts that heat flow from cold to hot objects is unlikely.

Note. The tendency to maximize multiplicity does not always result in a draining of energy from higher to lower.

Consider two systems ($\varepsilon_1 = 0, \varepsilon_2 = 1$) having the same energies, but different particle numbers. Suppose system A has $N_A = 10, U_A = 2$ and system B has $N_B = 4, U_B = 2$.

The total multiplicity of the isolated systems is

$$W_{AB} = W_A W_B = \frac{10!}{2!8!} \frac{4!}{2!2!} = 270.$$

Now let the systems thermally interact. If the larger system absorbs energy from the smaller one, so that $U_A = 3, U_B = 1$,

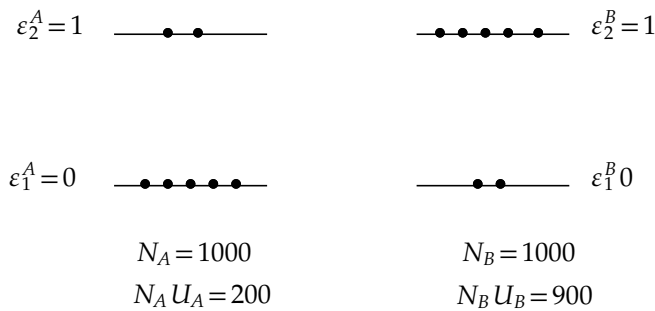
$$W_{AB} = W_A W_B = \frac{10!}{3!7!} \frac{4!}{1!3!} = 480,$$

the multiplicity increased.

We shall later see that the concept of *temperature* describes the driving force for energy exchange. The tendency toward maximum multiplicity is a tendency toward equal temperatures.

Example. Calculating maximized multiplicity distribution of particles.

Let there be two non-interacting systems, A and B , each having two possible states:



The total energy of the system per particle is $\frac{U}{N} = \sum_i p_i \varepsilon_i$.

What is the distribution of states within each system?

For system A,

$$U_A = \frac{200}{1000} = \varepsilon_1^A p_1^A + \varepsilon_2^A p_2^A = p_2^A,$$

$$p_1^A = 1 - p_2^A = 0.8.$$

Similarly, for system B,

$$U_B = \frac{900}{1000} = \varepsilon_1^B p_1^B + \varepsilon_2^B p_2^B = p_2^B,$$

$$p_1^B = 1 - p_2^B = 0.1.$$

Now we let the systems exchange energy. What would be the new equilibrium distribution of states?

According to the First Law of Thermodynamics, energy is conserved.

$$U_{\text{total}} = U_A + U_B = \frac{N_A U_A + N_B U_B}{N_A + N_B} = 0.55. \quad (3.3)$$

This is a constraint equation!

We wish to maximize the entropy.

$$\frac{S}{k} = -\sum p_i \ln p_i = -p_1^A \ln p_1^A - p_2^A \ln p_2^A - p_1^B \ln p_1^B - p_2^B \ln p_2^B. \quad (3.4)$$

The other constraint equations:

$$g = p_1^A + p_2^A + p_1^B + p_2^B = 1 \quad (3.5)$$

$$h = \varepsilon_1^A p_1^A + \varepsilon_2^A p_2^A + \varepsilon_1^B p_1^B + \varepsilon_2^B p_2^B \quad (3.6)$$

According to Boltzmann's law,

$$p_i^* = \frac{e^{-\beta \varepsilon_i}}{q}, \quad q = e^{-\beta \varepsilon_1^A} + e^{-\beta \varepsilon_2^A} + e^{-\beta \varepsilon_1^B} + e^{-\beta \varepsilon_2^B} = 2(1 + e^{-\beta}).$$

Accordingly,

$$p_1^{A,*} = p_1^{B,*} = \frac{1}{2(1 + e^{-\beta})}, \quad p_2^{B,*} = p_2^{A,*} = \frac{e^{-\beta}}{2(1 + e^{-\beta})}. \quad (3.7)$$

What is the value of β ? Insert into the constraint equation, eq. (3.4).

$$U_{\text{total}} = 2 \left(0 \cdot \frac{1}{2(1 + e^{-\beta})} + 1 \cdot \frac{e^{-\beta}}{2(1 + e^{-\beta})} \right) = 0.55,$$

$$\beta = -\ln \frac{U_{\text{total}}}{1 - U_{\text{total}}} = -0.2.$$

Plug β into eq. (3.5) to get (after normalization per system) $p_1^{A,*} = p_1^{B,*} = 0.54$ and $p_2^{A,*} = p_2^{B,*} = 0.46$. We can infer that particles in system A moved to the higher energy state, and particles in system B moved to the lower energy state.

3.4 Thermodynamic systems and the fundamental thermodynamic equations

A thermodynamic system is a collection of matter in any form, delineated from its surroundings by (real or imaginary) boundaries. Defining the boundaries is important, as it specifies thermodynamic properties of the system.

Types of systems:

Open system. An open system can exchange energy, volume, and matter with its surroundings.

Closed system. Energy can cross the boundary of a closed system, but matter cannot.

Isolated system. Energy and matter cannot cross the boundaries of an isolated system. Also, volume does not change. The total internal energy of an isolated system is constant.

Types of boundaries:

Semipermeable membrane. A semipermeable membrane is a boundary that restricts the flow of some kinds of particle, while allowing others to cross.

Adiabatic boundary. Prevents heat from flowing between the system and its surroundings.

We've seen that maximizing entropy with respect to different parameters, such as volume, number of particles, and internal energy, we predict different phenomena, such as expansion of gas, change in composition, and heat flow, respectively.

Many systems, however, allow multiple parameters to change simultaneously. The *fundamental thermodynamic equation* for entropy is multivariate: $S = S(U, V, \mathbf{N})$. In this formulation, the energy U , the volume V , and the number of particles of different categories N_1, N_2, \dots, N_M are all free to change.

Note that history first conjured the relations in the form of energy: $U = U(S, V, \mathbf{N})$. The fundamental definitions of pressure, chemical potential, and temperature are based on the form of $U = U(S, V, \mathbf{N})$. The microscopic driving forces, though, are better understood in terms of the entropy equation $S = S(U, V, \mathbf{N})$, so we need a way to switch between them. In any case, both formulations completely specify the state of a system.

Note. Thermodynamics does not en-tell the specific mathematical dependence of S on (U, V, \mathbf{N}) or U on (S, V, \mathbf{N}) . *Equations of state*, which come from microscopic models or experiments, specify interrelations among these variables.

In this section, we transition from Statistical Mechanics to Classical Thermodynamics.

$$S = -k \sum p_i \ln p_i \rightarrow S = f(U, V, \mathbf{N}).$$

3.5 The fundamental equations define the thermodynamic driving forces

According to the fundamental entropy equation,

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V, \mathbf{N}} dU + \left(\frac{\partial S}{\partial V} \right)_{U, \mathbf{N}} dV + \sum_{j=1}^M \left(\frac{\partial S}{\partial N_j} \right)_{U, V, N_{i \neq j}} dN_j. \quad (3.8)$$

Similarly, using the fundamental energy equation,

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V,N} dS + \left(\frac{\partial U}{\partial V} \right)_{S,N} dV + \sum_{j=1}^M \left(\frac{\partial U}{\partial N_j} \right)_{S,V,N_{i \neq j}} dN_j \quad (3.9)$$

It turns out that the partial derivatives in (3.9) correspond to measurable physical quantities.

Definition 3.3

Temperature, pressure, and chemical potential.

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N'} \quad p = - \left(\frac{\partial U}{\partial V} \right)_{S,N'} \quad \mu_j = \left(\frac{\partial U}{\partial N_j} \right)_{S,V,N_{i \neq j}}. \quad (3.10)$$

Note. T, P and μ are intensive properties, that are conjugate to extensive quantities, U, S, V and N .

Substituting (3.10) into (3.9) gives the *differential form of the fundamental energy equation*:

$$dU = T dS - p dV + \sum_{j=1}^M \mu_j dN_j. \quad (3.11)$$

Alternatively, substituting into (3.8) gives the *differential form of the fundamental entropy equation*:

$$dS = \left(\frac{1}{T} \right) dU + \left(\frac{p}{T} \right) dV - \sum_{j=1}^M \left(\frac{\mu_j}{T} \right) dN_j. \quad (3.12)$$

From which we identify,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N'} \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{U,N'} \quad \frac{\mu_j}{T} = - \left(\frac{\partial S}{\partial N_j} \right)_{U,V,N_{i \neq j}}. \quad (3.13)$$

We shall later see how equations (3.11) and (3.12) can be used to identify states of equilibrium.

4 Laboratory conditions and free energies

Up until now we dealt with systems with known energy that exchange it across their boundaries. These systems tend toward states of maximum entropy. That logic helped explain gas expansion, particle mixing, and the interconversion of heat. We now wish to explore a different class of systems, such as test tubes in laboratory heat baths, processes open to the air, and processes in biological systems. In these systems, it is not work or heat flow that is controlled at the boundaries, but temperature and pressure. This change requires new thermodynamic quantities—the *free energy* and the *enthalpy*—and reformulated extremum principles. Systems held at constant temperature do not tend toward their states of maximum entropy. They tend toward their states of *minimum free energy*.

When an intensive variable, such as T, p , or μ is controlled or measured at the boundary, it means that the conjugate variables, U, V , or N , can exchange freely back and forth across the boundary with the *bath*, the external reservoir that is large enough that it can hold V, p , or μ fixed, no matter what happens in the system. Such exchanges are called *fluctuations*.

When T is constant, heat can exchange between the system and the surroundings, so the energy of the system fluctuates. When p is held constant, the volume fluctuates. When μ is constant, a particle bath is in contact with the system—particles leave or enter the system to and from the particle bath. In this case, the number of particles in the system can fluctuate.

Consider a process in a system that we call the *test tube*, immersed in a *heat bath*. a heat bath refers to any surroundings of a system that hold the temperature of the system constant. If the combined test tube plus heat bath are isolated from the greater surroundings, equilibrium will be the state of maximum entropy for the total system. However, we are only interested in what happens in the test tube itself. We need a new extremum principle that applies to the test tube, where the independent variables are (T, V, N) .

Note. If the extremum of a function such as $S(U)$ predicts equilibrium, the variable U is called the *natural variable* of S . T is not a natural variable of S . Now we show that (T, V, N) are natural variables of a function F , the *Helmholtz free energy*.

An extremum in $F(T, V, N)$ predicts equilibria in systems that are constrained to constant temperature at their boundaries.

4.1 Free energy defines another extremum principle

4.1.1 The Helmholtz free energy

Consider a process inside a test tube, sealed so that it has constant volume V and no interchange of its N particles with the surroundings. A heat bath holds the test tube at constant temperature T .



Figure 4.1. A heat bath is a reservoir that holds the system (the test tube in this case) at constant temperature by allowing heat flow in or out, as required. The properties that do not change inside the system are (T, V, N) .

The process inside the test tube might be complex. It might vary in rate from a quasi-static process to an explosion. It might or might not involve chemical or phase changes. It might give off or absorb heat. Processes within the test tube will influence the heat bath only through heat exchange, because its volume does not change and no work is done.

If the combined system (sub-system plus heat bath) is isolated, equilibrium will be the state of maximum entropy of the combined system. Any change toward equilibrium must increase the entropy of the combined system, $dS_{\text{combined}} \geq 0$.

Because the entropy is extensive,

$$dS_{\text{combined}} = dS_{\text{sys}} + dS_{\text{bath}} \geq 0. \quad (4.1)$$

Since the combined system is isolated,

$$dU_{\text{bath}} + dU_{\text{sys}} = 0. \quad (4.2)$$

We wish to relate dS_{bath} to some property of the test tube system. Use (3.12) to get, in our case,

$$dS_{\text{bath}} = \left(\frac{1}{T}\right) dU_{\text{bath}}. \quad (\mathbf{N}, V) = \text{constant} \quad (4.3)$$

Combine with eq. (4.2) to get

$$dS_{\text{bath}} = -\frac{dU_{\text{sys}}}{T}. \quad (4.4)$$

Substitute eq. (4.4) into (4.1) to get

$$dS_{\text{sys}} = -\frac{dU_{\text{sys}}}{T} \geq 0 \quad \Rightarrow \quad dU_{\text{sys}} - T dS_{\text{sys}} \leq 0. \quad (4.5)$$

We got an expression describing the approach to equilibrium in terms of the test tube sub-system alone. Define a quantity F , the *Helmholtz free energy*:

Definition 4.1

Helmholtz free energy.

$$F \equiv U - TS. \quad (4.6)$$

$$dF = dU - T dS - S dT. \quad (4.7)$$

Comparison of eq. (4.7) with eq. (4.5) shows that when a system in which (T, V, \mathbf{N}) are constant is at equilibrium, the quantity F is at minimum. It also follows from eq. (4.6) that to minimize F , the system in the tube will tend toward *both* high entropy and low energy, depending on the temperature. At high temperatures, the entropy dominates. At low temperatures, the energy dominates.

4.1.2 The fundamental equation for the Helmholtz free energy

Just as the functional form $S(U, V, \mathbf{N})$ implies a fundamental entropy equation for dS , the form $F(T, V, \mathbf{N})$ implies a fundamental equation for dF :

$$dF = d(U - TS) = dU - T dS - S dT.$$

Substitute the fundamental energy equation (3.11) into (4.7) to get:

$$\begin{aligned} dF &= \left(T dS - p dV + \sum_{j=1}^M \mu_j dN_j \right) - T dS - S dT \\ &= -S dT - p dV + \sum_{j=1}^M \mu_j dN_j. \end{aligned} \quad (4.8)$$

Because dF is also defined by its partial derivative expression,

$$dF = \left(\frac{\partial F}{\partial T} \right)_{V, \mathbf{N}} dT + \left(\frac{\partial F}{\partial V} \right)_{T, \mathbf{N}} dV + \sum_{j=1}^M \left(\frac{\partial F}{\partial N_j} \right)_{V, T, N_{i \neq j}} dN_j, \quad (4.9)$$

we get additional thermodynamic relations by comparing eq. (4.9) with (4.8):

$$S = -\left(\frac{\partial F}{\partial T} \right)_{V, \mathbf{N}}, \quad p = -\left(\frac{\partial F}{\partial V} \right)_{T, \mathbf{N}}, \quad \mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{V, T, N_{i \neq j}}. \quad (4.10)$$

Note. We derived $F(T, V, \mathbf{N})$ from $S(U, V, \mathbf{N})$ by physical arguments. You can also switch from one set of independent variables to another by purely mathematical arguments, called *Legendre transforms*.

A function $y = f(x)$ can be described as a list of pairs $(x_1, y_1), (x_2, y_2), \dots$. You can express the same function instead as a list of different pairs: the slopes $c(x)$ and the intercepts $b(x)$: $(c_1, b_1), (c_2, b_2), \dots$.

For a small change dx , the change dy in the function can be described by the slope $c(x)$ at that point:

$$dy = \left(\frac{\partial y}{\partial x} \right) dx = c(x) dx. \quad (4.11)$$

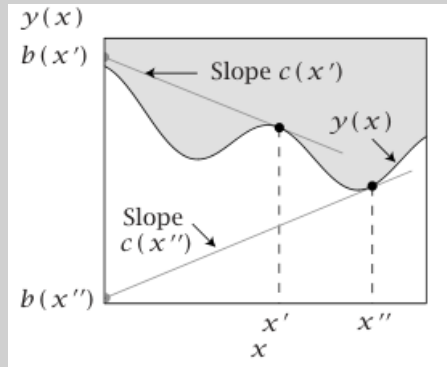


Figure 4.2. To create the Legendre transform, a function $y(x)$ is expressed as a tangent slope function $c(x)$, and a tangent intercept function $b(x)$. The tangent slopes and intercepts of points x' and x'' are shown here.

Actually, the full function $y(x)$ (not just small changes) can be regarded as a set of slopes and intercepts—one slope $c(x)$ and one intercept $b(x)$ for each point x :

$$y(x) = c(x)x + b(x) \quad \Rightarrow \quad b(x) = y(x) - c(x)x. \quad (4.12)$$

We are interested in the function that expresses the series of intercepts versus slopes, $b(c)$. To see how small changes in the slope c lead to small changes in the intercept b , take the differential of (4.12) and substitute in (4.11), to get

$$db = dy - c dx - x dc = -x dc. \quad (4.13)$$

Now generalize to a multivariate function $y = y(x_1, x_2, x_3)$. The differential element is

$$dy = c_1 dx_1 + c_2 dx_2 + c_3 dx_3, \quad (4.14)$$

where

$$c_1 = \left(\frac{\partial y}{\partial x_1} \right)_{x_2, x_3}, \quad c_2 = \left(\frac{\partial y}{\partial x_2} \right)_{x_1, x_3}, \quad c_3 = \left(\frac{\partial y}{\partial x_3} \right)_{x_1, x_2}.$$

We want the intercept function b_1 along the x_1 axis:

$$b_1(c_1, x_2, x_3) = y - c_1 x_1. \quad (4.15)$$

Take the differential of (4.15) and substitute (4.14) to get

$$db_1 = dy - c_1 dx_1 - x_1 dc_1 = -x_1 dc_1 + c_2 dx_2 + c_3 dx_3. \quad (4.16)$$

From (4.16), you can see that

$$x_1 = - \left(\frac{\partial b_1}{\partial c_1} \right)_{c_2, c_3}, \quad c_2 = \left(\frac{\partial b_1}{\partial x_2} \right)_{c_1, c_3}, \quad c_3 = \left(\frac{\partial b_1}{\partial x_3} \right)_{c_1, c_2}. \quad (4.17)$$

4.1.3 The enthalpy

The enthalpy is a function of the natural variables (S, p, \mathbf{N}) . Enthalpy is seldom used as an extremum principle, because it is not usually convenient to control the entropy. However, it can be obtained from calorimetry experiments, and it gives an experimental route to the Gibbs free energy, which is of central importance in chemistry and biology.

To find the enthalpy, you could reason in the same way as we did for the Helmholtz free energy, but instead let's use a simple math argument. Start with the internal energy $U(S, V, \mathbf{N})$. We seek to replace a dV term in the energy function with a dp term to get the enthalpy function dH . Add a pV term to the energy so that when you differentiate it, the dV term will disappear and a dp term will appear:

$$H = H(S, p, \mathbf{N}) \equiv U + pV. \quad (4.18)$$

Now differentiate:

$$dH = dU + p dV + V dp. \quad (4.19)$$

Substitute eq. (3.11) into (4.19) to get

$$dH = T dS - p dV + \sum_{j=1}^M \mu_j dN_j + p dV + V dp$$

$$dH = T dS + V dp + \sum_{j=1}^M \mu_j dN_j. \quad (4.20)$$

4.1.4 The Gibbs free energy

The Gibbs free energy G is a function of (T, p, \mathbf{N}) . Constant temperature and pressure are the easiest constraints to impose in the laboratory, because the atmosphere provides them.

$G = G(T, p, \mathbf{N})$ has a minimum at equilibrium. To find the fundamental equation, start with the enthalpy, $H = H(S, p, \mathbf{N})$. You want to replace the dS term with a dT term in eq. (4.20). Define a function G :

$$G \equiv H - TS. \quad (4.21)$$

The total differential dG is

$$dG = dH - T dS - S dT. \quad (4.22)$$

Substitute eq. (4.20) into (4.22) to get

$$dG = -S dT + V dp + \sum_{j=1}^M \mu_j dN_j. \quad (4.23)$$

Similarly to $F(T, V, \mathbf{N})$, if a process occurs in a test tube held at constant pressure and temperature, it will be at equilibrium when the Gibbs free energy is at minimum.

Note. Equilibrium is the state at which the entropy of the combined system *plus* surroundings is at maximum. However, for the test tube system itself, which is at constant (T, p, \mathbf{N}) , equilibrium occurs when the Gibbs free energy is at minimum.

dG can be expressed as

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p, \mathbf{N}} dT + \left(\frac{\partial G}{\partial p} \right)_{T, \mathbf{N}} dp + \sum_{j=1}^M \left(\frac{\partial G}{\partial N_j} \right)_{p, T, N_{i \neq j}} dN_j. \quad (4.24)$$

So,

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p, \mathbf{N}}, \quad V = \left(\frac{\partial G}{\partial p} \right)_{T, \mathbf{N}}, \quad \mu_j = \left(\frac{\partial G}{\partial N_j} \right)_{p, T, N_{i \neq j}}. \quad (4.25)$$

Note. For equilibrium phase changes, which occur at constant temperature, pressure, and particle number, the Gibbs free energy does not change.

4.1.5 Summary

Function	Fundamental equation	Definition
$U(S, V, \mathbf{N})$	$dU = T dS - p dV + \sum_j \mu_j dN_j$	
$S(U, V, \mathbf{N})$	$dS = \left(\frac{1}{T} \right) dU + \left(\frac{p}{T} \right) dV - \sum_j \left(\frac{\mu_j}{T} \right) dN_j$	
$H(S, p, \mathbf{N})$	$dH = T dS + V dp + \sum_j \mu_j dN_j$	$H = U + pV$
$F(T, V, \mathbf{N})$	$dF = -S dT - p dV + \sum_j \mu_j dN_j$	$F = U - TS$
$G(T, p, \mathbf{N})$	$dG = -S dT + V dp + \sum_j \mu_j dN_j$	$G = H - TS = F + pV$

Table 4.1. Fundamental equations and their natural variables.

4.2 Uses of internal energy, entropy and enthalpy; heat capacity

These non-fundamental component functions are important because they can be measured in calorimeters, and can be combined to give the fundamental functions, such as $F(T, V, \mathbf{N})$ and $G(T, p, \mathbf{N})$. You measure the temperature dependence of a material's heat capacity $C_V(T)$ in a constant-volume calorimeter. Then, using $\Delta U = \int C_V(T) dT$ and $\Delta S = \int \frac{C_V}{T} dT$ to find ΔF . Alternatively, if ΔG is desired, then you can measure the heat capacity in a constant pressure calorimeter, and use $dH = dU + p dV + V dp = \delta q$. The heat capacity C_p is

$$C_p = \left(\frac{\delta q}{dT} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p. \quad (4.26)$$

Rearranging, you get

$$\Delta H(T, p) = \int_{T_A}^{T_B} C_p(T) dT. \quad (4.27)$$

$$\Delta S(T, p) = \int_{T_A}^{T_B} \frac{C_p(T)}{T} dT.$$

And then use these to calculate ΔG .

4.2.1 The third law of thermodynamics

Suppose you want to know the absolute entropy of a material at a temperature T . You can integrate the heat capacity, $S(T) = \int_0^T (C_V/T') dT' + S(0)$, where $S(0)$ is the entropy at absolute zero temperature. The third law of thermodynamics states that $S(0) = 0$ at for a pure perfectly crystalline substance at zero Kelvin.

4.2.2 Thermodynamic cycles

The following example shows how to combine a thermodynamic cycle with heat capacities to compute properties for which measurements are difficult or impossible.

Example. Measuring enthalpies under standard conditions and computing them for other conditions. Suppose you want to know the enthalpy of boiling water, $\Delta H_{\text{boil}(0^\circ\text{C})}$, at the freezing point of water 0°C and $p = 1$ atm. boiling water, $\Delta H_{\text{boil}(0^\circ\text{C})}$, at the freezing point of water 0°C and $p = 1$ atm. Since you cannot boil water at water's freezing point, why would you want to know that quantity? We will see later that $\Delta H_{\text{boil}(0^\circ\text{C})}$ from the heat capacities of water and steam and the enthalpy of vaporization of water, $\Delta H_{\text{boil}(100^\circ\text{C})}$, under more standard boiling conditions, by using a simple thermodynamic cycle.

The standard state enthalpy has been measured to be $\Delta H_{\text{boil}(100^\circ\text{C})} = 540 \text{ cal g}^{-1}$. The heat capacity of steam is $C_p = 0.448 \text{ cal K}^{-1} \text{ g}^{-1}$ and the heat capacity of liquid water is $C_p = 1.00 \text{ cal K}^{-1} \text{ g}^{-1}$. To obtain $\Delta H_{\text{boil}(0^\circ\text{C})}$, construct the following thermodynamic cycle.

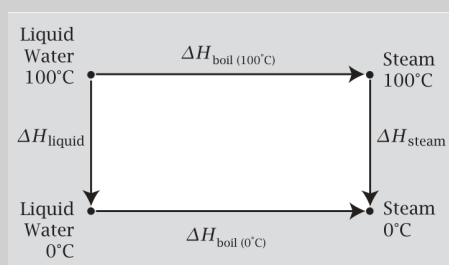


Figure 4.3. A thermodynamic cycle allows you to calculate the enthalpy for boiling water at the freezing temperature of water if you have measured the enthalpy at the boiling temperature.

With the directions of the arrows shown, summing to zero around a cycle means that

$$\Delta H_{\text{boil}(0^\circ\text{C})} = \Delta H_{\text{boil}(100^\circ\text{C})} - \Delta H_{\text{liquid}} + \Delta H_{\text{steam}}.$$

Because there is no phase change for the steam or liquid, and because the heat capacities are reasonably independent of temperature, you have

$$\Delta H_{\text{liquid}} = \int_{100}^0 C_{p,\text{liquid}} dT = C_{p,\text{liquid}} \Delta T = \left(1.00 \frac{\text{cal}}{\text{K g}}\right)(-100 \text{ K}) = -100 \text{ cal g}^{-1}$$

and

$$\Delta H_{\text{steam}} = \int_{100}^0 C_{p,\text{steam}} dT = C_{p,\text{steam}} \Delta T = \left(0.448 \frac{\text{cal}}{\text{K g}}\right)(-100 \text{ K}) = -44.8 \text{ cal g}^{-1}.$$

Thus,

$$\Delta H_{0^\circ\text{C}} = (540 + 100 - 44.8) \text{ cal g}^{-1} = 585.2 \text{ cal g}^{-1}.$$

5 The Boltzmann distribution law and partition functions

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This chapter deals with modeling of the probability distributions of the energies of atoms and molecules. The motivations is that averages over these distributions correspond to experimental measurements, and may be used to predict equilibria.

5.1 Developing the Boltzmann distribution law

Consider a system having N particles of a single type, and suppose the system has t different energy levels, $E_j, j = 1, \dots, t$. We aim to compute the probabilities p_j that the system is in each level j . Suppose (T, V, N) are held constant. Then the condition for equilibrium is $dF = dU - T dS = 0$. We need to find dS and dU .

dS is given by eq. (2.1):

$$\frac{S}{k} = - \sum_{j=1}^t p_j \ln p_j.$$

Differentiating with respect to p_j gives

$$dS = -k \sum_{j=1}^t (1 + \ln p_j) dp_j. \quad (5.1)$$

dU is given by eq. (2.6):

$$U = \langle E \rangle = \sum_{j=1}^t p_j E_j.$$

Take the derivative:

$$dU = \sum_{j=1}^t (E_j dp_j + p_j dE_j). \quad (5.2)$$

Like the macroscopic energy U , the energy levels E_j depend on (V, N) , but not on S or T . We take as a fundamental principle of quantum mechanics that only the populations $p_j(T)$, and not the energies E_j , depend on temperature. However, the *average energy* $\langle E \rangle$ does depend on the temperature. $dE_j = (\partial E_j / \partial V) dV + (\partial E_j / \partial N) dN = 0$ because both V and N are held constant. Thus,

$$d\langle E \rangle = \sum_{j=1}^t E_j dp_j. \quad (5.3)$$

The first law of thermodynamics gives $dU = \delta q + \delta w$, which reduces to $d\langle E \rangle = dU = \delta q$ when V, N are constant. Because eq. (5.3) applies when V is constant, it follows that the term $\sum E_j dp_j$ is the heat and $\sum p_j dE_j$ is the work.

We want the probability distribution that satisfies the equilibrium condition $dF = d\langle E \rangle - T dS = 0$ subject to the normalization constraint, which can be expressed in terms of a Lagrange multiplier α :

$$\alpha \sum_{j=1}^t dp_j = 0. \quad (5.4)$$

Substitute eq. (5.1) and (5.2)–(5.4) into $dF = dU - T dS = 0$ to get

$$dF = \sum_{j=1}^t [E_j + kT (1 + \ln p_j^*) + \alpha] dp_j^* = 0. \quad (5.5)$$

According to the Lagrange multiplier equation (2.3), the term in the brackets must equal zero for each j , so we have t equations of the form

$$\ln p_j^* = -\frac{E_j}{kT} - \frac{\alpha}{kT} - 1. \quad (5.6)$$

Exponentiate eq. (5.6) to find

$$p_j^* = e^{-E_j/kT} e^{(-\alpha/kT)-1}. \quad (5.7)$$

To eliminate α , write the constraint equation

$$\sum_{j=1}^t p_j^* = 1$$

as

$$1 = \sum_{j=1}^t e^{-E_j/kT} e^{(-\alpha/kT)-1}.$$

Divide eq. (5.7) by this form to get the *Boltzmann distribution law*

$$p_j^* = \frac{e^{-E_j/kT}}{\sum_{j=1}^t e^{-E_j/kT}} = \frac{e^{-E_j/kT}}{Q}, \quad (5.8)$$

where Q is the *partition function*,

$$Q \equiv \sum_{j=1}^t e^{-E_j/kT}. \quad (5.9)$$

The relative populations of particles in energy levels i and j at equilibrium are given by

$$\frac{p_i^*}{p_j^*} = e^{-(E_i - E_j)/kT}. \quad (5.10)$$

Note. Comparison of eq. (5.9), which we obtained by minimizing the free energy, with eq. (2.5), which we obtained by maximizing entropy subject to normalization constraint, shows that the Lagrange multiplier that enforces the constraint of average energy is $\beta = 1/(kT)$.

Note. The Boltzmann distribution says that more particles will have low energies and fewer particles will have high energies, because there are more rearrangements of the system that way. It is extremely unlikely that one particle would have such a high energy that it would leave all the others no energy. There are far more arrangements in which most particles have energies that are relatively low, but nonzero.

5.2 Properties of the partition function

The partition function is the connection between macroscopic thermodynamic properties and microscopic models. It is a sum of *Boltzmann factors* $e^{-E_j/kT}$ that specify how particles are partitioned throughout the accessible states. eq. (5.9) gives

$$Q = e^{-E_1/kT} + e^{-E_2/kT} + \dots + e^{-E_t/kT}.$$

It is also common to express Q in an alternative form. Experiments usually give information in form of energy differences (rather than absolute energies). So it is often convenient to define the ground-state energy as zero, $E_1 = 0$, and re-write the partition function as follows:

$$Q = 1 + e^{-(E_2-E_1)/kT} + e^{-(E_3-E_1)/kT} + \dots + e^{-(E_t-E_1)/kT}. \quad (5.11)$$

Another way to think about the partition function is as the number of states that are *effectively* accessible to the system. Look at limits of Q . when the energies are small, or the temperature is high, all the states become equally populated.

$$\left\{ \begin{array}{l} E_j \rightarrow 0 \\ \text{or} \\ T \rightarrow \infty \end{array} \right. \Rightarrow \frac{E_j}{kT} \rightarrow 0 \Rightarrow p_j^* \rightarrow \frac{1}{t} \Rightarrow Q \rightarrow t. \quad (5.12)$$

In this case, all t states become accessible. At the other extreme, as the energy intervals become large or as the temperature approaches zero, the particles only occupy the ground state.

$$\left\{ \begin{array}{l} E_{j \neq 1} \rightarrow \infty \\ \text{or} \\ T \rightarrow 0 \end{array} \right. \Rightarrow \frac{E_{j \neq 1}}{kT} \rightarrow \infty \Rightarrow \left\{ \begin{array}{l} p_1^* \rightarrow 1 \\ \text{and} \\ p_{j \neq 1}^* \rightarrow 0 \end{array} \right. \Rightarrow Q \rightarrow 1. \quad (5.13)$$

In other words, only the ground state becomes accessible. The magnitude E_j/kT determines whether state j is “effectively accessible”. Therefore, kT may be used as a reference value. States that have energies $E_j > kT$ are relatively inaccessible at temperature T , while states with $E_j < kT$ are well populated. Increasing kT increases the *threshold* for effective population. Note that the term ‘effective’ is used, because the number of accessible states is always t , which is determined by the physics of the system.

5.2.1 Densities of states

Sometimes there is a different number of ways that a system can occupy one energy level than another. In such a case, we define $W(E)$ as the *density of states*—the total number of ways a system can occur in energy level E . When $W(E) > 1$, an energy level is called *degenerate*.

When we have a density of states, we can express the partition function as a sum over energy levels $\ell = 1, 2, \dots, \ell_{\max}$:

$$Q = \sum_{\ell=1}^{\ell_{\max}} W(E_\ell) e^{-E_\ell/kT}. \quad (5.14)$$

The probability that a system is in **macrostate** energy level ℓ is

$$p_\ell = Q^{-1} W(E_\ell) e^{-E_\ell/kT}. \quad (5.15)$$

5.2.2 Partition functions for independent and distinguishable particles

The Boltzmann distribution law applies to system of any degree of complexity. In the simplest case, the particles do not interact, and therefore are considered independent. In this case, the **system** partition function is the product of **particle** partition functions.

Before we prove the statement above, we need to emphasize the difference between distinguishable particles and indistinguishable ones. For example, the atoms in a crystal are spatially distinguishable because each one has its own private location in the crystal over the timescale of a typical experiment. Its location serves as a marker. In contrast, the particles in a gas are indistinguishable. As they interchange locations, you can't tell which is which.

Consider distinguishable particles in a system with energy levels E_j . Suppose the system has two independent subsystems (e.g., two particles), labeled A and B , with energy levels ε_i^A and ε_m^B , where $i = 1, 2, \dots, a$ and $m = 1, 2, \dots, b$. The system energy is

$$E_j = \varepsilon_i^A + \varepsilon_m^B.$$

Because the subsystems are independent, we can write partition functions for each subsystem.

$$q_A = \sum_{i=1}^a e^{-\varepsilon_i^A/kT}, \quad q_B = \sum_{m=1}^b e^{-\varepsilon_m^B/kT}. \quad (5.16)$$

The partition function Q for the entire system is the sum of Boltzmann factors over all $j = ab$ energy levels.

$$Q = \sum_{i=1}^a \sum_{m=1}^b e^{-(\varepsilon_i^A + \varepsilon_m^B)/kT} = \sum_{i=1}^a \sum_{m=1}^b e^{-\varepsilon_i^A/kT} e^{-\varepsilon_m^B/kT} = q_A q_B. \quad (5.17)$$

More generally, for a system having N independent and distinguishable particles, each with partition function q , the partition function Q for the whole system is

$$Q = q^N. \quad (5.18)$$

5.2.3 Partition functions for independent and indistinguishable particles

For a system of two indistinguishable particles, the total energy is $E_j = \varepsilon_i + \varepsilon_m$, where $i = 1, 2, \dots, t_1$ and $m = 1, 2, \dots, t_2$. The system partition function is

$$Q = \sum_{j=1}^t e^{-E_j/kT} = \sum_{i=1}^{t_1} \sum_{m=1}^{t_2} e^{-(\varepsilon_i + \varepsilon_m)/kT}. \quad (5.19)$$

If one particle occupied energy level 27 and other particle occupied energy level 56, we could not distinguish that from the reverse. Because of this indistinguishability, we would have overcounted by a factor of $2!$.

For this system, we have $Q = q^2/2!$, to a good approximation. (We are neglecting the case that both particles occupy the same energy level, which doesn't need a correction factor, but for a large number of available energy levels and limited amount of particles, the chance of the above event occurring is very small.) For N indistinguishable particles, the system partition function is

$$Q \approx \frac{q^N}{N!}. \quad (5.20)$$

5.3 Thermodynamic properties can be predicted from partition functions

5.3.1 Computing the internal energy

Consider a system having fixed (T, V, N) . The internal energy for a system with energies E_j , substitute eq. (5.8) into eq. (2.6):

$$U = \sum_{j=1}^t p_j^* E_j = Q^{-1} \sum_{j=1}^t E_j e^{-\beta E_j}, \quad (5.21)$$

where $\beta = 1/kT$. Notice that it follows from eq. (5.9) that we can write

$$\left(\frac{dQ}{d\beta} \right) = \frac{d}{d\beta} \sum_{j=1}^t e^{-\beta E_j} = - \sum_{j=1}^t E_j e^{-\beta E_j}. \quad (5.22)$$

Substituting eq. (5.22) into (5.21) simplifies it:

$$U = -\frac{1}{Q} \left(\frac{dQ}{d\beta} \right) = - \left(\frac{d \ln Q}{d\beta} \right). \quad (5.23)$$

Since $\beta = 1/kT$, we have

$$\left(\frac{d\beta}{dT} \right) = -\frac{1}{kT^2}. \quad (5.24)$$

So we can multiply the left side of (5.23) by $-1/kT^2$ and the right side by $d\beta/dT$ to get

$$\frac{U}{kT^2} = \left(\frac{d \ln Q}{dT} \right). \quad (5.25)$$

A useful alternative expression is

$$\frac{U}{kT} = \frac{d \ln Q}{d \ln T} = \frac{T}{Q} \left(\frac{dQ}{dT} \right). \quad (5.26)$$

5.3.2 Computing the average particle energy

If particles are independent and distinguishable, the average energy $\langle \epsilon \rangle$ **per particle** is

$$\langle \epsilon \rangle = \frac{U}{N} = \frac{kT^2}{N} \left(\frac{\partial \ln q^N}{\partial T} \right)_{V,N} = kT^2 \left(\frac{\partial \ln q}{\partial T} \right) = - \left(\frac{\partial \ln q}{\partial \beta} \right). \quad (5.27)$$

5.3.3 Computing the entropy

The entropy of a system is given by

$$\frac{S}{k} = - \sum_{j=1}^t p_j \ln p_j.$$

Substituting the Boltzmann distribution $p_j^* = Q^{-1} e^{-E_j/kT}$ gives

$$\frac{S}{k} = - \sum_{j=1}^t \left(\frac{1}{Q} e^{-E_j/kT} \right) \left[\ln \left(\frac{1}{Q} \right) - \frac{E_j}{kT} \right]. \quad (5.28)$$

Substituting eq. (5.9) and (5.21) into (5.28) gives

$$S = k \ln Q + \frac{U}{T} = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right). \quad (5.29)$$

For systems of N independent distinguishable particles ($Q = q^N$),

$$S = kN \ln q + \frac{U}{T}. \quad (5.30)$$

Because S increases linearly with N , the system entropy is the num of the entropies of the independent particles.

5.3.4 Computing the free energy and chemical potential

From U and S derived above, thermodynamic relationships can produce the rest—the Helmholtz free energy, chemical potential, and pressure.

$$F = U - TS = -kT \ln Q. \quad (5.31)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -kT \left(\frac{\partial \ln Q}{\partial N} \right)_{T,V}. \quad (5.32)$$

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}. \quad (5.33)$$

5.3.5 The Schottky two-state model

Consider a system that has N distinguishable particles with two energy levels for each particle: a ground state with energy zero and an excited state with energy $\varepsilon_0 > 0$. Find the average particle energy $\langle \varepsilon \rangle$, the heat capacity C_V , the entropy, and the free energy per particle from the partition function.

The partition function for a two-state level system is

$$q = 1 + e^{-\beta \varepsilon_0}. \quad (5.34)$$

The relative populations are given by the Boltzmann distribution.

$$p_1^* = \frac{1}{q}, \quad p_2^* = \frac{e^{-\beta \varepsilon_0}}{q}. \quad (5.35)$$

The average energy per particle is

$$\langle \varepsilon \rangle = \sum_i p_i^* \varepsilon_i = \frac{1}{q} \cdot 0 + \frac{e^{-\beta \varepsilon_0}}{q} \cdot \varepsilon_0 = \frac{\varepsilon_0 e^{-\beta \varepsilon_0}}{1 + e^{-\beta \varepsilon_0}}. \quad (5.36)$$

The heat capacity is defined as $\partial U / \partial T$.

$$U = N \langle \epsilon \rangle = \frac{\epsilon_0 e^{-\beta \epsilon_0}}{1 + e^{-\beta \epsilon_0}}.$$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial U}{\partial \beta} \frac{\partial \beta}{\partial T} = -\frac{N}{kT^2} \left(\frac{\partial \langle \epsilon \rangle}{\partial \beta} \right). \quad (5.37)$$

After some algebra we get

$$C_V = \frac{N \epsilon_0^2}{kT^2} \frac{e^{-\beta \epsilon_0}}{(1 + e^{-\beta \epsilon_0})^2}. \quad (5.38)$$

Note. Peaks in the heat capacity plot are characteristic of bond-breaking and melting processes. At low temperatures, the thermal energy kT from the bath is too small to excite the system to its higher energy level. At intermediate temperatures, the system can absorb heat from the bath, and particles are excited into the higher-energy state. At the highest temperatures, the system takes up no further energy from the bath because it has already taken up the maximum energy it can contain.

To get the entropy, substitute eq. (5.34) for q and $Q = q^N$ for distinguishable independent particles into (5.27) and (5.29):

$$\frac{S}{k} = \frac{\epsilon_0 e^{-\beta \epsilon_0}}{T (1 + e^{-\beta \epsilon_0})} + k \ln (1 + e^{-\beta \epsilon_0}). \quad (5.39)$$

To get the free energy, substitute Q into (5.31).

$$\frac{F}{NkT} = -\ln q = -\ln (1 + e^{-\beta \epsilon_0}). \quad (5.40)$$

As $\epsilon_0 \rightarrow \infty$, the excited state becomes inaccessible, so $S \rightarrow 0$ and $F \rightarrow 0$. On the other hand, as $\epsilon_0 \rightarrow 0$, both states become accessible, so $S \rightarrow Nk \ln 2$ and $F \rightarrow -NkT \ln 2$.

5.3.6 Temperature of a two-state system (and the notion of negative temperature)

Eq. (3.13) tells us that $T^{-1} = (\partial S / \partial U)_{V,N}$. Let's use the Schottky model to see the meaning of T .

In the two-state model, n (out of N) particles populate the excited state. When energy enters the system as heat, it excites particles to move from the ground state to the excited state. We've seen that the energy U of the system abides by

$$U = n \epsilon_0 \quad \Rightarrow \quad n = \frac{U}{\epsilon_0}. \quad (5.41)$$

The multiplicity of states in a binary system is given by the binomial:

$$W = \frac{N!}{n! (N-n)!},$$

so

$$\frac{S}{k} = \ln W \approx -n \ln \left(\frac{n}{N} \right) - (N-n) \ln \left(\frac{N-n}{N} \right). \quad (5.42)$$

To get $S(U)$, replace (5.41) into (5.42).

$$\frac{1}{T} = k \left(\frac{\partial \ln W}{\partial U} \right)_{V,N} = k \left(\frac{\partial \ln W}{\partial n} \right)_{V,N} \left(\frac{dn}{dU} \right). \quad (5.43)$$

$$\begin{aligned} \frac{1}{T} &= \frac{k}{\varepsilon_0} \left[-1 - \ln \left(\frac{n}{N} \right) + 1 + \ln \left(\frac{N-n}{N} \right) \right] \\ &= -\frac{k}{\varepsilon_0} \ln \left(\frac{n/N}{1 - (n/N)} \right) = -\frac{k}{\varepsilon_0} \ln \left(\frac{U/N \varepsilon_0}{1 - U/N \varepsilon_0} \right) \\ &= \frac{k}{\varepsilon_0} \ln \left(\frac{f_{\text{ground}}}{f_{\text{excited}}} \right), \end{aligned} \quad (5.44)$$

where $f_{\text{excited}} = n/N$ and $f_{\text{ground}} = 1 - n/N$. Eq. (5.44) shows that the temperature of a two-state system depends on the energy spacing ε_0 , the number of particles N , and the total energy U , through quantity n . The following figure shows $S(U)$ for a two-state system with $N = 3$ particles.

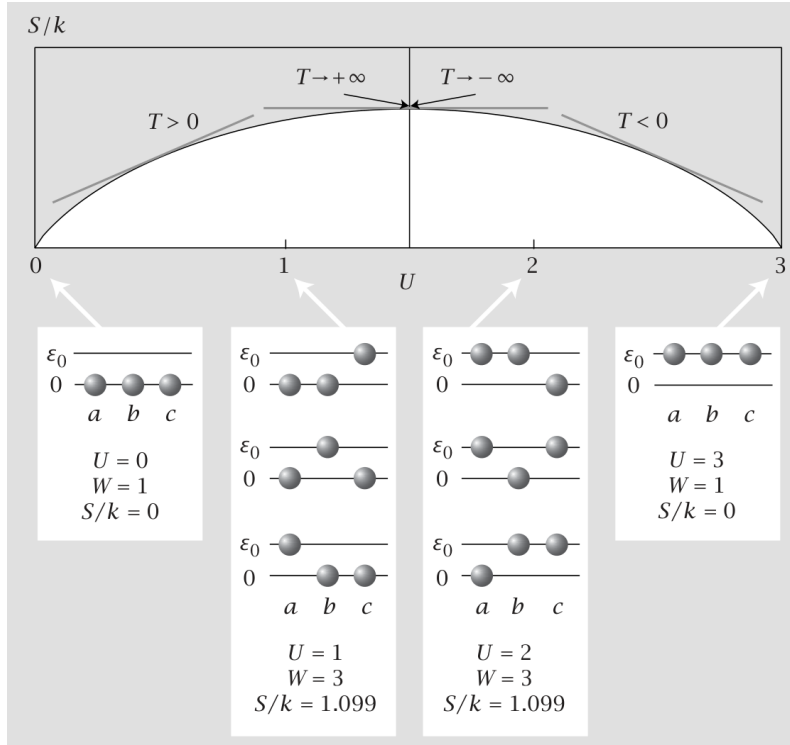


Figure 5.1. The entropy of a two-state system as a function of its energy.

For any value of U , $1/T$ is the slope of the curve $S(U)$ at that point. There are 3 regions in the graph:

1. *Positive temperature, $T > 0$.* At low U , most particles are in the ground state. According to (5.44), the temperature is positive. If an external source of energy is available, the system will tend to absorb energy from it, and particles will transition to the excited state. **Systems having positive temperature absorb energy to gain entropy.**
2. *Infinite temperature, $T \rightarrow \infty$.* At intermediate energy U , with equal populations in the ground and excited states, $1/T \rightarrow 0$. This is the point where $S(U)$ is maximal. **Systems at infinite temperature cannot gain additional entropy by absorbing energy.**

3. *Negative temperature*, $T < 0$. At high energy U , most particles are in the excited state. It follows from (5.44) that the temperature is negative. If the system were to absorb additional energy, shifting the last few particles from the ground state to the excited state would lead to a lower multiplicity of states. **Systems at negative temperature give off energy.**

A system at negative energy is *hotter* than at positive energy, since ‘hotness’ is a tendency to give up energy. Negative temperatures occur only in saturable systems that have finite numbers of energy levels. Ordinary materials have practically infinite ladders of energy levels and are not saturable, because their particles have translational, rotational, vibrational, and electronic freedom.

A system at negative temperature, with more excited than ground-state particles, is said to have a population inversion. A population inversion cannot be achieved by equilibration with a normal heat bath, because heat baths invariably have positive temperatures. Using a heat bath that has a positive temperature, the most that increasing the bath temperature can achieve is equal populations of excited- and ground-state particles of the system. A population inversion can be caused by incident electromagnetic radiation entering the system to excite the particles into a nonequilibrium state. The excited particles will typically then spontaneously emit radiation to give off energy in order to reach a state of higher entropy.

5.3.7 Energy fluctuations in a system

The probability that an arbitrary system is in a particular energy level is (from eq. (5.14))

$$p(E) = \frac{W(E) e^{-\beta E}}{Q}. \quad (5.45)$$

We shall show that $p(E)$ is a highly peaked function with a width that is determined by the heat capacity. Let E represent one particular energy level of the system and U represent the equilibrium value of the energy. Near the peak, the function $p(E)$ is approximately Gaussian, and its width is proportional to C_V . Express $\ln p(E)$ as a Taylor series around the mean value $\langle E \rangle = U$:

$$\ln p(E) = \ln p(U) + \left(\frac{\partial \ln p(E)}{\partial E} \right)_{E=U} (E - U) + \frac{1}{2} \left(\frac{\partial^2 \ln p(E)}{\partial E^2} \right)_{E=U} (E - U)^2 + \dots \quad (5.46)$$

The peak of this function defines the equilibrium state: the fluctuations are deviations from it. We are interested in the variations away from equilibrium. At the peak, the entropy $S(E)$ equals its equilibrium value $S(U)$. At the peak, the temperature $T(E)$ equals its equilibrium value T_0 , which is the temperature of the bath.

Insert (5.45) into (5.46) and. Q is not a function of E , but a sum over E . So Q does not contribute to the partial derivatives. Use $S(E) = k \ln W(E)$ and $(\partial S / \partial E) = 1/T(E)$ to get:

$$\begin{aligned} \left(\frac{\partial \ln p(E)}{\partial E} \right) &= \left(\frac{\partial \ln W(E)}{\partial E} \right) - \beta \\ &= \left(\frac{\partial (S/k)}{\partial E} \right) - \beta = \frac{1}{kT(E)} - \frac{1}{kT_0}. \end{aligned} \quad (5.47)$$

To get the second derivative, use the relation $(\partial E / \partial T) = C_V$ to get:

$$\left(\frac{\partial^2 \ln p(E)}{\partial E^2} \right) = - \left(\frac{1}{kT^2} \right) \left(\frac{\partial T}{\partial E} \right)_{E=U} = - \left(\frac{1}{kT_0^2 C_V} \right). \quad (5.48)$$

Substituting (5.48) into (5.46) and exponentiating shows that $p(E)$ is approximately a Gaussian function.

$$p(E) = p(U) \exp \left[- \frac{(E - U)^2}{2kT_0^2 C_V} \right] = \exp [U - T_0 S(U)] \exp \left[- \frac{(E - U)^2}{2kT_0^2 C_V} \right]. \quad (5.49)$$

By the definition of variance,

$$\sigma^2 = \langle (E - U)^2 \rangle = \langle E^2 \rangle - U^2 = k T_0^2 C_V. \quad (5.50)$$

This equation shows that you can determine the magnitude of the energy fluctuations if you know C_V .

Sometimes, it is useful to express the variance in terms of the partition function:

$$\sigma^2 = \frac{d^2 \ln Q}{d\beta^2} = \frac{d}{d\beta} \left(\frac{1}{Q} \frac{dQ}{d\beta} \right) = \frac{Q''}{Q} - \frac{Q'}{Q^2}. \quad (5.51)$$

5.4 What is an ensemble?

A term commonly used in statistical mechanics is *ensemble*. The term is usually used in one of two ways. First, it can refer to which set of variables you are controlling: 'the (U, V, N) ensemble' or 'the (T, p, N) ensemble'.

- The (T, V, N) ensemble is called the *canonical ensemble*.
- The (U, V, N) ensemble is called the *microcanonical ensemble*.
- The (T, p, N) ensemble is called the *isobaric-isothermal ensemble*.
- The (T, V, μ) ensemble is called the *grand canonical ensemble*.

The term ensemble also has another meaning. An ensemble is the collection of all the possible microstates, or snapshots, of a system.

5.4.1 The microcanonical ensemble

The microcanonical ensemble is qualitatively different from the canonical and grand canonical ensembles. In the canonical ensemble, the temperature is fixed, which is equivalent to fixing the average energy $U = \langle E \rangle$. The energy can fluctuate. But in the microcanonical ensemble, every microstate has exactly the same fixed energy, so $U = E$, and there are no fluctuations.

For the microcanonical ensemble, it is more useful to focus on the $i = 1, 2, \dots, W(E, V, N)$ microstates of the system, than of t energy levels, since there is only one energy level. In the microcanonical ensemble, each microstate is equivalent. So you can express the probability that the system is in microstate $i = 1, 2, \dots, W$ as

$$p_i^* = \frac{1}{W}. \quad (5.52)$$

Using the definition of the entropy, we have

$$\frac{S}{k} = - \sum_{i=1}^W p_i \ln p_i = - \sum_{i=1}^W \left(\frac{1}{W} \right) \ln \left(\frac{1}{W} \right) = \ln W(E, V, N). \quad (5.53)$$

6 Solutions and Mixtures

6.1 Lattice models describe mixtures

In this section we wish to derive the relationship between the chemical potential μ of a molecule and its concentration x in the solution. We shall use the (T, V, \mathbf{N}) ensemble rather than (T, p, \mathbf{N}) , because it allows us to work with a simple lattice model that captures the principles of solution theory. The appropriate extremum principle is based on the Helmholtz free energy F , where S is the entropy of the solution and U accounts for the interaction energies between lattice particles.

6.1.1 The entropy of a solution

Suppose there are N_A, N_B molecules of species A and B respectively. Particles A and B are the same size; each occupies one lattice site and together they completely fill a lattice of N lattice sites.

$$N = N_A + N_B. \quad (6.1)$$

The multiplicity here is given by the binomial

$$W = \frac{N!}{N_A! N_B!}. \quad (6.2)$$

The translational entropy of the mixed system can be computed using the $S = k \ln W$ and Stirling's approximation.

$$\begin{aligned} \Delta S_{\text{solution}} &= k (N \ln N - N_A \ln N_A - N_B \ln N_B) \\ &= k (N_A \ln N + N_B \ln N - N_A \ln N_A - N_B \ln N_B) \\ &= -Nk \left[\frac{N_A}{N} \ln \left(\frac{N_A}{N} \right) + \frac{N_B}{N} \ln \left(\frac{N_B}{N} \right) \right] \\ &= -k (N_A \ln x_A + N_B \ln x_B). \end{aligned} \quad (6.3)$$

This entropy can be expressed in terms of the *relative concentrations* of A and B . We shall use *mole fractions* $x = N_A/N$ and $(1 - x) = N_B/N$.

$$\frac{\Delta S_{\text{solution}}}{Nk} = -x \ln x - (1 - x) \ln (1 - x). \quad (6.4)$$

This dependence is shown in Figure 6.1.

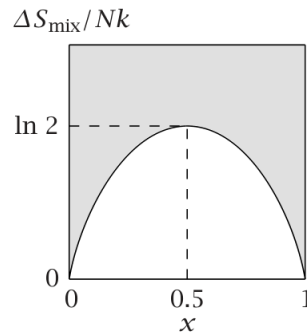


Figure 6.1. The entropy of solution as a function of the mole fraction.

Note though that x is a fixed property of the system, and is not a degree of freedom.

Definition 6.1

Ideal solutions. A solution is called *ideal* if its free energy is given by $\Delta F_{\text{solution}} = -T \Delta S_{\text{solution}}$. Mixing an ideal solution involves **no** change in energy, and it involves no other entropies due to changes in volume, structuring, or ordering in the solution.

Examples of ideal solutions: toluene/benzene and n-hexane/n-heptane.

6.1.2 The energy of a solution (and the mean-field approximation)

Real (non-ideal) solutions involve interactions between molecules. In the lattice model, the total energy of solution is the sum of the contact interactions of noncovalent bonds of all the pairs of nearest neighbors in the mixture. There are three types of contact: an *AA* bond, a *BB* bond, or and *AB* bond.

The total energy of the system is

$$U = m_{AA} w_{AA} + m_{BB} w_{BB} + m_{AB} w_{AB}, \quad (6.5)$$

where m_{AA} is the number of *AA* bonds and w_{AA} is the contact energy of the *AA* bond. These are negative quantities.

In general, m_{ij} are not known. Express these in terms of N_A and N_B . Each lattice site has z ‘sides’; every contact involves two sides.

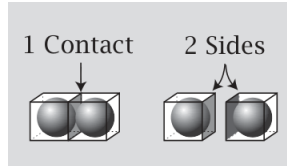


Figure 6.2. One contact between lattice particles involves two lattice site sides.

The total number of sides of type *A* particles is $z N_A$, which can be expressed in terms of the number of contacts as

$$z N_A = 2 m_{AA} + m_{AB}, \quad (6.6)$$

because the number of *A* side equals

$$(\#AA \text{ bonds}) \times \left(\frac{2 A \text{ sides}}{AA \text{ bond}} \right) + (\#AB \text{ bonds}) \times \left(\frac{1 A \text{ side}}{AB \text{ bond}} \right).$$

Similarly, for type *B* particles,

$$z N_B = 2 m_{AB} + m_{BB}. \quad (6.7)$$

Combining (6.6) and (6.7) gives

$$m_{AA} = \frac{z N_A - m_{AB}}{2}, \quad m_{BB} = \frac{z N_B - m_{AB}}{2}. \quad (6.8)$$

Substitute into the expression for the total energy, to get

$$\begin{aligned} U &= \left(\frac{z N_A - m_{AB}}{2} \right) w_{AA} + \left(\frac{z N_B - m_{AB}}{2} \right) w_{BB} + m_{AB} w_{AB} \\ &= \left(\frac{z w_{AA}}{2} \right) N_A + \left(\frac{z w_{BB}}{2} \right) N_B + \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) m_{AB}. \end{aligned} \quad (6.9)$$

Before we continue, we must first introduce a new approximation: the *mean-field approximation*.

Different arrangements of the system's particles will have different values of m_{AB} . In principle, we should consider each configuration of the system, and we should account for its appropriate Boltzmann weight. Instead, we assume that for any given numbers N_A and N_B , the particles are mixed **as randomly and uniformly as possible**. This gives a new way to estimate m_{AB} .

Consider a specific site next to an A molecule. What is the probability that a B occupies that neighboring site? According to the mean-field approximation,

$$p_B = \frac{N_B}{N} = x_B = 1 - x. \quad (6.10)$$

Because there are z nearest-neighbor sites for each molecule of A , the average number of AB contacts made by that particular molecule of A is $zN_B/N = z(1 - x)$. Therefore,

$$m_{AB} \approx \frac{zN_A N_B}{N} = zNx(1 - x). \quad (6.11)$$

Now compute the total contact energy of the mixture from the known quantities N_A and N_B by inserting (6.11) into (6.9):

$$\begin{aligned} U &= \left(\frac{zw_{AA}}{2}\right)N_A + \left(\frac{zw_{BB}}{2}\right)N_B + \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2}\right)zNx(1 - x) \\ &= \left(\frac{zw_{AA}}{2}\right)N_A + \left(\frac{zw_{BB}}{2}\right)N_B + kT\chi_{AB}\frac{N_A N_B}{N}, \end{aligned} \quad (6.12)$$

where we define the *exchange parameter* χ_{AB} as

$$\chi_{AB} \equiv \frac{z}{kT} \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right). \quad (6.13)$$

The mean-field approximation does not always hold. If AB interactions are more favorable than AA and BB interactions, then the mixing will not be random. Conversely, if the self-attractions are stronger, then A 's and B 's will tend to form independent clusters.

6.1.3 The free energy of a solution

Combine the previous terms to form $F = U - TS$.

$$\frac{F(N_A, N_B)}{kT} = N_A \ln \left(\frac{N_A}{N} \right) + N_B \ln \left(\frac{N_B}{N} \right) + \left(\frac{zw_{AA}}{2} \right) N_A + \left(\frac{zw_{BB}}{2} \right) N_B + kT\chi_{AB} \frac{N_A N_B}{N}. \quad (6.14)$$

The difference between the mixed, final state and the initial pure states of A and B , $\Delta F_{\text{solution}}$ is

$$\Delta F_{\text{solution}} = F(N_A, N_B) - F(N_A, 0) - F(0, N_B). \quad (6.15)$$

$F(N_A, 0)$ is found by substituting $N = N_A$ and $N_B = 0$ into (6.14).

$$\frac{\Delta F_{\text{solution}}}{NkT} = x \ln x + (1 - x) \ln (1 - x) + \chi_{AB} x (1 - x). \quad (6.16)$$

This model is also called the *regular solution model*, coined by JH Hildebrand in 1929. While ideal solutions are driven only by the entropy of solution of particles of roughly equal size, regular solutions are driven also by the energy of the mean-field form described above.

6.1.4 The chemical potentials

The chemical potential of species A is $\mu_A = (\partial F / \partial N_A)_{T, N_B}$.

$$\begin{aligned} \frac{\mu_A}{kT} &= \left[\frac{\partial}{\partial N_A} \left(\frac{F}{kT} \right) \right]_{T, N_B} \\ &= \ln \left(\frac{N_A}{N} \right) + 1 - \frac{N_A}{N} - \frac{N_B}{N} + \frac{z w_{AA}}{2kT} + \chi_{AB} \frac{(N_A + N_B) N_B - N_A N_B}{(N_A + N_B)^2} \\ &= \ln x_A + \frac{z w_{AA}}{2kT} + \chi_{AB} (1 - x_A)^2. \end{aligned} \quad (6.17)$$

Similarly, for B ,

$$\frac{\mu_B}{kT} = \left[\frac{\partial}{\partial N_B} \left(\frac{F}{kT} \right) \right]_{T, N_A} = \ln x_B + \frac{z w_{BB}}{2kT} + \chi_{AB} (1 - x_B)^2. \quad (6.18)$$

The main result is an equation of the form

$$\mu = \mu^0 + kT \ln \gamma x, \quad (6.19)$$

where γ is called the *activity coefficient*.

Note that because the lattice is fully filled, no work can be done and pV effects are neglected.

Equations (6.17)–(6.19) provide the foundation for treatment of mixing, solubility, partitioning, solvation, and colligative properties. Chemical potential describes the tendency of particles to change phases, or states. Particles of type A tend to leave regions of high relative concentration to gain solution entropy, and are attracted to regions or phases characterized by high chemical affinity, described by μ^0 and χ_{AB} .

Note. What is the physical meaning of χ_{AB} ? It describes the **energetic cost** of beginning with the pure states of A and B and transferring one B into a medium of pure A 's and one A into a medium of pure B 's.

$$\frac{1}{2} z(AA) + \frac{1}{2} z(BB) \longrightarrow z(AB), \quad \chi_{AB} = -\ln K_{\text{exch.}}$$

where $K_{\text{exch.}}$ is the *equilibrium constant* for the exchange process.

If the mixing is favorable, then $K_{\text{exch.}} > 1$. According to Hildebrand's principle, for most systems the AB affinity is weaker than the pure affinities, so usually $\chi_{AB} > 0$. The quantity χ_{AB} also contributes to the interfacial free energy between two materials.

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6.1.5 The Partition Function in the Mean-Field Approximation

The partition function Q should be a sum over all the possible states of the system. It should be a sum of the number of states with small numbers of AB contacts, m_{AB} , and states with large m_{AB} rather than a mean-field estimate of the number of uniformly mixed conformations. In this way, we have made the approximation that

$$Q = \sum_{m_{AB}} w(N_A, N_B, m_{AB}) e^{-E(N_A, N_B, m_{AB})/kT} \approx \frac{N!}{N_A! N_B!} e^{-U/kT}, \quad (6.20)$$

where E is the energy of a configuration having m_{AB} contacts and w is the density of states, the number of configurations having the given value of m_{AB} . U is the mean-field average energy from (6.12). The partition function is useful, because we can use it to calculate other properties of the system, such as the heat capacity.

7 Phase Transitions

7.1 Two States Can Be Stable at the Same Time

At water's boiling point, two different phases are stable at the same time: liquid water is in equilibrium with steam. A phase transition is a dramatic change in a system's physical properties. Other phase transitions among different states of matter include freezing, the magnetization of metals, solubilization and precipitation in liquids, the formation of membranes and micelles, and sharp transitions in the alignments of liquid crystal molecules.

While the term *phase transition* usually applies to macroscopic systems, *cooperativity* more broadly also refers to sharp changes of properties of single molecules, for example in protein folding, helix-coil transitions, or ligand binding.

To understand how multiple states can be stable at the same time, first recall the principle of stability of a single state. If a system at fixed temperature has a degree of freedom x , the stable state occurs at $x = x^*$, where the free energy $F(x)$ is at minimum. Note that $F(x)$ is convex in this case; the free energy increases in either direction away from this minimum. Water gets no denser than $\rho = \rho^*$ because steric repulsions among the molecules would increase the free energy. Water gets no looser than $\rho = \rho^*$ because the loss of water-water attractions would increase the free energy. **When two or more phases are in equilibrium, it implies that the free energy function of a system has multiple minima.**

7.2 Energy Landscapes Describe Stabilities and Transitions

Energy landscape diagrams show how changing the temperature shifts a system from one stable state to another through the course of a phase transition. A *phase* is a region in which the composition and properties are uniform.

There are two types of phase transitions: *first-order* and *higher-order*. First-order transitions are between two states, such as liquid and vapor. At the midpoint temperature of a first-order transition, i.e., exactly at the boiling temperature, the landscape has two equal minima in free energy, representing two equally stable states. At the midpoint of a higher-order transition, the landscape has one broad minimum in the free energy.

At the midpoint of a first-order transition, some clusters of molecules would be observed having low density (like vapor) and other having high density (like liquid), but rarely with properties in between. In contrast, at the midpoint of a higher-order transition, some clusters would have intermediate densities between those of vapor and liquid. **Energy landscapes represent free energy functions of the degrees of freedom of a system and give a graphical way to think about phase transitions.**

Simple experimental observables typically do not tell you whether a transition is first-order or higher-order. For boiling, you could measure the average density of water molecules, $\rho(T)$, as a function of temperature. You would observe a sharp decline in $\rho(T)$, which indicates on a phase transition, but not on its type. The quantity $\rho(T)$ gives only the *average* density of all the clusters.

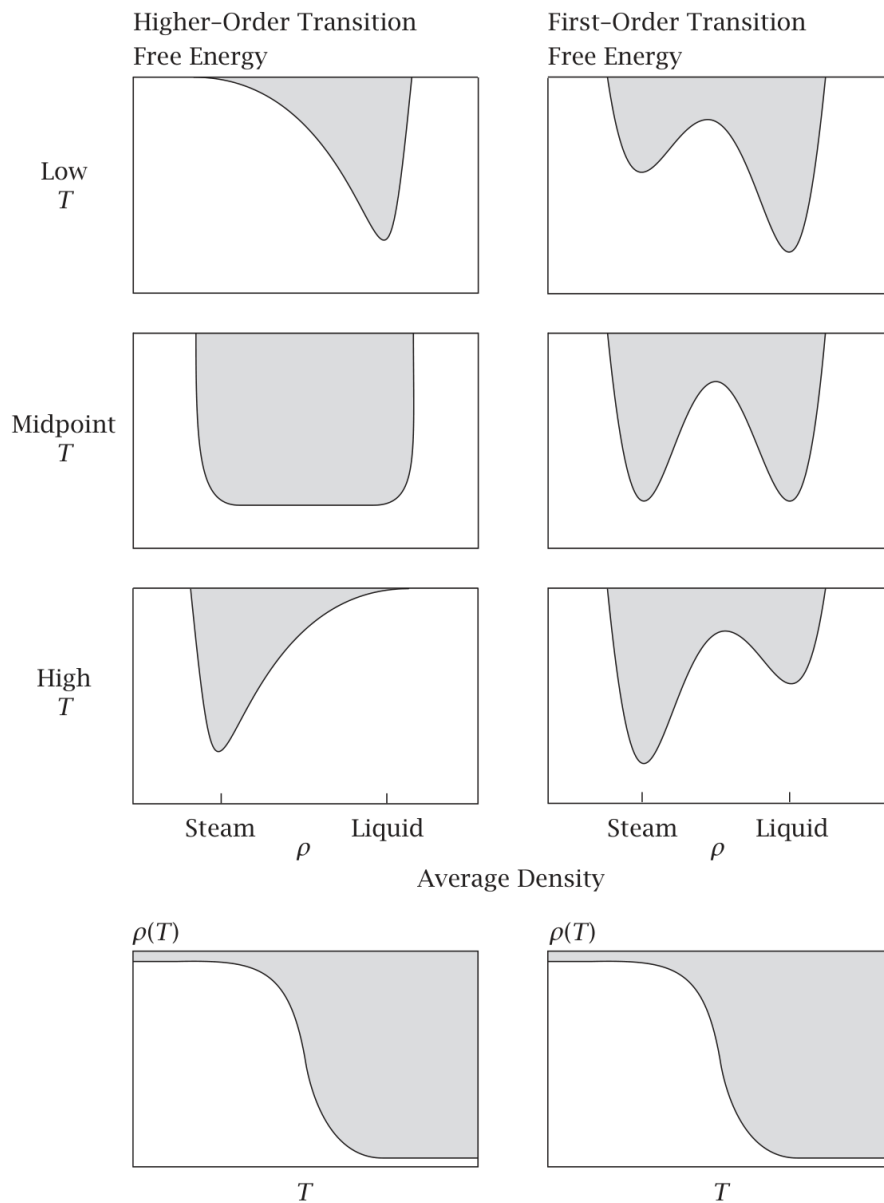


Figure 7.1. Free energy landscapes/profiles showing how the stable state of water shifts from liquid to steam. Left column: at the midpoint of a higher-order transition, states are stable that have a wide range of densities. Right column: at the midpoint of a first-order transition, only two states are stable. The bottom figure shows that the average density versus temperature can be the same for these two different types of transformations. Quantities such as the density do not give the landscape shape, because they are averaged over the different landscape states.

7.3 Phase Diagrams Describe What Phases Are Stable Under Which Conditions

In the boiling example above, we considered temperature as our *control* variable: changing the temperature switches the stable state from liquid water to steam. You can also boil water by changing the pressure. Or, you can boil water by different combinations of pressure and temperature. With two control variables, such as pressure and temperature, you can make a two-dimensional plot, called a phase diagram. A phase diagram tells you which phases are stable under what conditions. A different type of phase diagram can describe the mixing and de-mixing of two liquids. In this case, the two control variables are the temperature (T) and composition (x).

7.3.1 Liquids or Solids May Mix at High Temperatures but Not at Low Temperatures

Observe the following phase diagram of oil and water:

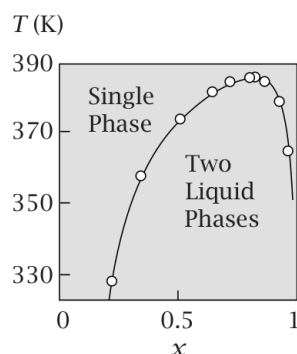


Figure 7.2. A phase diagram for liquid benzene (mole fraction x) in perfluorooheptane.

How would one obtain this diagram experimentally? Make six solutions, numbered 1–6, having different compositions of oil and water. Beaker 1 has mostly water, and beaker 6 has mostly oil. All solutions are at the same temperature T_0 . In the figure above, the vertical axis represents the temperature of the solutions, and the horizontal axis represents the composition (mole fraction) of one solution. In the figure below, $x_B = 1$ means pure oil and $x_B = 0$ means pure water.

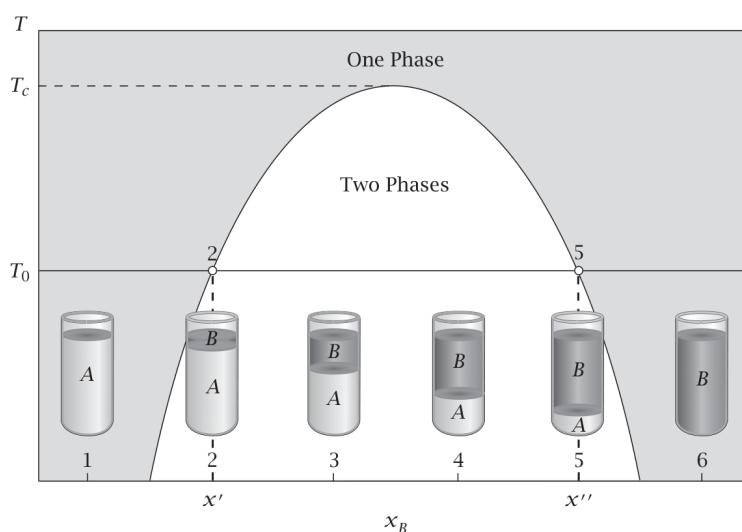


Figure 7.3. Six different solutions help to map out the phase diagram. T_0 is the temperature of the solution, x' is the concentration of B that saturates liquid A , and x'' is the concentration of B at which A saturates B . T_c is the critical temperature.

Let's examine the different beakers:

1. **A small amount of oil dissolved in water.** The oil fully dissolves in the water, meaning that most of the individual oil molecules are dispersed and surrounded by water molecules. This is a *single-phase* solution.
2. **The solubility limit of oil in water.** The oil concentration in test tube 2 is greater than in tube 1. This is the lowest oil concentration at which you can detect a second phase, a thin layer of oil on the water. Tube 2 has enough oil to *saturate* the capacity of the water to hold oil. This mark defines one point on the *phase boundary*.

3. **An oil phase on top of a water phase.** Test tube 3 has a higher oil concentration than tube 2. This is a *two-phase* solution. The top phase is mostly oil (but contains some water) and the bottom phase is mostly water (but contains some oil). The water-rich phase on the bottom is saturated with oil, having oil concentration x' . The oil-rich phase on top is saturated with water, having oil concentration x'' .
4. **More oil phase on top of the water phase.** Tube 4 has a larger volume of the oil-rich phase than tube 3, and a smaller volume of the water-rich phase. But the compositions of the oil-rich and water-rich phases remain the same as they are in test tube 3: the bottom phase still has oil concentration x' , and the top phase still has oil concentration x'' .
5. **The solubility limit of water in oil.** Beyond this point, the system becomes a single phase again. At this point, the water-rich phase disappears and you have only an oil-rich phase saturated with water. This mark defines another point on the *phase boundary*.
6. **A small amount of water dissolved in oil.** Test tube 6 contains a single phase, in which a very small amount of water is fully dissolved in a large amount of oil.

From the six experiments at temperature $T = T_0$, the phase boundary is defined by two compositions: x' and x'' .

Now perform the same experiment with another series of tubes of different compositions at a higher temperature $T = T_1$. Again, mark the two phaseboundary points $x'(T_1)$ and $x''(T_1)$. At higher temperatures, the phase boundaries are closer together: more oil dissolves in water and more water dissolves in oil. Continue increasing the temperature and finding the two phaseboundary points for each temperature. For any temperature higher than the *critical point* T_c , the two components are *miscible in all proportions*. That is, there are not two distinct phases; any proportion of the two components form a single mixed system.

In this series of test tubes, we fixed the temperature and varied the composition. Now, instead, fix the composition and change the temperature, say of solution 4. Read the results from the same phase diagram. At low temperatures, the solution has two phases. At a higher temperature, above the phase boundary, the two components dissolve in each other.

7.3.2 The Lever Rule: Computing the Amounts of the Stable Phases

You can determine the amounts (the volumes) of the phases from the phase diagram by using the lever rule. The amounts of B in each phase must sum to the total amount that were put into the solution. Let the relative amount of material in the A -rich phase be represented by the fraction

$$f = \frac{\text{number of molecules in } A\text{-rich phase}}{\text{total number of molecules in both phases}},$$

so $(1 - f)$ is the fraction of all molecules that are in the B -rich phase. You also have

$$x' = \frac{\text{number of } B \text{ molecules in } A\text{-rich phase}}{\text{number of molecules in } A\text{-rich phase}}$$

and

$$x'' = \frac{\text{number of } B \text{ molecules in } B\text{-rich phase}}{\text{number of molecules in } B\text{-rich phase}}.$$

Combining the two gives

$$fx' = \frac{\text{number of } B \text{ molecules in } A\text{-rich phase}}{\text{total number of molecules in both phases}}.$$

$$(1 - f)x'' = \frac{\text{number of } B \text{ molecules in } B\text{-rich phase}}{\text{total number of molecules in both phases}}.$$

So,

$$fx' + (1-f)x'' = x_0.$$

Rearranging leads to the lever rule.

$$f = \frac{x_0 - x''}{x' - x''}.$$

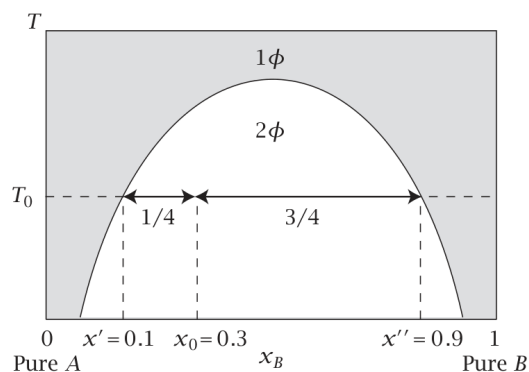


Figure 25.6 The lever rule. Suppose you are given the phase diagram points $x' = 0.1$ and $x'' = 0.9$. Now you mix together two components to have a B composition $x_0 = 0.3$. To find the relative amounts of the two phases, compute f using Equation (25.2). This gives $f = (0.9 - 0.3) / (0.9 - 0.1) = 3/4$, the relative length of the right side of the lever arm. So, the left side of the lever arm has relative length $(1 - f) = 1/4$. Three-quarters of the system is in the x' (mostly A) phase. The other one quarter of the system is in the mostly- B phase.

Now, let's use energy landscapes to understand when a system will be stable as a single phase or when it be unstable and split into multiple phases in equilibrium.

7.4 Peaks on Energy Landscapes Are Points of Instability

Suppose you put into a beaker two components A and B , with B concentration $x_0 = 0.5$. The landscape has two stable states (the minima). The system has two options: two balls metaphorically stay at the top of the hill or one ball rolls down to the left energy well and the other ball rolls down to the right well. Of these two options, the system can achieve its lowest possible total free energy by forming separate phases. That is, $F_{\text{hilltop}} = 2F_0$ and $F_{\text{valleys}} = 2F_1$. Since $F_1 < F_0$ you see $F_{\text{valleys}} < F_{\text{hilltop}}$.

Why roll two balls on this hill, rather than one? Our system has a constraint. If one ball rolled from the top of the hill to the valley on the left, it would represent changing the composition of the system from x_0 to x' . But this is not possible. The composition of the system is fixed to be x_0 by the total amount of oil and water that you put into the beaker in the first place. The system does not have the freedom to change its overall composition. But, the system can divide into two component subsystems having compositions x' and x'' , where $x' + x'' = 2x_0$.

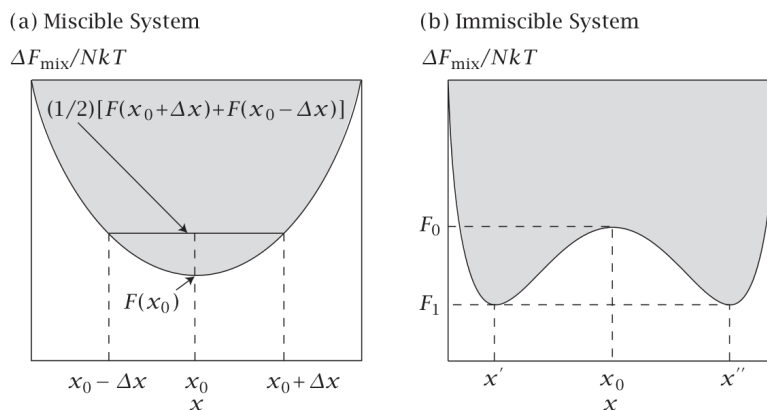


Figure 7.4. (a) if a system's free energy $\Delta F_{\text{mix}}(x)$ is concave upwards, the system is miscible. (b) for compositions where $\Delta F_{\text{mix}}(x)$ is concave downwards, the system is immiscible.

7.4.1 The Common Tangent Predicts the Compositions of Phases

Here is a way that you can predict the compositions of the two phases in general if you know the function $F(x)$. Find the compositions x' and x'' by drawing a line that is tangent to $F(x)$ at two points. The two points of tangency predict the compositions of the two phases.

To get the free energy $F(x)$ at fixed T and V , start with eq. (4.23). For a system having N_A particles of type A with chemical potential μ_A (and similarly for B),

$$F = \mu_A N_A + \mu_B N_B = N (\mu_A x_A + \mu_B x_B) . \quad (7.1)$$

$$\left(\frac{\partial F}{\partial x_B} \right) = N (\mu_B - \mu_A) . \quad (7.2)$$

In a two-phase equilibrium, the chemical potential of each component must be the same in both phases, so $\mu'_A = \mu''_A$ and $\mu'_B = \mu''_B$. Subtract $\mu'_A = \mu''_A$ from $\mu'_B = \mu''_B$ and multiply by N to get

$$N (\mu'_B - \mu'_A) = N (\mu''_B - \mu''_A) . \quad (7.3)$$

Substitute (7.2) into (7.3) for each phase reveal that the slope of $F(x)$ must be the same at x' and x'' .

$$\left(\frac{\partial F}{\partial x} \right)_{x=x'} = \left(\frac{\partial F}{\partial x} \right)_{x=x''} . \quad (7.4)$$

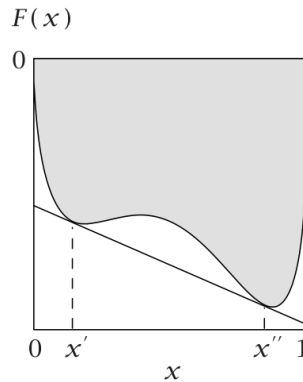


Figure 7.5. The common tangent to $F(x)$, the free energy as a function of composition, identifies the stable phases having compositions x' and x'' .

If the function $F(x)$ has minima of two different depths, the common tangency condition means that the points x' and x'' are not exactly the points at which the free energy is a local minimum.

Now, let's model the underlying driving forces for phase equilibria.

7.4.2 Thermal Phase Equilibria Arise from a Balance between Energies and Entropies

Suppose you have two liquid phases, one of pure A and one of pure B . Combine them to give a mole fraction x of B in A . The free energy of mixing ΔF_{mix} is given in the lattice model by eq. (6.16):

$$\frac{\Delta F_{\text{mix}}}{NkT} = x \ln x + (1-x) \ln (1-x) + \chi_{AB} x (1-x) ,$$

where $N = N_A + N_B$ is the total number of molecules. Recall that $\chi_{AB} = c_1/T$ is a dimensionless free energy quantity that is inversely proportional to temperature and describes the interactions between A and B molecules, where

$$c_1 = \frac{z}{k} \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right), \quad (7.5)$$

is a constant independent of temperature.

We wish to predict the phase diagram and the energy landscapes using this lattice model. Choose a temperature of interest, $T = T_1$. For two given materials A and B , c_1 is known. Compute $\Delta F_{\text{mix}}(x)$. Then, calculate the corresponding curves for T_2, T_3, \dots . These should look like this:

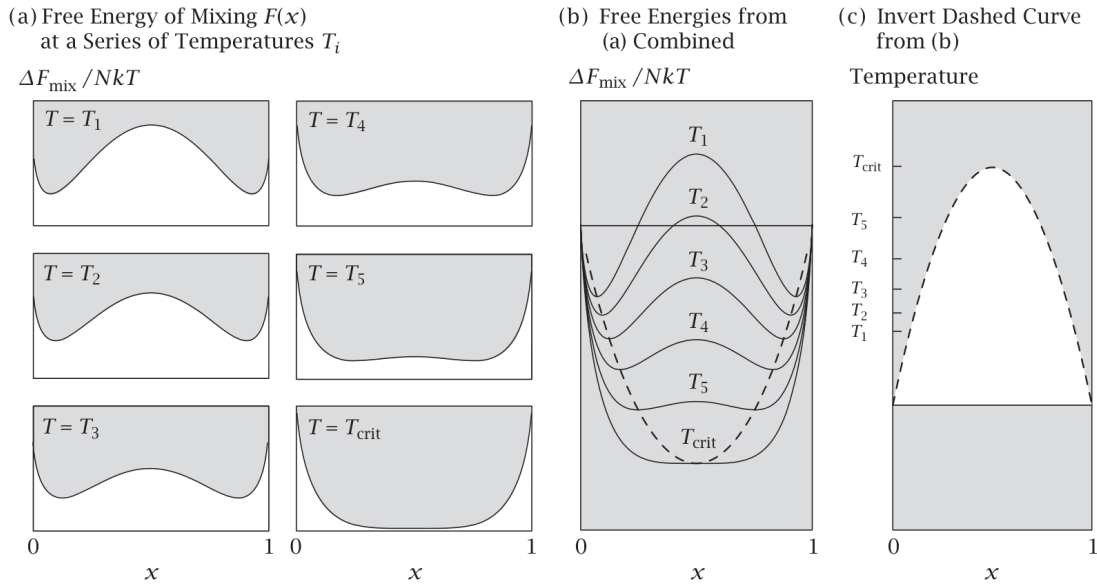


Figure 7.6. Use the lattice model to compute the mixing phase diagram. (a) Compute $\Delta F_{\text{mix}}(x)/NkT$ for a series of temperatures given c_1 . (b) Put those curves onto a single figure. The dashed curve represents the two minima in $\Delta F_{\text{min}}(x)$ for each temperature. Inside the dashed curve is the two-phase region. (c) Replot the dashed curve of (b) so that the temperatures of the free energy minima are on the vertical axis.

If A and B ‘dislike’ each other enough at a given temperature ($\chi_{AB} > 2$), then the free energy has two minima, and the system will form separate phases at appropriate concentrations. Conversely, if $\chi_{AB} < 2$, then A and B are miscible in all proportions. The critical point is at $\chi_{AB} = 2$.

Now, find the one or two minima of each curve, where $\partial \Delta F_{\text{mix}} / \partial x = 0$. The dashed curve above connects all the minima, defining the coexistence curve predicted by the model. Lastly, put the coexistence curve on a new figure, where the vertical axis is now the temperature. The theory (of a simple model) predicts a phase diagram that is symmetrical around $x = 0.5$.

Example. The phase diagram for the lattice model of solutions.

We want locate the minima in the free energy function. Substitute the lattice model free energy.

$$\left(\frac{\partial \Delta F}{\partial x} \right)_{x=x' \text{ or } x''} = NkT \left[\ln \left(\frac{x}{1-x} \right) + \chi_{AB} (1-2x) \right]_{x=x' \text{ or } x''} = 0.$$

You can compute x' and x'' for a series of different values of χ_{AB} by rearranging and solving the equation

$$\ln \left(\frac{x'}{1-x'} \right) = -\chi_{AB}(T) (1-2x'). \quad (7.6)$$

This is a *transcendental* equation. You can solve for $x'(T)$ by iterative methods. Because the lattice model free energy is symmetrical around $x=0.5$, you have $x''=1-x'$. If the solute is only sparingly soluble, then $x' \ll 1$. In that case, (7.6) simplifies and predicts that the solubility is

$$\ln x' \approx \chi_{AB} \quad \text{or} \quad x' = e^{-\chi_{AB}}. \quad (7.7)$$

If χ_{AB} is large (A has very little affinity for B), then the solubility is small, according to (7.7).

7.5 The Spinodal Curve Describes the Limit of Metastability

So far, we have discussed the coexistence curve, also called the binodal curve. It describes the global stability of a system against phase separation. Here we describe another property, called *metastability* or local stability or the *spinodal* curve. Previously, we found that a solution having overall composition x_0 that is inside the two-phase region should form separate phases having compositions x' and x'' in order to lower its total free energy. But, sometimes a system that is inside its two-phase region, if handled very gently and not shaken or stirred, does not actually form separate phases.

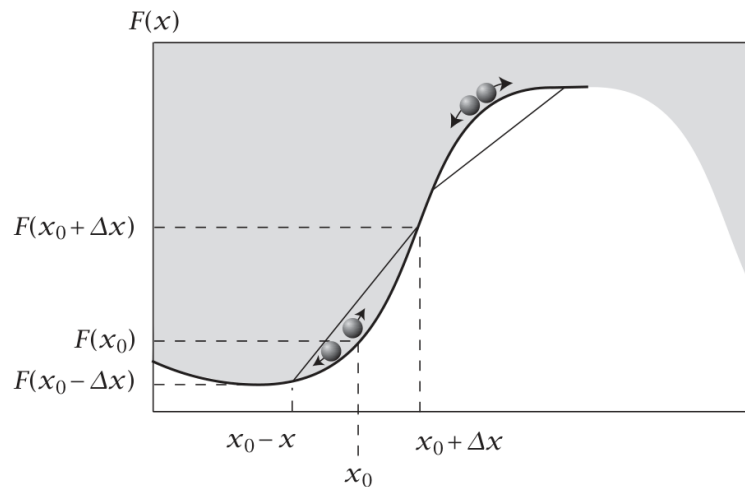


Figure 7.7. Metastability. Where the free energy is concave upwards (balls on the bottom left), the system at x_0 does not undergo local phase separation into phases having compositions $x_0 + \Delta x$ and $x_0 - \Delta x$ because a local phase separation would increase the total free energy (indicated by the straight sloping line on the left). But, where the free energy is concave downwards, the system will undergo a local phase separation to lower its net free energy.

Such solutions are called *metastable solutions*.

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For example, a solution can be *supersaturated*. It can have slightly more oil dissolved in water than would be predicted by the coexistence curve: x can be larger than x' for a given temperature. Or, a solution can be *supercooled*: it can remain mixed even at a lower temperature T for a given x than would be predicted by its coexistence curve. Gentle handling can postpone phase separation.

A system has local stability where the energy landscape is concave upwards ($\partial^2 F / \partial x^2 > 0$) and local instability where the landscape is concave downwards ($\partial^2 F / \partial x^2 < 0$). To see this, compare the free energy $2F(x_0)$ of the mixed system with the free energy $F(x_0 + \Delta x) + F(x_0 - \Delta x)$ of a system that locally separates into slightly different compositions ($x_0 + \Delta x$) and ($x_0 - \Delta x$). This system is locally stable as a single phase when

$$F(x_0 + \Delta x) + F(x_0 - \Delta x) > 2F(x_0) . \quad (7.8)$$

Rearrange to get the condition for stability against small fluctuations:

$$F(x_0 + \Delta x) - F(x_0) - [F(x_0) - F(x_0 - \Delta x)] > 0. \quad (7.9)$$

This equation is a difference of a difference: $\Delta\Delta F > 0$.

As $\Delta x \rightarrow 0$, this double difference can be expressed as a second derivative,

$$\left(\frac{\partial^2 F}{\partial x^2} \right)_{x=x_0} > 0. \quad (7.10)$$

When this second derivative is positive, the mixed system is locally stable and does not form separate phases. When the second derivative is negative, the system will locally divide into separate phases, and then will also proceed further to global instability and full phase separation.

The following figures shows the metastable region. The spinodal curve is inside the binodal curve. The binodal curve is where $(\partial F / \partial x) = 0$. The spinodal curve is where $(\partial^2 F / \partial x^2) = 0$. In the region M between the curves, the system is *metastable*. In the M region, if you don't perturb the system (like shake it), it won't form separate phases. However, inside the spinodal curve, in the two-phase region labeled $2P$, the system will always separate into two phases.

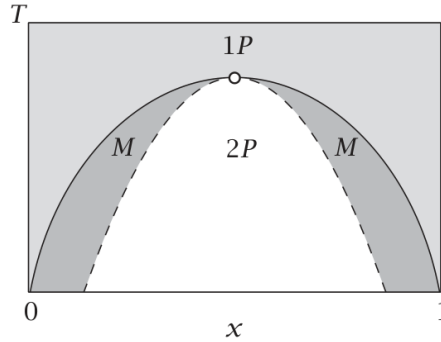


Figure 7.8. In region $1P$, the system is always in one phase. M is the metastable region: the system is in one phase if perturbations are small. In region $2P$ the system is always in two phases. Continuous line is the binodal curve and the dashed line is the spinodal curve. They meet at the critical point.

7.6 The Critical Point is Where Coexisting Phases Merge

The critical point is where the binodal and spinodal curves intersect. Above the critical temperature T_c , the two components are miscible in all proportions.

At the critical point the two compositions x' and x'' approach each other. The spinodal points also merge. So, the critical point is also where the third derivative is zero:

$$\lim_{x' \rightarrow x''} \left[\left(\frac{\partial^2 F}{\partial x^2} \right)_{x=x'} - \left(\frac{\partial^2 F}{\partial x^2} \right)_{x=x''} \right] = 0 \quad \Rightarrow \quad \left(\frac{\partial^3 F}{\partial x^3} \right) = 0. \quad (7.11)$$

Example. Lattice model critical point. To find the critical point (x_c, χ_c, T_c) for the lattice mixture model, determine the point where both the second and third derivatives of the free energy equal zero. Recall eq. (6.16):

$$\frac{\Delta F_{\text{solution}}}{NkT} = x \ln x + (1-x) \ln (1-x) + \chi_{AB} x (1-x).$$

$$\left(\frac{\partial^2 F}{\partial x^2} \right) = NkT \left(\frac{1}{x} + \frac{1}{1-x} - 2\chi_{AB} \right). \quad (7.12)$$

$$\left(\frac{\partial^3 F}{\partial x^3} \right)_{x=x_c} = NkT \left[\frac{1}{(1-x_c)^2} - \frac{1}{x_c^2} \right] = 0 \quad \Rightarrow \quad x_c = \frac{1}{2}. \quad (7.13)$$

Now use $x_c = 0.5$ and eq. (7.12) to get

$$\left(\frac{\partial^2 F}{\partial x^2} \right)_{x=x_c} = \frac{1}{0.5} + \frac{1}{1-0.5} - 2\chi_c = 4 - 2\chi_c \quad \Rightarrow \quad \chi_c = 2. \quad (7.14)$$

From (7.13) and (7.14) the critical point x_c and T_c can be computed.

Because $\chi_c = c_1 / T_c = 2$, you can compute the intermolecular interaction quantity $c_1 = 2 T_c$. If $c_1 = 0$ then the system is fully miscible at all temperatures, and there is no two-phase region at all.

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7.7 Boiling a Liquid Mixture Involves Two Types of Phase Transition

Consider a combined phase equilibria: a system that undergoes both liquid-liquid immiscibility and boiling. Consider a liquid having two components A and B. The system may have a miscibility phase transition, but it will also boil at a sufficiently high temperature. Typically, each component boils at a different temperature. Boiling a mixture, e.g. alcohol and water, is the basis for *fractional distillation*. Below are three typical temperature-composition phase diagrams for boiling a mixture.

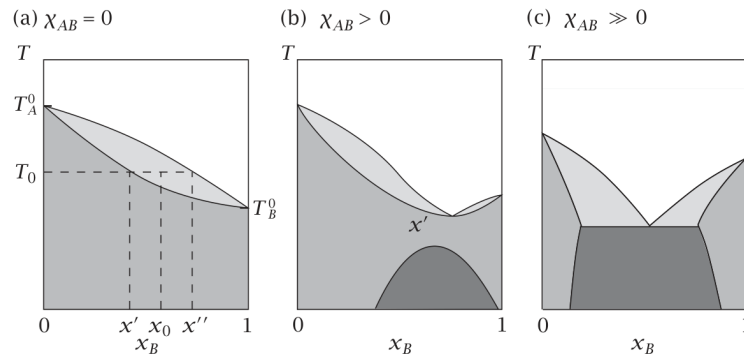


Figure 7.9. Phase diagrams for boiling liquid mixtures. *White*: both components in vapor phase; *Light gray*: vapor phase enriched component is in equilibrium with a liquid phase enriched component; *Dark gray*: two liquid phases in equilibrium; *Gray*: A single liquid-phase solution. T_A^0 is the pure A boiling temperature (and similarly T_B^0 for pure B).

Left: an ideal mixture ($\chi_{AB}=0$), having no liquid-liquid two-phase region. The progression from the left figure to the right represents decreased affinity of A for B (increasing χ_{AB}). The two-phase region grows and the one-phase liquid region shrinks.

At low temperatures, below the canoe-shaped region, both components are liquids. Their liquids are miscible in all proportions. At high temperatures, above the canoe, both components are gases. Inside the canoe is a two-phase region: a liquid and a gas. Pure B boils at T_B^0 . If B is more volatile than A , then $T_B^0 < T_A^0$.

Mix alcohol in water at concentration x_0 . Heat the mixture to $T_B^0 < T^0 < T_A^0$. Follow the tie-line to the left to see that the liquid that remains behind is purified water (alcohol concentration $x' < x_0$). Follow the tie-line to the right to see that the vapor phase is purified alcohol (concentration $x'' > x_0$). This is the basis for distillation of liquids.

8 Cooperativity

Cooperativity addresses macroscopic phase transitions or single-molecule conformational changes, and is predicted from the shape of a *free energy landscape*.

8.1 Transitions and Critical Points are Universal

In the last chapter we noted that the shapes of coexistence curves for liquid-liquid immiscibility are about the same as for boiling. Both display critical points, and both are described approximately by the same simple model.

8.1.1 Some history

In 1944, L Onsager derived an exact solution to the two-dimensional version of a better model of the coexistence curve, called the *Ising model*. The Ising model treats nearest-neighbor interactions, and captures the shape of the coexistence curves more accurately.

During the 1960s and 1970s, a highly successful theory of critical phenomena emerged, called renormalization group theory. Renormalization group theory shows that the flaws in the simpler models do not lie in their structural simplifications—the use of lattices or beads to represent atoms and molecules, or the use of simplified energies. Rather, the flaws in simpler models are due to their mean-field approximations and their neglect of large fluctuations near critical points. Renormalization group theory also shows that behavior near critical points can be described by *universality classes*: many different types of transition share the same behaviors, depending mainly on an order parameter and the dimensionality of the system.

To mathematically express the shape of a coexistence curve near the critical point, you need to first define the **order parameter** of the system. An order parameter is a quantity m on which the free energy depends. $m = 0$ above the critical temperature, indicating that the system is disordered, or randomly mixed. $m > 0$ below the critical temperature, indicating that the system is ordered, or phase-separated in some way.

For liquid-liquid immiscibility, a good choice of order parameter is the difference in phase compositions $m = x'' - x'$. A conveniently normalized order parameter is $m(T) = 2x'' - 1$, since $m \rightarrow 1$ at low temperatures and $m = 0$ at the critical temperature.

For boiling, a good order parameter is the difference in density between the liquid and gas phases. A function with a similar shape near the critical point is the enthalpy vaporization as a function of temperature.

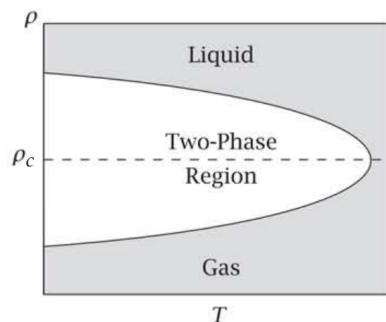


Figure 26.2 For boiling, a useful order parameter is the difference between liquid and gas densities $\Delta\rho = \rho_{\text{liquid}} - \rho_{\text{gas}}$. ρ_c is the density of the fluid at the critical point.

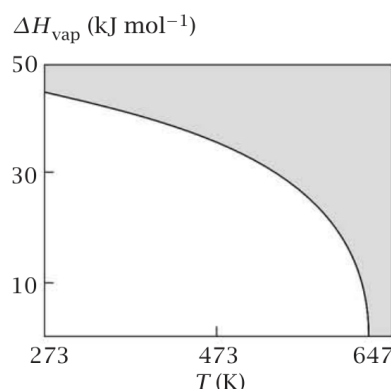


Figure 26.3 The enthalpy of vaporization of water as a function of temperature has a functional form similar to the order parameter, becoming zero at the critical point. Source: JN Murrell and AD Jenkins, *Properties of Liquids and Solutions*, Wiley, New York, 1982.

The disordering with temperature is called an order-disorder transition, and the process is called *symmetry-breaking*. To predict these transitions, we wish to compute the mathematical form of $m(T)$ near the critical temperature, where $m(T) \rightarrow 0$. We will find the result from the *Landau model*.

8.2 The Landau Model is a General Description of Phase Transitions and Critical Exponents

The Landau model was named after the Russian physicist LD Landau (1908-1968). It is a generic treatment of phase transitions and critical points. It is based on the idea that coexistence curves have two minima at low temperatures, merging into a single minimum at higher temperatures. This behavior can be captured mathematically by expressing the free energy $F(m)$ as a polynomial function of an order parameter m

$$F(m) = F(0) + a_1 m + a_2 m^2 + \dots \quad (8.1)$$

The a_i 's are coefficients that depend on the physical problem at hand. For simple problems we want $F(m)$ to be symmetrical around $m=0$, so we can eliminate the terms involving odd powers. To allow for the possibilities of either one or two minima, we must keep terms at least up to fourth order. A minimal model is therefore

$$F(m) = F(0) + a_2 m^2 + a_4 m^4. \quad (8.2)$$

If we apply the constraint $a_4 > 0$, then the sign of a_2 predicts different states of the system. $F(m)$ has a single minimum if $a_2 > 0$, a flat broad minimum if $a_2 = 0$, and two minima if $a_2 < 0$.

A flat broad minimum implies large fluctuations in m .

Lowering a_2 affects the $F(m)$ the same way that reducing the temperature affects phase equilibria free energy functions:

- At $T > T_c$ the free energy has one minimum.

- At $T = T_c$ the free energy minimum is broad.
- At $T < T_c$ the free energy has two minima.

To capture the correspondence between a_2 and T , let t represent the fractional deviation of the temperature T away from the critical temperature T_c (also called the *reduced temperature*):

$$t \equiv \frac{T - T_c}{T_c}. \quad (8.3)$$

If you take a_2 to be proportional to t , $a_2 = at$, and choose a to be positive, then the function $F(m)$ behaves as planned:

$$F(m) = F(0) + atm^2 + a_4m^4. \quad (8.4)$$

To determine how the equilibrium value of the order parameter m^* depends on T near T_c , find the value $m = m^*$ that minimizes $F(m)$.

$$\left(\frac{dF}{dm} \right)_{m=m^*} = 2at(m^*) + 4a_4(m^*)^3 = 0, \quad (8.5)$$

which simplifies into

$$(m^*)^2 = -\frac{at}{2a_4}. \quad (8.6)$$

We got a solution of the form

$$m^* = \text{constant} \times t^\beta, \quad (8.7)$$

where β is called the *critical exponent*. In the Landau model $\beta = 1/2$.

In general, independently of the model, the critical exponent λ for a function $g(x)$ is

$$\lambda = \lim_{x \rightarrow 0} \frac{\ln |g(x)|}{\ln |x|}. \quad (8.8)$$

Different physical properties of a system, which are different functions of the free energy, have different critical exponents. Because physical properties are often related through thermodynamic relationships, there are algebraic relationships among critical exponents.

The importance of critical exponents is their **universality**. While the critical temperature depends on the details of the interatomic interactions, the critical exponent does not. For example, $\beta = 1/2$ arises in the Landau model irrespective of whether the transition involves boiling, mixing, metal alloy order-disorder, or magnetization, and irrespective of microscopic parameters such as χ_{AB} . It can be shown that van der Waals and lattice mean-field models also give a critical exponent of $\beta = 1/2$.

Experimental evidence shows that $\beta \approx 1/3$, in disagreement with the Landau model. The reason for the discrepancy is that near the critical point, higher-order terms beyond m^4 are needed in $F(m)$. The true free energy surfaces are flatter near critical points, so the fluctuations are broader than would be predicted by mean-field or Landau models.

A model in which $F(m)$ can be expressed exactly, without mean-field approximations or low-order expansions in m , is the *Ising model*, also called the *nearest-neighbor model*. It handles critical behavior more accurately. It was originally derived to treat the magnetization of metals.

8.3 The Ising Model Describes Magnetization

You can magnetize certain materials, such as iron, by putting them into a magnetic field. Below a certain critical temperature, such materials have a net magnetic moment. If you heat them above that temperature, they lose magnetization. Why is the basis for this behavior?

Atomic spins act like small magnets: they are magnetic dipoles with north and south poles that become aligned in applied magnetic fields. At high temperatures, the spins are randomly oriented, but below a critical temperature T_c , the spins align with each other.

Magnetic alignment is cooperative because of the nearest-neighbor interactions. At low temperatures, the spins in ferromagnets line up to satisfy the favorable nearest-neighbor interactions; but at high temperatures, the arrow directions (see fig. below) randomize to maximize the entropy.

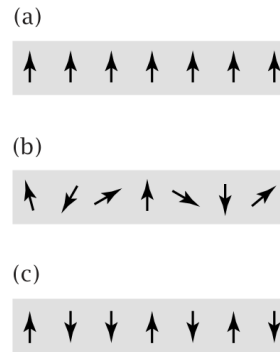


Figure 8.1. Magnetic spins in a one-dimensional system: (a) fully aligned, for example at low temperatures; (b) disordered, at high temperatures; (c) a simple 'binary' model of the disordered states in which spins are either up or down.

In a ferromagnet, such as iron, certain iron oxides, or cerium antimonide, each spin prefers to orient in the same direction as its neighbors. In antiferromagnets, like MnO, each spin prefers to orient in the direction opposite to its neighbors.

In the Ising model, each atomic magnet occupies one lattice site with a spin that is either up or down. The model is named for the physicist E Ising (1925).

On a one-dimensional lattice, the partition function is simple to compute. The Boltzmann weights are $q(\uparrow\uparrow) = q(\downarrow\downarrow) = e^J$ and $q(\uparrow\downarrow) = q(\downarrow\uparrow) = e^{-J}$, where $J = J_0/kT$ is a dimensionless energy. Ferromagnets are modeled by $J > 0$ and antiferromagnets by $J < 0$.

For a single site, the partition function is $Q_1 = 2$, because there are two states: \uparrow or \downarrow . To get the two-site partition function, multiply Q_1 by $(e^J + e^{-J})$, because the second arrow can point in either the same direction as the first or in the opposite direction. In terms of the hyperbolic cosine function, $\cosh x = (e^x + e^{-x})/2$, you have

$$Q_2 = Q_1 (e^J + e^{-J}) = Q_1 (2 \cosh J). \quad (8.9)$$

Every site that is added to the one-dimensional array of spins multiplies the partition function by a factor of $(e^J + e^{-J})$, so the partition function for a linear lattice of N magnetic spins is

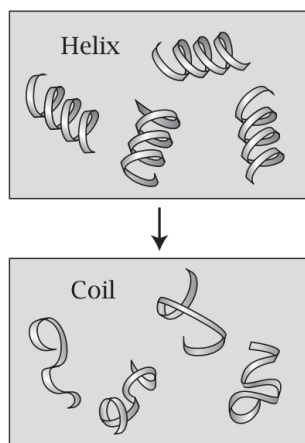
$$Q_N = Q_1 (2 \cosh J)^{N-1} = 2^N \cosh^{N-1} J. \quad (8.10)$$

The thermodynamic properties of the one-dimensional Ising model are computed from the partition function in the standard way. (See Table 4.1.)

Real magnets are three-dimensional. However, computing the properties of the Ising model in two or three dimensions is much more challenging. The two dimensional Ising model has an analytical solution that was found by the Norwegian–American physicist L Onsager (1968). The three dimensional Ising model must be solved by computer simulations.

8.4 Polymers Undergo Helix-Coil Transitions

Some polymers undergo a helix-coil transition. In the single-helical conformation, the polymer molecule is ordered. The coil state is a collection (ensemble) of disordered conformations. This ensemble often appears in aqueous solutions at high temperatures.



When the temperature is lowered, each molecule undergoes a transition to a helix. These transitions are called *cooperative*, which is sometimes taken to mean the following.

1. Some property (the amount of helices, for example) changes in a sigmoidal way as a function of an external variable (such as temperature or solvent).
2. The sigmoidal curve steepens with increasing size of the system (the chain length, in this case).

Interestingly, some of the most important protein helix-coil cooperativity data were taken in a solvent that inverts the transition: increasing the temperature increases the helix content.

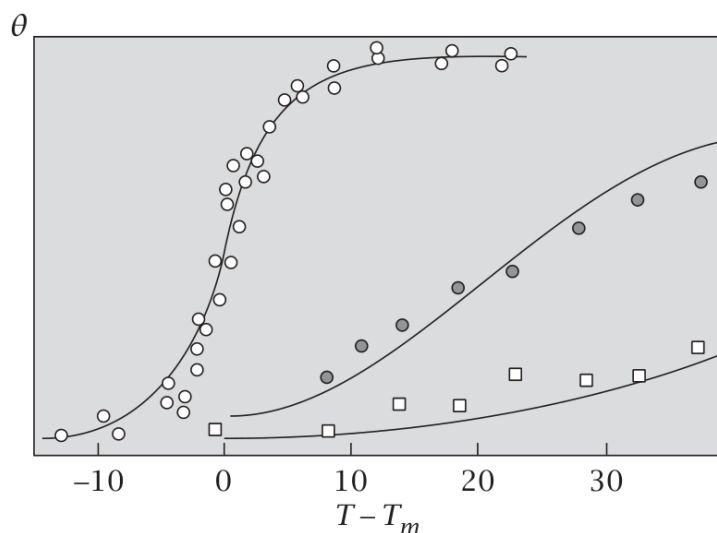


Figure 8.2. The helix-coil transition of poly- γ -benzyl-L glutamate chains. White squares—26-mers, gray circles—46-mers, white circles—1500-mers. Fractional helicity $f_H = \theta$ versus temperature T , relative to the midpoint T_m for the long chains (from optical-rotation data).

The simplest models of this cooperative behavior suppose that each monomeric unit along the chain has one of two possible states: H (helix) or C (coil). The chain conformations are represented as one-dimensional sequences of H and C units.

Our aim is to compute the partition function, based on the combinatorics for counting the numbers of arrangements of H and C units in the chain. We will consider three different models for the partition function. To show the nature of cooperativity, it is useful to start with a model that has no cooperativity.

8.4.1 Noncooperative Model: Neighboring Units are Independent of Each Other

Assume the chain has N monomer units, and that the state of each monomer (H or C) $j=1,2,\dots,N$ in the chain is independent of the state of every other monomer. Let q_C (q_H) be the partition function for each C (H) unit.

Because we are interested only in relative populations among different states, we are free to choose $q_C = 1$, which is equivalent to defining the free energy of a coil unit as zero. Let $q_H = \exp(-\beta \Delta \epsilon)$, where $\Delta \epsilon < 0$ represents the energy of forming a helical unit relative to a coil unit, and $\beta = 1/kT$. The ratio

$$s = \frac{q_H}{q_C} = e^{-\beta \Delta \epsilon} \quad (8.11)$$

defines the relative probabilities of H and C states for a unit of the chain and represents its helix-coil equilibrium constant. Note that $s(T)$ increases as T decreases.

The probability $p(n_H)$ that an N -mer chain has n_H of its units in the helical state (and $n_C = N - n_H$ in the coil state) is given by the statistics of independent coin flips:

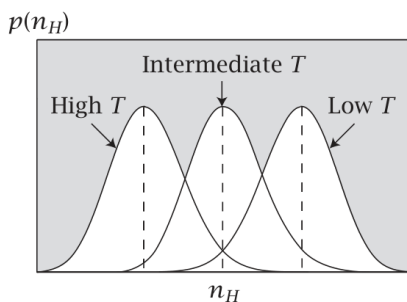
$$p(n_H) = \frac{N!}{n_H! n_C!} q_H^{n_H} q_C^{n_C} = \frac{N!}{n_H! (N - n_H)!} s^{n_H}. \quad (8.12)$$

The partition function Q is the sum of all the possible sequences of H and C :

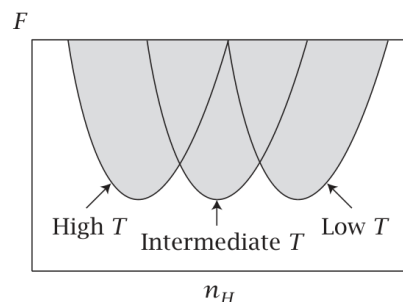
$$Q = \sum_{n_H=0}^N p(n_H) = (q_C + q_H)^N = q_C^N (1 + s)^N = (1 + s)^N. \quad (8.13)$$

This model predicts a gradual transition between coil and helical states, not a sharp transition.

(a) Distribution of Helical Units



(b) Free Energy



To convert the probability distributions to the energy landscapes, you can compute the free energy function $F(n_H) = -kT \ln p(n_H)$. The population distribution shifts smoothly as the temperature is changed.

Now compute $f_H = \langle n_H \rangle / N$, the equilibrium fraction of the N monomers that are H 's, as a function of the chain length N and the temperature T . To calculate $f_H(T)$, you could compute the free energy for each T , find the value of $n = \langle n_H \rangle$ that causes F to be at a minimum, and then plot $\langle n_H \rangle$, as a function of T . An easier way is to take the derivative of eq. (8.13) [not shown here].

We have

$$\left(\frac{dQ}{ds} \right) = N (1+s)^{N-1},$$

which leads to

$$\langle n_H \rangle = \frac{s}{Q} \left(\frac{dQ}{ds} \right) = \frac{Ns (1+s)^{N-1}}{(1+s)^N} = \frac{Ns}{1+s}.$$

So the average helicity is

$$f_H(T) = \frac{\langle n_H \rangle}{N} = \frac{s(T)}{1+s(T)}. \quad (8.14)$$

The noncooperative model predicts that the helicity changes gradually, not sharply, with temperature. Cooperativity requires some interdependence of the interactions among the monomers. Eq. (8.14) fails to predict a sufficiently sharp dependence of f_H on chain length that is indicated by experiments (which is clear from the figure above).

Gradual noncooperative changes are characterized by free energy functions in which a single minimum $m^*(T)$ shifts with T or with some other external variable. Let's inspect the opposite of this model, the maximum cooperativity model.

8.4.2 The Two-State Model: Maximum Cooperativity

Suppose we model the helix-coil system as having only two possible states: $CCC \dots C$ or $HHH \dots H$. Maximum cooperativity means that if one monomer is H , all are H . The partition function for the system is

$$Q = q_C^N + q_H^N = q_C^N (1 + s^N) = 1 + s^N. \quad (8.15)$$

In this case, the populations of the only two states of the system are

$$p_{\text{all } C} = \frac{1}{1+s^N}, \quad p_{\text{all } H} = \frac{s^N}{1+s^N}.$$

In this model, at low temperatures all molecules are fully helical, and at high temperatures all molecules are in coil conformation. At the midpoint of the transition, the average helicity is 1/2, not because the individual molecules are half helix and half coil, but because half of the molecules are all-helix, and half of the molecules are all-coil. There is no intermediate state.

Get the average helicity for the two-state model by taking the derivative of Q :

$$\langle n \rangle = \frac{s}{Q} \left(\frac{dQ}{ds} \right) = \frac{s N s^{N-1}}{1+s^N} = N \frac{s^N}{1+s^N} \quad \Rightarrow \quad f_H = \frac{s^N}{1+s^N}.$$

This model doesn't predict the data well either.

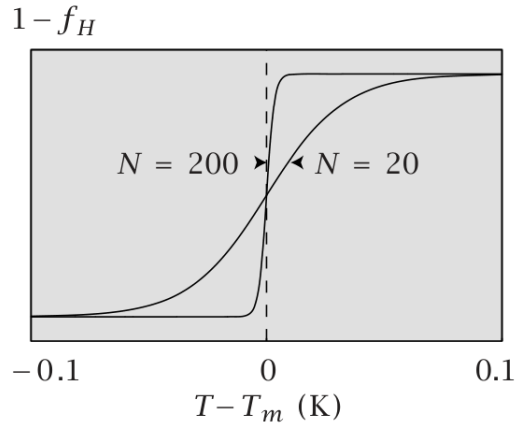


Figure 8.3. The two-state model for $N = 20$ and $N = 200$ units. The model predicts more cooperativity than is observed in experiments.

In summary, one-state and two-state transformations are distinguished by the shapes of their free energy functions $F(m)$, where m (the order parameter) here stands for the fractional helicity. At the midpoint of a twostate transition, the free energy function has two minima.

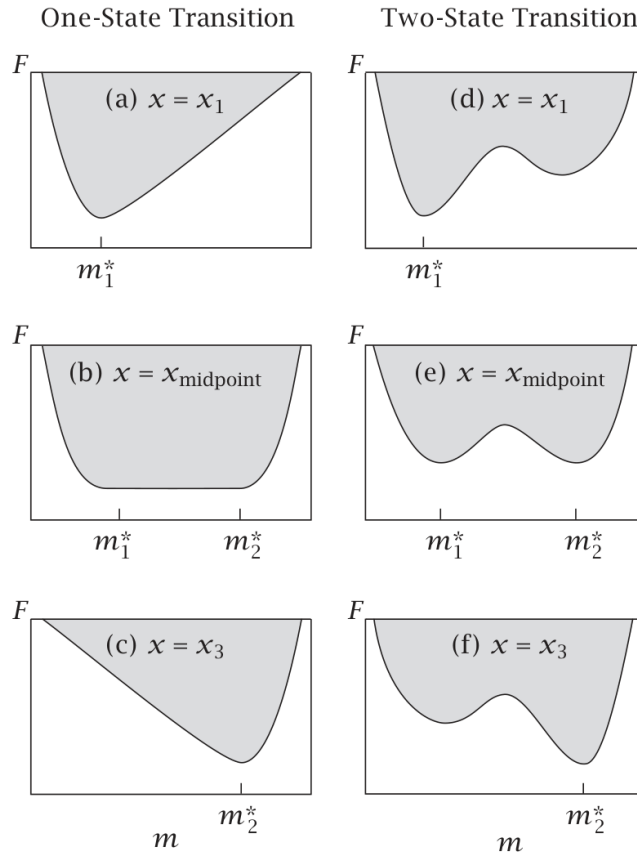


Figure 8.4. Transitions are two-state if there are two minima in the free energy and one-state if there is one minimum. In both types of system, the system changes from state m_1^* when $x = x_1$ to m_2^* when $x = x_2$. At the midpoint $x = x_{\text{midpoint}}$ of a two-state transition, there are two stable states: m_1^* and m_2^* . At the midpoint of a one-state transition, there is a broad distribution of stable states from m_1^* to m_2^* .

Under those conditions, half the molecules are in state m_1^* and half are in state m_2^* . There is little or no population of 'intermediate states' having intermediate values of the order parameter. In contrast, at the midpoint of a one-state transition, the free energy function has a single minimum, and the molecules in those systems have a distribution of order parameter values, $m_1^* \leq m \leq m_2^*$.

How can experiments determine whether a transition is one-state or two-state? Both models can give sigmoidal curves of $f_H(T)$, so a sigmoidal shape alone is not sufficient to establish whether the free energy has one or two minima. The strongest proof of a two-state transition would be direct evidence of two populations. Three other methods are commonly accepted evidence for two-state transitions: (1) when the enthalpy measured by calorimetry equals the enthalpy based on a two-state model, (2) when different experimental methods give superimposable sigmoidal curves, and when there is an isodichroic or isosbestic point in the spectra.

Now we explore a third model, in which the monomers are neither fully independent of each other nor totally cooperative. This Ising-like nearest-neighbor model gives deeper insights into cooperativity.

8.4.3 The Zimm–Bragg Model of the Helix–Coil Transition: Nearest-Neighbor Cooperativity

In this model, developed by BH Zimm and JK Bragg, the probability that monomer j is in state C or H depends on whether its neighboring monomer $j - 1$ is in state C or H . The statistical weight q for monomer j is *conditional* on the state of its neighboring monomer.

There are four different monomer conditional statistical weights: $q(C|C)$, $q(C|H)$, $q(H|C)$, and $q(H|H)$. Statistical weights are quantities that describe relative populations or probabilities. For example, $q(C|H)$ is the relative amount of monomer j that is in state C if monomer $j - 1$ is in state H . You can multiply together appropriate monomer statistical weights to get the sequence statistical weight for a chain of H and C monomers of length N . The partition function is the sum over the statistical weights of all the possible sequences.

Every coil unit C is assigned a statistical weight of 1, by convention, whether the preceding monomer is an H or C . Any helical unit H is assigned a statistical weight s . You can think of s as an equilibrium constant for converting a C into an H :

$$s \equiv \frac{[H]}{[C]}.$$

Assign a statistical weight σs if an H follows a C or if the H is the first monomer in the chain. Think of σ as the *nucleation parameter* for initiating a helix. For most amino acids, s is slightly greater than 1 and $\sigma \approx 10^{-3}$. **Propagation is easy but nucleation is difficult.**