Lecture 1 - Macroscopics, entropy, and temperature - Summary

- **Main motivation of SM.**

  An isolated system would exhibit *macroscopic properties* (like energy, magnetization etc.) that correspond to the highest number of *microscopic states*.

- **Entropy**

  The natural log of the number of microscopic states, for a given set of Macroscopic measurables, $\{E\}$:

$$S(\{E\}) = \ln \Omega. \tag{1}$$

  E could be total energy, total magnetization, volume, etc.

- **System of N electronic spins**

  Magnetization:

$$M^z = \gamma \sum_i \hat{S}_i^z \tag{2}$$

  $\gamma = g\mu_B = g\frac{e}{2m}$ is the gyromagnetic ratio, and $\hat{S}_i^z$ is the z-direction spin of the i'th electron.
  M_z is a *conserved quantity*: it remains constant in an isolated system. Also, it is a prime example of a *macroscopic measurable*. The energy in a magnetic field H:

$$U = -HM_z = -H\gamma \sum_i \hat{S}_i^z. \tag{3}$$

  Entropy with $N_\uparrow - N_{downarrow} = L$:

$$S(L) = \ln \Omega(L) \approx N \ln N - \frac{1}{2}(N+L)\ln\left(\frac{1}{2}(N+L)\right) - \frac{1}{2}(N-L)\ln\left(\frac{1}{2}(N-L)\right) + \mathcal{O}(\ln N) \tag{4}$$

  As a function of U (for small U) it is:

$$\begin{aligned} S(U) &= N\ln N - \tfrac{1}{2}(N + \tfrac{2U}{H\gamma})\ln\left(\tfrac{1}{2}(N+\tfrac{2U}{H\gamma})\right) - \tfrac{1}{2}(N - \tfrac{2U}{H\gamma})\ln\left(\tfrac{1}{2}(N-\tfrac{2U}{H\gamma})\right) + \mathcal{O}(\ln N) \\ &\approx N\ln 2 - \tfrac{1}{2N}\left(\tfrac{2U}{H\gamma}\right)^2 \end{aligned} \tag{5}$$

  This is called the **equation of state**.
  The entropy was obtained using the Stirling formulae:

$$\ln n! = n\ln n - n + \mathcal{O}(\ln n). \tag{6}$$

- **Temperature**

$$\frac{1}{T} = \frac{\partial S(U)}{\partial U} \tag{7}$$

- **2nd law of Thermodynamics: Entropy always rises in non-equilibrium situations**

  When two bodies come in contact and exchange energy:

$$\begin{aligned} \delta S_{total} &= \tfrac{\partial S_1(U_1)}{\partial U_1}\delta U_1 + \tfrac{\partial S_2(U_2)}{\partial U_2}\delta U_2 \\ &= \left(\tfrac{\partial S_1(U_1)}{\partial U_1} - \tfrac{\partial S_2(U_2)}{\partial U_2}\right)\delta U_1 \\ &= \left(\tfrac{1}{T_1} - \tfrac{1}{T_2}\right)\delta U_1 \geq 0 \end{aligned} \tag{8}$$

  δU_1 has the same sign as $1/T_1 - 1/T_2$. So it is positive if $T_1 < T_2$. Heat flows from hot to cold.

- **First law of thermodynamics**

  S is a **a state function** of the macroscopic measurables of the systems.Generally, in addition to energy U, these will be volume V, number of particles N, and could anything else, which we mark X_i. As a state function, it is differentiable in all of its arguments. Therefore:

$$dS(U,\, V\, N\, \{X_i\}) = \frac{\partial S}{\partial U}dU + \frac{\partial S}{\partial V}dV + \frac{\partial S}{\partial N}dN + \sum_i \frac{\partial S}{\partial X_i}dX_i \tag{9}$$

  Now:

$$\tfrac{\partial S}{\partial U} = \tfrac{1}{T} \quad \tfrac{\partial S}{\partial V} = \tfrac{p}{V} \quad \tfrac{\partial S}{\partial N} = -\tfrac{\mu}{T} \tag{10}$$

  p is the pressure, and you see that if we change V, while keeping S constant, and also keeping N and the X's constant, the energy changes by:

$$dU = -pdV. \tag{11}$$

  The first law of thermodynamics:

$$TdS = dU + pdV - \mu dN + \dots \tag{12}$$

- **3rd law of Thermodynamics - Nernst Law: Entropy is a minimum at zero temperature**

  The third law has a very simple quantum mechanical statement: The system is always at its quantum ground state at zero temperature. If the ground state is singly degenerate, the entropy at $T = 0$ is $S = 0$.

- **Negative temperature**

  In the spin system discussed in lecture:

$$T = -\frac{N}{U}\left(\frac{H\gamma}{2}\right)^2 \tag{13}$$

  Which is negative for $U > 0$. Although counterintuitive, negative temperatures were measured using NMR in LiF[1].

Some definitions:

- **Adiabatic process.** A process in which the entropy remains unchanged, and no absorption of heat occurs .

- **Extensive and intensive quantities.** If we magnify the system by factor b, and *extensive* quantity also grows by a factor b: $X \to bX$. Examples are total energy U, entropy S, volume V, number of particles N. *Intensive* quantities do not change under magnification. Examples: temperature T, pressure p, density $n = N/V$.

  Typically for extensive quantities we use upper-case letters, and for intensive quantities lower-case letters (with the exception of temperature).

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[1] E. M. Purcell, R. V. Pound, Phys. Rev. **81**, 279 (1951).