FREELY-JOINTED CHAIN

A strand of polymer is a chain of repeating units, the monomers. The monomers are joined by covalent bonds. Two bonded monomers may rotate relative to each other. The rotation is not entirely free in that the energy is a function of the angles between the two molecules.

But we will develop a model, called the freely-jointed chain model, assumes that the monomers can rotate freely relative to one another. In a simple-minded interpretation, the model represents a monomer by a link, a bond between the two monomers a joint, and a strand of polymer by a chain of links.

As the monomers rotate relative to one another, and the polymer rapidly changes from one configuration to another. When the two ends of the polymer are pulled by a force, the distance between the two ends changes.

By excluding all effects of internal energy, this model makes the polymer a purely entropic spring.

Boltzmann Distribution

A system in contact with a reservoir of energy. We list the key results of the Boltzmann distribution. A small system is in thermal contact with a large system. To keep track of names, we call the small system just the system, and call the large system the reservoir of energy, or just the *reservoir* for brevity. The system and the reservoir exchange energy by heat. All other modes of interactions between the system and the reservoir are blocked: no exchange of energy by work, and no exchange of matter.

Reservoir of energy, kT
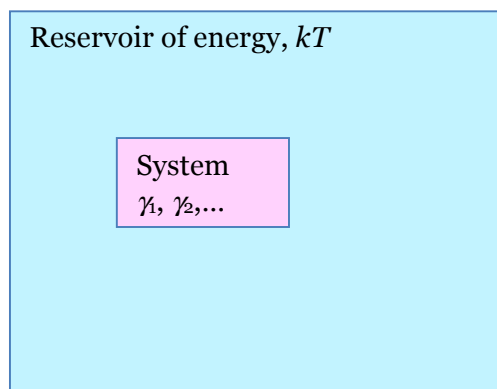
System
$\gamma_1, \gamma_2, \ldots$

The reservoir is much larger than the system. Consequently, when the reservoir exchanges energy with the system, the temperature of the reservoir is unchanged, and is denoted by kT. The situation is analogous to a reservoir of

water. When we use a cup to take water out of the reservoir, the level of the reservoir changes negligibly. In this analogy, water is analogous to energy, and the level of the reservoir of water is analogous to the temperature of the reservoir of energy.

Probability for the system to be in a microstate. The system flips rapidly and ceaselessly among a set of microstates, $\gamma_1, \gamma_2, ...$ Let the energy of these microstates by $U_1, U_2, ...$ Because the system is not isolated, these microstates may have different amounts of energy, and the system may flip to these microstates with unequal probability. After the system and the reservoir are in thermal contact for a long time, the system and the reservoir in combination reach thermal equilibrium. In equilibrium, the probability for the system to be in a microstate γ_s is proportional to the Boltzmann factor

$$\exp\left(-\frac{U_s}{kT}\right).$$

The system has to be in one of its microstates, so that the sum of the probabilities of microstates is unity. Thus, the probability for the system in any microstate s is

$$P_s = \frac{\exp\left(-\frac{U_s}{kT}\right)}{Z},$$

where

$$Z = \sum \exp\left(-\frac{U_i}{kT}\right)$$

The sum is taken over all the microstates of the system. The distribution of probability is called the Boltzmann distribution, and the sum Z is called the partition function.

Mean value of a property. Let Y be a property of the system. When the system is in microstates $\gamma_1, \gamma_2, ...$, this property takes values $Y_1, Y_2, ...$ In the theory of probability, a property of the system is called a random variable: it maps a microstate of the system to a scalar. The mean value of the property is defined as

$$\langle Y \rangle = \sum_i P_i Y_i .$$

The sum is over all the microstates of the system.

For example, the energy of the system is a property. When the system is

in the microstates $\gamma_1, \gamma_2, \ldots$, the energy of the system takes values $U_1, U_2, \ldots$ The mean value of the energy of the system is

$$\langle U \rangle = \frac{\sum U_i \exp\left(-\dfrac{U_i}{kT}\right)}{\sum \exp\left(-\dfrac{U_i}{kT}\right)}.$$

Each sum is taken over all the microstates of the system.

Exercise. Consider a harmonic oscillator of frequency ω. According to quantum mechanics, the oscillator has a set of microstates, labeled as 1, 2,... In microstate *n*, the oscillator has energy

$$U_n = \left(\frac{1}{2} + n\right)\hbar\omega,$$

where the Planck constant is $\hbar \approx 10^{-34}\,\mathrm{J \cdot s}$. Calculate the mean value of the energy of the oscillator when it is in thermal contact with a reservoir of temperature *kT*.

Helmholtz free energy. The Helmholtz free energy of the system is given by

$$F = -kT \log Z.$$

Freely-Jointed Chain

A rigid rod subject to a fixed force. A rigid rod, length *b,* is subject to a force of constant magnitude *f* and fixed direction. We picture the force as a hanging weight. The rod can rotate freely. As the rod rotates, the potential energy of the weight changes. We regard the rod and the weight together as a system.   This system is in thermal contact with a reservoir held at a fixed temperature *kT*.

A microstate of the system is specified by two angles: the angle between the direction of the rod and that of the force, θ, as well as the angle around the direction of the force, ϕ. The two angles vary in the intervals $0 \le \theta \le \pi$ and $0 \le \varphi \le 2\pi$.

The energy of the system is the potential energy of the weight. We set the potential energy of the weight to be zero when the rod is horizontal, $\theta = \pi/2$. When the rod rotates from the horizontal direction, the potential energy of the weight is

$$U = -fb\cos\theta.$$

The potential energy is minimal when $\theta = 0$, increases with the angle θ, and is maximal when $\theta = \pi$. The minimal-energy microstate is a single microstate. By contrast, microstates with $\theta \neq 0$ are numerous. Consequently, the main value of the angle θ will not be zero.

The probability of the rod in a microstate is proportional to the Boltzmann factor:

$$\exp\left(\frac{fb\cos\theta}{kT}\right).$$
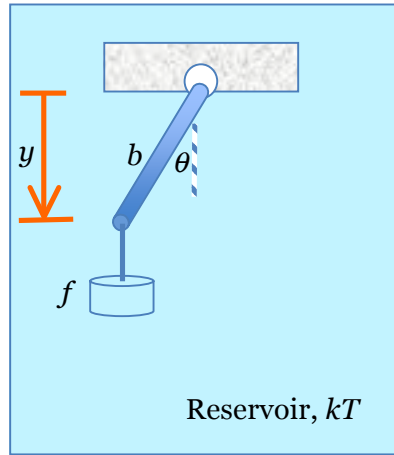
Reservoir, kT

Competition between the force and temperature. The system is in thermal contact with a reservoir of energy held at a fixed temperature kT. The dimensionless parameter fb/kT measures the competition between the force and the temperature. When $fb/kT \ll 1$, the temperature prevails, and the rod is nearly in any orientation. When $fb/kT \gg 1$, the force prevails, and the rod is nearly aligned in the direction of the force.

The force and the temperature are competitive when $fb/kT \sim 1$, or when

$$f \sim \frac{kT}{b}.$$

The magnitude of this force is

$$f \sim \frac{\left(1.38 \times 10^{-23}\,\text{J/K}\right)\left(300\text{K}\right)}{10^{-9}\,\text{m}} = 4.14 \times 10^{-12}\,\text{N}.$$

In this estimate, we have assumed that the reservoir is at room temperature, $T =$

300 K, and that the length of the rod is b = 1 nm. This pico-Newton force is used in experiments with individual polymer chains.

In what follows we write

$$\beta = \frac{fb}{kT} .$$

This dimensionless number measures the competition between the force and the temperature.

The mean value of the displacement. The displacement associated with the force equals the length of the rod projected onto the axis of the force:

$$y = b\cos\theta .$$

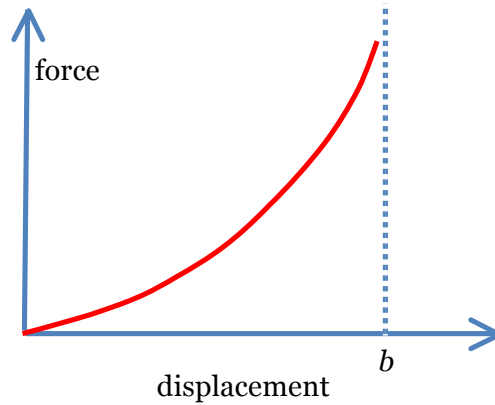The orientation θ of the rod fluctuates, and so does y.

The number of microstates is proportional to the area of the element on the unit sphere, $2\pi\sin\theta d\theta$. The mean value of y is given by

$$\langle y \rangle = \frac{\int\limits_{0}^{\pi}(b\cos\theta)2\pi\exp(\beta\cos\theta)\sin\theta d\theta}{\int\limits_{0}^{\pi}2\pi\exp(\beta\cos\theta)\sin\theta d\theta} .$$

Integrating, we obtain that

$$\langle y \rangle = b\left(\frac{1}{\tanh\beta} - \frac{1}{\beta}\right).$$

The relation between the force and the mean displacement is sketched in the figure.

Recall that $\beta = fb/kT$. To stretch the chain by a certain displacement, the force needed is linear in the temperature.

Limiting behavior. In the absence of the force, $\beta = 0$, the orientation of the rod is equally probable in any direction, and the mean value of the displacement is $\langle y \rangle = 0$. Because of thermal fluctuation, the rigid rod acts as a spring—the entropic spring.

When the force is small, $fb/kT << 1$, we obtain that

$$\langle y \rangle = \frac{fb^2}{3kT} \, .$$

The force f is linear in the displacement $\langle y \rangle$, and the stiffness is $3kT/b^2$.

When the force is large, $fb/kT >> 1$, we obtain that

$$\langle y \rangle = b\left(1 - \frac{1}{fb/kT}\right).$$

The large force prevails over the temperature, and the rod will be nearly vertical, $\langle y \rangle \to b$.

Exercise. Carry out the integral. Confirm the two limits.

Free energy. The partition function is the sum of the Boltzmann factor over all microstates. The number of microstates is proportional to the area of the element on the unit sphere, $2\pi \sin\theta d\theta$. Thus, the partition function is

$$Z = \int_0^\pi 2\pi \exp(\beta\cos\theta)\sin\theta \, d\theta \, .$$

Integrating, we obtain that

$$Z = 2\pi\frac{\sinh\beta}{\beta} \, .$$

Recall that the Helmholtz free energy of the system is
$$g = -kT\log Z \, ,$$
giving that

$$g = kT\log\frac{\beta}{\sinh\beta} \, .$$

We have dropped an additive term independent of the force.

The "system" includes both the rod and the weight. The Helmholtz free energy of the weight is the mean potential energy $-\langle y \rangle f$. Consequently, the Helmholtz free energy of the rod is

$$w = g + \langle y \rangle f \,.$$

A combination of the above relations gives the Helmholtz free energy of the rod:

$$w = kT \left(\frac{\beta}{\tanh \beta} + \log \frac{\beta}{\sinh \beta} \right).$$

Exercise. Note that g is the Gibbs free energy of the rod. Confirm that

$$\langle y \rangle = - \frac{\partial g \left(kT, f \right)}{\partial f} \,.$$

Freely-jointed chain. A strand of polymer consists of a large number of monomers joined together by covalent bonds. The freely jointed chain model represents a polymer by a chain of n links, each link being of length b. Two neighboring links can rotate freely relative to each other. The chain is pulled at the two ends by a constant force f in a fixed direction. Every link is subject to the same force f, and behaves in the same way as a rigid rod.

Let y be the length of the entire chain projected onto the axis of the force. The mean value of the displacement is given by

$$\langle y \rangle = nb \left(\frac{1}{\tanh \beta} - \frac{1}{\beta} \right),$$

where $\beta = fb / kT$ is the normalized force.

The Helmholtz free energy of the single strand of polymer is

$$w = nkT \left(\frac{\beta}{\tanh \beta} + \log \frac{\beta}{\sinh \beta} \right).$$

Exercise. Calculate the stiffness of a polymer chain.

Exercise. Water is a polar molecule. The dipole moment of each water molecule is $p = 1.85$ debye. Consider an isolated water molecule, such as a water molecule in a vapor. Under no electric field, the temperature prevails, and the orientation of the dipole is random. Under an electric field E, the dipole will have a tendency to align with the direction of the electric field. Form a dimensionless number to measure the competition between the electric field and the temperature. Estimate the electric field needed to be competitive with the room temperature. Reference: Section 11-3, Volume II, The Feynman Lectures on Physics.

Exercise. A water molecule is at a finite temperature and is subject to an

electric field. Calculate the mean value of the dipole moment projected onto the direction of the applied electric field.

Exercise. At a small electric field, the mean value of the dipole moment projected onto the direction of the applied electric field is linear in the electric field. Calculate the coefficient of proportionality.

Exercise. This model assumes isolated water molecules. Suppose we simply apply the results to liquid water at room temperature. Calculate the permittivity using this idealized model. Compare your prediction to the experimental value of the permittivity of water. Comment on the comparison.

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REFERENCES
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