Lecture 11 - Thermodynamics

What's Important:
- laws of thermodyncamics
- determination of k_B
- why does thermodynamics work?

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Laws of thermodynamics

Starting with the microscopic picture of statistical mechanics, we have now established the laws of thermodynamics:

Zeroth Law Two systems each in thermal equilibrium with a third system must be in thermal equilibrium with each other.

First Law $\Delta\bar{E} = Q - W$

Second Law $\Delta S \geq 0$; for small changes $dS = \frac{đQ}{T}$

Third Law The entropy decreases to some minimal value S_o as T decreases to zero (this law is necessary to describe some spin systems, particularly if they do not order at T = 0).

How do we determine k_BT?

One approach is to invoke the ideal gas law. We showed previously that

$$\frac{\bar{E}}{f} = \frac{1}{2}k_BT$$

which doesn't tell us k_B unless we can measure $\bar{E}$. A more direct route is to use a generalized force relation

$$\phi = \frac{1}{ß}\frac{\partial \ln\Omega}{\partial h}$$

and apply it directly to pressure and volume:

$$\bar{p} = \frac{1}{ß}\frac{\partial \ln\Omega}{\partial V}$$

But Ω is proportional to $V^N E^{f/2}$ for an ideal gas, so

$$\bar{p} = \frac{1}{ß}\frac{\partial N \ln V}{\partial V} = k_BTN\frac{1}{V}$$

$$\bar{p}V = Nk_BT$$

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To determine k_B:

· set the temperature scale (*e.g.*, freezing points)
· find Avodardro's number
· extract k_B.

Why does thermodynamics work?

What we have described at length is how the fluctuations of a many-particle system behave. The temperature of the system was established through

$$ß = \frac{\partial \ln\Omega}{\partial E} \tag{11.1}$$

and related to the average energy. But why is the temperature a useful quantity? Why doesn't E fluctuate strongly with time? To answer these questions, we now evaluate the energy fluctuations.

As usual, we begin with a Taylor expansion around the most likely energy $\tilde{E}$ in the distribution of accessible states. We define a small parameter η as the difference between the instantaneous energy and the most likely energy:

$$\eta = E - \tilde{E}$$

such that

$$E' - \tilde{E}' = (E' - E_o) - (\tilde{E}' - E_o) = -E + \tilde{E} = -\eta.$$

The expansion is then

$$\ln\Omega(E) = \ln\Omega(\tilde{E}) + \left(\frac{\partial \ln\Omega}{\partial E}\right)\eta + \frac{1}{2}\frac{\partial^2 \ln\Omega}{\partial E^2}\eta^2 ... \tag{11.2}$$

and

$$\ln\Omega'(E') = \ln\Omega'(\tilde{E}') + \left(\frac{\partial \ln\Omega'}{\partial E'}\right)(-\eta) + \frac{1}{2}\frac{\partial^2 \ln\Omega'}{\partial E'^2}(-\eta)^2 ... \tag{11.3}$$

Substituting Eq. (11.1) for $ß$ and defining

$$\lambda \equiv -\frac{\partial^2 \ln\Omega}{\partial E^2} = -\frac{\partial ß}{\partial E} \tag{11.4}$$

then Eqs. (11.2) and (11.3) become

$$\ln\Omega(E) = \ln\Omega(\tilde{E}) + ß\eta - \frac{1}{2}\lambda\eta^2 + ... \tag{11.5}$$

$$\ln\Omega'(E') = \ln\Omega'(\tilde{E}') - ß'\eta - \frac{1}{2}\lambda'\eta^2 + ... \tag{11.6}$$

Adding (11.5) and (11.6) together, and equating $ß' = ß$ (same temperature) eliminates the linear term (replace a sum of logs with a log of a product):

$$\ln\Omega(E)\Omega'(E') = \ln\Omega(\tilde{E})\Omega'(\tilde{E}') - \frac{1}{2}(\lambda + \lambda')\eta^2$$

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The product of the two Ω's gives the probability for the energy states, or

$$\ln P(E) = \ln P(\tilde{E}) - \frac{1}{2}(\lambda + \lambda')\eta^2$$

or

$$P(E) = P(\tilde{E})e^{-\frac{\lambda+\lambda'}{2}\eta^2} \qquad (11.7)$$

This implies that the mean energy is equal to the most likely energy, within this approximation. So, the probability distribution is peaked at η = 0, and falls off with the usual Gaussian form. The question is, what is λ? Let's determine this for an ideal gas.

Ideal gas

The number of accessible states in an ideal gas is given by

$$\Omega \sim V^N E^{f/2}$$

Evaluating Eq. (11.6) then

$$\lambda = -\frac{\partial^2 \ln\Omega}{\partial E^2} = -\frac{\partial^2}{\partial E^2}\left(\frac{f}{2}\ln E\right) = -\frac{\partial}{\partial E}\left(\frac{f}{2E}\right)$$

$$= (-1)^2\left(\frac{f}{2E^2}\right)$$

The derivative is evaluated at the most likely energy, so

$$\lambda = \left(\frac{f}{2\tilde{E}^2}\right) \qquad (11.8)$$

With Eq. (11.7), the argument of the exponential in (11.7) becomes

$$-\frac{1}{4}\left(\frac{f}{\tilde{E}^2} + \frac{f'}{\tilde{E}'^2}\right)\left(E - \tilde{E}\right)^2$$

If *A′* is large, and *E′* ~ *f′*, then the second term is much smaller than the first term (*i.e.*, f/E^2 scales like $1/f$). Dropping the second term gives

$$-\frac{1}{4}\frac{f}{\tilde{E}^2}\left(E - \tilde{E}\right)^2 = -\frac{f}{2}\left(1 - \frac{E}{\tilde{E}}\right)^2$$

Why thermodynamics works is the factor of *f*: the larger the value of *f*, the faster the probability drops as $E/\tilde{E}$ moves away from unity. For $f \sim 10^{23}$, the drop-off is precipitous.

Note: Although the above result was derived for an ideal gas, in general it is found that

$$\frac{\sigma(E)}{E} \sim \frac{1}{\sqrt{f}}$$

where σ is the width of the distribution.

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