Lecture 9 - Temperature and specific heat

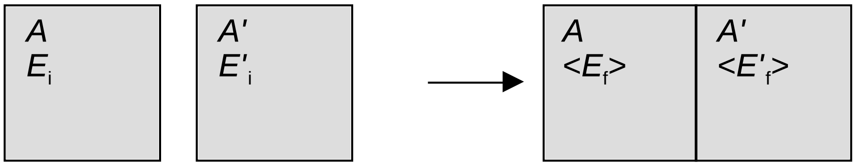
What's Important:

- thermal equilibrium
- temperature
- zeroth law of thermodynamics
- equipartition theorem
- specific heat of an ideal gas

Text: Reif

Approach to equilibrium (thermal)

Let's return to the problem of two systems A and A' being brought into thermal (but not mechanical) contact.



Notes:

- After contact, averages are made over the energies because the systems can exchange energy.
- The most probable energies are very close to the average energies.

By conservation of energy:

$$\bar{E}_f + \bar{E}'_f = E_i + E'_i$$

Note that no averages need be performed over the initial states, as they are in isolation and their energies are constant.

Defining Q as the energy **absorbed** by A, (and Q' by A') then

$$Q = \bar{E}_f - E_i = E'_i - \bar{E}'_f = -Q'$$

or

$$Q + Q' = 0. \qquad (9.1)$$

What about the entropy? Recall that the probability in the combined system is given by

$$P(E) = \text{const} \bullet \Omega(E)\, \Omega'(E')$$

The probability of being in the final state is always greater than, or equal to, the probability of being in the initial state, reflecting the number of accessible states:

$$\text{(after) } \ln \Omega_f(E_f) + \ln \Omega'_f(E'_f) \geq \ln \Omega_i(E_i) + \ln \Omega'_i(E'_i) \qquad \text{(before)}$$

But we know that entropy is related to Ω by $S = k_B \ln\Omega$. Hence,

$$S(\bar{E}_f) + S'(\bar{E}'_f) \geq S(E_i) + S'(E'_i)$$

or

$$\Delta S \equiv S(\bar{E}_f) - S(E_i) \geq S'(E'_i) - S'(\bar{E}'_f) \equiv -\Delta S' \qquad (9.2)$$

Rearranging,

$$\Delta S + \Delta S' \geq 0. \qquad (9.3)$$

Hence, the entropy of the combined system *increases* or remains the same.

Temperature

We said before that the parameter ß in

$$ß \equiv \frac{\partial \ln \Omega}{\partial E} \equiv \frac{1}{k_B T} \qquad (9.4)$$

is the same for two systems once they have reached equilibrium. We can then imagine detaching the systems and putting them in contact with another systems. If the third system has the same temperature as the original two systems, then it will be in equilibrium with them as well. This is the **zeroth** law of thermodynamics:

If two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.

This leads to the idea of thermometers: "test" systems which can be used to measure the equilibrium properties (*ß*) of other systems.

Ideal gas temperature

With the definition of temperature in hand, we return to the ideal gas situation where we have established that

$$\Omega(E) \quad V^N E^{f/2}.$$

Then, at equilibrium

$$ß = \frac{1}{k_B T} = \left.\frac{\partial \ln \Omega}{\partial E}\right|_{\bar{E}} = \left.\frac{\partial}{\partial E}(N \ln V + \frac{f}{2} \ln E)\right|_{\bar{E}}$$

$$= 0 + \frac{f}{2} \cdot \frac{1}{\bar{E}}$$

Rearranging,

$$\bar{E} = f \frac{k_B T}{2}$$

$$\frac{\bar{E}}{f} = \frac{1}{2} k_B T \qquad (9.5)$$

This is the equipartition theorem:

The average energy per translational degree of freedom for classical

particles is equal to $k_BT/2$.

Some notes and caveats:

- $\langle E \rangle$ increases linearly with temperature
- there is no upper limit on T; as more energy is dumped into the system, $\langle E \rangle$ just increases.
- quantum effects modify the prefactor (1/2) but not dramatically (see later lectures on photons, bosons and fermions).

Spin temperatures (covered in Prob. 2.2)

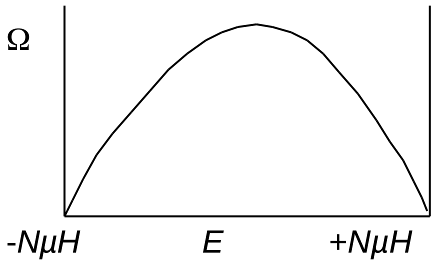
Let's return to a system investigated previously: non-interacting spin - 1/2 particles in a magnetic field H, with energy

$$E = -\Sigma_i \mu_i H. \tag{9.6}$$

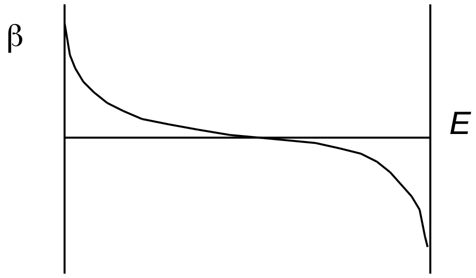
This system has an interesting behaviour as a function of temperature. Let's consider what happens with just three spins:

Energy	Configurations		
$+3\mu H$		↓↓↓	
μH	↓↓↑	↓↑↓	↑↓↓
$-\mu H$	↑↑↓	↑↓↑	↓↑↑
$-3\mu H$		↑↑↑	

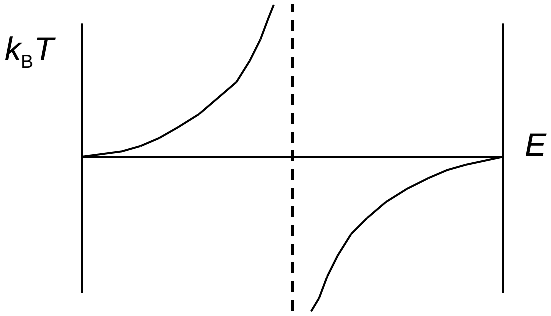
The number of accessible states is peaked at $E = 0$, not at large E. This becomes ever more clear as the number of spins N becomes large. As we know from the random walk problem, the distribution of states is Gaussian at large N:



Taking the derivative of the logarithm yields the inverse temperature $ß$:



which can be inverted to give the temperature:



What is the meaning of the divergence in the temperature? As heat is added to the system, it becomes increasingly disordered until it saturates at $<E> = 0$.

Specific heat of an ideal gas

We established above that the energy per degree of freedom of an ideal gas (translation only) increases linearly with temperature as

$$\frac{\bar{E}}{f} = \frac{1}{2} k_B T \qquad (9.7)$$

Put another way, as energy is added to the system, its temperature rises. The heat capacity of a system C is the amount of heat required to change the temperature by a specific amount:

$$C \sim \frac{\partial \bar{E}}{\partial T} \qquad (9.8)$$

Now, the amount of heat added depends upon

- the conditions under which the system is heated (*e.g.*, constant pressure or constant temperature)
- the amount of material in the system.

Under constant volume conditions, there is no mechanical work done on the system, and the energy is just $f k_B T / 2$:

$$C_V = \frac{\partial}{\partial T}(\bar{E}) = \frac{\partial}{\partial T}\left(\frac{f k_B T}{2}\right) = \frac{f}{2} k_B \qquad (9.9)$$

For a gas of N particles in three dimensions, $f = 3N$, and

$$C_V = \frac{3}{2} N k_B$$

To obtain the molar heat c_V, an intensive quantity, we evaluate C_V for one mole: N_o (Avogadro's number, 6.023×10^{23} per gram-mole). That is

$$c_V = \frac{3}{2} N_o k_B = \frac{3}{2} R \qquad (9.10)$$

The constant

$$R = N_o k_B, \qquad (9.11)$$

is called the universal gas constant, and has the value

R = 8.31 J/mole-K.