Physics 7230: Statistical Mechanics

Lecture set 2: Microcanonical Ensemble

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(Dated: 20 January, 2021)

Abstract

In this set of lectures we will introduce and discuss the microcanonical ensemble description of quantum and classical statistical mechanics. We will apply it to a study of three canonical systems, spin-1/2 paramagnet, Boltzmann gas, quantum and classical harmonic oscillators, with details worked out by you in the homework.

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I. REVIEW OF FUNDAMENTALS

Let’s begin with reviewing the basics from lecture 1:

- **microstates**: labeled by \{q_i\}

- **ergodicity**:
  - time averages replaced by ensemble averages with probability \( P(\{q_i\}) \)
  - every microstate is equally likely to occur in a closed system (for fixed conserved quantities, \( E, N, V, \ldots \))

- \( \langle O \rangle = \sum_{\{q_i\}} O(\{q_i\}) P(\{q_i\}) \)

- \( P(\{q_i\}) = f[H(\{q_i\})] \), dictated by Liouville’s theorem, so that probability distribution is stationary (time independent)
  - Microcanonical ensemble: fixed \( E, V, N \rightarrow S(E, V, N) \)
  - Canonical ensemble: fixed \( T, V, N \rightarrow F(T, V, N) = E - TS \)
  - Grandcanonical ensemble: fixed \( T, V, \mu \rightarrow \Pi(T, V, \mu) = E - TS - \mu N \)

All we need is \( P(\{q_i\}) \) and from it any thermodynamic average can be computed, at least in principle.

II. MICROCANONICAL ENSEMBLE FUNDAMENTALS

A. Liouville’s Theorem

![Diagram](image)

FIG. 1: An illustration of conservation of phase space microstates \( \{q_i\} \) in arbitrary volume \( V \).
Above we have mentioned in passing that stationarity of equilibrium demands that $\mathcal{P}(\{q_i\})$ must be a function of the Hamiltonian, $H(\{q_i\})$. It is worth pausing briefly to see the derivation of this Liouville’s theorem dating back to 1838.

To this end, focussing on a classical particle system, let’s consider a region of phase space $V$ and discuss the number density $\rho(\{p_i, r_i\})$ of microstates confined to $V$ at time $t$. Since microstates are conserved locally, the change in number inside $V$ can only come from current flow out of the region, as summarized by,

$$\frac{d}{dt} \left( \int \rho(\{p_i, r_i\}) d^{4N} p d^{4N} r \right) = - \int dA \cdot \rho \mathbf{v},$$

where phase space velocity $\mathbf{v} = (\dot{p}_i, \dot{r}_i)$. Using divergence theorem to transform the right hand side, we find that phase space density $\rho(\{p_i, r_i\})$ satisfies the continuity equation, $\partial_t \rho + \nabla \cdot \rho \mathbf{v} = 0$, where $\nabla \equiv (\frac{\partial}{\partial p_i}, \frac{\partial}{\partial q_i})$. Applying the divergence to the current and using Hamilton’s equations, we find,

$$\partial_t \rho + \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} = 0.\tag{2}$$

Demanding that in equilibrium $\partial_t \rho = 0$, we find a vanishing of the Poisson bracket or $H$ with $\rho$,

$$\{H, \rho\} = 0.\tag{3}$$

The solution for this is $\rho(\{p_i, r_i\}) = f[H(\{p_i, r_i\})]$, as advertized above.

B. Microcanonical Probability Distribution

So what is the probability distribution $P(\{q_i\})$?

Since all microstates appear with equal probability then,

$$P[\{q_i\}] = \begin{cases} 
  1/\Omega(E), & \text{for } E(\{q_i\}) = E, N(\{q_i\}) = N, \ldots \\
  0, & \text{otherwise}
\end{cases} \tag{4}$$

where

$$\Omega(E, V, N, ...) = \sum_{\{q_i\}} \delta_{E,E(\{q_i\})} = \sum_{\{q_i\}} 1 \tag{5}$$
is the total number of states - “multiplicity” - subject to the constraint of fixed conserved quantities, like \( E, V, N \), as indicated by the prime on the conditional sum in the second line. By definition, \( P[\{q_i\}] \) is normalized to 1.

This is illustrated in Fig. 2, where we allowed the constraint to extend over energies between \( E \) and \( E + \Delta \) to get a finite number of states in this infinitesimal shell. In the thermodynamic limit, the results will be independent of the width \( \Delta \).

We note in passing that \( \Omega(E) \) can be best thought of as the density of states, that allows us to change from energy-unconstrained sums over microstates \( \{q_i\} \) to an integral over energy \( E \) with an extra Jacobian factor \( \Omega(E) \). This will become clear when we study other e.g., canonical ensemble without the energy constraint.

### III. Definition of Temperature, Pressure, Chemical Potential

Consider systems A and B in thermal contact, so energy can flow between them but total system A+B is still completely closed and isolated with \( E = E_A + E_B \) fixed. \( N_{A,B} \) and \( V_{A,B} \) are fixed for each of the systems.

For this situation, for a state with a given \( E_A \) and \( E_B \), multiplicity for the combined
system is
\[
\Omega(E_A, E_B) = \Omega_A(E_A)\Omega_B(E_B),
\]
with probability of this state therefore given by
\[
P(E_A, E_B) = \frac{\Omega_A(E_A)\Omega_B(E_B)}{\Omega(E)},
\]
where \(\Omega(E) = \int_{E_A}^{E} dE_A\Omega_A(E_A)\Omega_B(E - E_A)\).

The state that dominates in the thermodynamic limit is the one with highest probability so we determine it by maximizing \(P(E_A, E_B)\) over \(E_A\) (or equivalently \(E_B\), under condition \(E_A + E_B = E\)).

Computing \(dP(E_A, E - E_A)/dE_A\) and setting it to zero, we find
\[
\frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial E_A} = \frac{1}{\Omega_B} \frac{\partial \Omega_B}{\partial E_B}, \tag{6}
\]
\[
\frac{\partial \ln \Omega_A}{\partial E_A} \bigg|_{V_A, N_A} = \frac{\partial \ln \Omega_B}{\partial E_B} \bigg|_{V_B, N_B}, \tag{7}
\]
\[
\frac{\partial S_A}{\partial E_A} \bigg|_{V_A, N_A} = \frac{\partial S_B}{\partial E_B} \bigg|_{V_B, N_B}, \tag{8}
\]
where we defined our key result, namely that entropy \(S\) is a logarithm of the multiplicity with the Boltzmann constant \(k_B = 1.38 \times 10^{-23}\) Joules/Kelvin as the proportionality constant that converts between energy and temperature,
\[
S(E, V, N) = k_B \ln \Omega(E, V, N). \tag{9}
\]
We note that \(S(E)\) is our first thermodynamic potential and its advantage over \(\Omega\) itself is that \(S\) is extensive (if system size increases by a factor of \(b\), \(\Omega\) increases exponentially with \(b\), while \(S\) increases by a factor of \(b\)).

Furthermore we observe that
\[
\frac{1}{T} \equiv \frac{\partial S(E)}{\partial E} \bigg|_{V, N} \quad \text{definition of temperature } T \tag{10}
\]
is the quantity that is equal between two subsystems A and B in thermal equilibrium, and so it is useful to give it a name. As you will see on the homework, one can also show that heat
FIG. 4: Graphical illustration of maximization of total multiplicity of system A+B by equality of logarithmic derivatives of the corresponding Ω for two systems in equilibrium.

will flow from a subsystem with a lower value of this derivative $\frac{\partial S}{\partial E}|_{V,N}$ (higher temperature) to one with a higher derivative (lower temperature). (Can you explain why this is the case?) It therefore makes sense to set this derivative to inverse of physical temperature to correlate with everyday physical notion of temperature. We therefore take Eq.(10) as the definition of temperature, and is the content of 0th law of thermodynamics. Graphical illustration of this is given in Fig.4.

We can repeat above analysis step by step for (i) keeping A and B insulating and impermeable ($E_{A,B}$ and $N_{A,B}$ fixed), but allowing the boundary between the two to adjust, such that only the total volume $V_A + V_B = V$ is fixed, and for (ii) fixed volumes and insulating A and B ($E_{A,B}$ and $V_{A,B}$ fixed), but separated by a permeable wall allows the number of particles to adjust such that the total number $N_A + N_B = N$ remains fixed. Maximizing the probability (or multiplicity) of the total system A+B in these two cases (i) and (ii) we obtain that mechanical equilibrium and chemical equilibrium conditions are respectively given by equality of:

$$\frac{\partial S}{\partial V}|_{E,N} \equiv P/T \quad \text{(mechanical equilibrium)}$$

$$\frac{\partial S}{\partial N}|_{E,V} \equiv -\mu/T \quad \text{(chemical equilibrium)},$$

where we respectively defined as pressure and chemical potential. The fact that these are sensible definitions that agree thermodynamics can be shown (see below) but comparing with the thermodynamic relations.

**Observations and consequences:**
• Note that if there is only 1 state is available, \( \Omega = 1 \) and \( S = k_B \ln 1 = 0 \) -> 3rd law of thermodynamics

• \( S(E) \) is extensive and thus is additive

• From Eq.(10), we have \( T = \frac{\partial E}{\partial S}|_{V,N} \), which gives \( dE|_{V,N} = TdS = Q \), where \( Q \) is the corresponding heat flow. This is the **1st law of thermodynamics - conservation of energy** showing that increase in internal energy is given by the amount of heat flowing into the system (if no work is done, \( V \) is fixed, \( dV = 0 \). More generally \( dE = W + Q \).

• By definition, the total differential of entropy \( S \) is given by

\[
dS = \frac{\partial S}{\partial E}|_{V,N} dE + \frac{\partial S}{\partial V}|_{E,N} dV + \frac{\partial S}{\partial N}|_{E,V} dN,
\]

which when compared to thermodynamics \( dE = TdS - PdV + \mu dN \), gives

\[
P = T \frac{\partial(k_B \ln \Omega)}{\partial V}|_{E,N}, \quad \mu = -T \frac{\partial(k_B \ln \Omega)}{\partial N}|_{E,V}.
\]

• Thermodynamics is most commonly probed by adding heat \( Q = TdS \) to the system and measuring how much temperature changes. This is probed by heat capacities at constant \( V \) or \( P \), given by

\[
C_v = T \left( \frac{\partial S}{\partial T} \right)|_{V,N} = \left( \frac{\partial E}{\partial T} \right)|_{V,N} \quad C_p = T \left( \frac{\partial S}{\partial T} \right)|_{P,N} = \left( \frac{\partial H}{\partial T} \right)|_{P,N}.
\]

**Thus, with multiplicity \( \Omega(E, V, N) \) in hand, we can compute any thermodynamic property!** (at least in principle, though it may be difficult.)

The problem thus reduces to computation of \( \Omega(E) \). Below we will sketch out such computations for a few canonical examples, relegating the details of the derivation to homework 1.

### IV. APPLICATIONS OF MICROCANONICAL STATISTICAL MECHANICS

Having established the foundation of microcanonical ensemble statistical mechanics, we now compute the associated thermodynamics for three common examples.
A. \( N \) noninteracting particles: Boltzmann gas

![Boltzmann gas diagram](image)

FIG. 5: An illustration of a Boltzmann (noninteracting, classical) gas of \( N \) particles, confined to a closed, insulating box.

Consider \( N \) identical noninteracting (low density) classical particles - Boltzmann gas - confined to a \( d \)-dimensional box of linear size \( L \), described by a Hamiltonian

\[
H(\{p_i\}) = \sum_i^N p_i^2/2m,
\] (11)

which for classical system is the energy \( E[\{r_i, p_i\}] = H(\{p_i\}) \), and,

**Microstates:** \( 2dN \) dimensional phase space with coordinates \( \{r_i, p_i\} \).

The multiplicity at energy \( E \) - a number of states in a shell between \( E \) and \( E + \Delta \) - is then given by,

\[
\Omega(E, V, N) = \frac{1}{N!} \sum_{\{r_i, p_i\}} \delta_{E,E[\{r_i, p_i\}]} = \frac{1}{N!} \sum_{\{r_i, p_i\}} 1,
\]

\[
= \frac{\Delta}{N!} \prod_i^N \left[ \int \frac{d^d r_i d^d p_i}{(2\pi \hbar)^d} \right] \delta(E - H(\{p_i\})),
\] (12)

**Comments:**

1. Gibbs “fudge” factor \( 1/N! \) crudely accounts for the identity of these classical particles and crucially ensures that \( S(E) \) is extensive. We will see later why this fix fails at low temperatures.
2. Phase space measure $1/2\pi^2\hbar$ is required by dimensionless analysis ($\Omega$ is a dimensionless number), with its precise form encoding one microstate state per phase space area $dxdp = 2\pi\hbar$. Classical physics does not know about this factor and therefore about the zero of the entropy, classically only defined up to additive constant (3rd law requires quantum mechanics). We will derive this below.

3. The total number of states $\Omega_T(E_T)$ up to energy $E_T$ is given as simply the total phase-space volume, which is given as the coordinate-volume, set by the box volume $V$ times a momentum-volume of a $dN$-dimensional sphere with radius set by $\sqrt{2mE}$:

$$\Omega_T(E_T) = \prod_i^n \left[ \int^{H(\{p_i\}) < E_T} d\tau_i d^{d}p_i \right]^{1/2},$$

$$= \int_0^{E_T} dE \prod_i^n \left[ \int \frac{d\tau_i d^d p_i}{(2\pi\hbar)^d} \right] \delta(E - H(\{p_i\})),

= VN \int_{\sqrt{2mE_T}} dR \left[ \frac{RN!}{m\Delta V^N} \Omega(R^2/2m) \right],$$

(14)

where in the last line we inserted an identity as an integral over a $\delta$-function, and the last equality demonstrates that $(2E/m)^{1/2}\Omega(E)N!/(\Delta V^N)$ is the “surface area” of the momentum-hypersphere with radius $\sqrt{2mE}$.

4. This last observation makes the evaluation (left for homework 1) easy to carry out exact, as a surface area and volume of a $d$-dimensional unit hypersphere are given by $S_d = 2\pi^{d/2}/\Gamma(d/2)$ (with $S_2 = 2\pi$, $S_3 = 4\pi$, …) and $V_d = \pi^{d/2}/\Gamma(d/2 + 1)$, respectively.

5. Quantum mechanical treatment treats particle as matter deBroglie waves with microstates given by an integer valued $dN$-dimensional vectors, $n_i$, related to components of momenta in the usual way (for periodic boundary conditions), e.g., $p_x = 2\pi\hbar n_x/L$. Thus, we have

$$\Omega(E) = 1/N! \sum_{\{n_i\}} 1 = 1/N! \prod\limits_i \left[ L^d \int d^dP_i / (2\pi\hbar)^d \right],$$

(15)

thereby deriving the aforementioned normalization of the classical computation of $\Omega$. 

6. Clearly, $\Omega(E,V,N) = \frac{V_N}{N!} f(N,E)$, from which we immediately obtain the celebrated ideal gas law $PV = Nk_B T$.

A straightforward computation (relegated to homework 1) gives in 3d $S = k_B \ln \Omega$,

$$
S(E,V,N) = k_B N \left[ \frac{5}{2} + \ln \left( \frac{V}{N} \left( \frac{4\pi m E^3}{3N h^2} \right)^{3/2} \right) \right]
$$

referred to as the Sackur-Tetrode equation.

We note that:

- The entropy expression is explicitly extensive as required on general physical grounds and Gibbs factor was crucial to have this happen.
- Straightforward computation also gives the so-called equipartition, $E = \frac{1}{2} d N k_B T$, a linear relation between the energy and the temperature, valid for systems with only quadratic degrees of freedom in the Hamiltonian and proportionality constant $d N$ counting the number of such quadratic degrees of freedom.
- The expression for entropy $S(E)$ becomes negative for sufficiently low $E$ (or $T$), and thus clearly the computation must break down as it violates 3rd law of thermodynamics and really more fundamentally violates its intrinsically position definition $S = k_B \ln \Omega$.
- From $S(E,V,N)$ we can explicitly obtain well known properties of the ideal $d$-dimensional Boltzmann gas:

$$
E(T) = \frac{d}{2} N k_B T, \quad \text{equipartition,} \quad (17)
$$

$$
E^{d/2} V = \text{const.,} \quad \text{adiabatic process,} \quad dS = 0, \quad (18)
$$

$$
C_V(T) = \frac{d}{2} N k_B, \quad \text{heat capacity at constant } V, \quad (19)
$$

$$
C_P(T) = \frac{d + 2}{2} N k_B, \quad \text{heat capacity at constant } P. \quad (20)
$$

We next turn to another two systems and treat them within the microcanonical ensemble.
B. $N$ harmonic oscillators: Einstein phonons in a solid

FIG. 6: An illustration of the Einstein phonon model in a solid of $N$ independent harmonic oscillator.

1. Classical

Consider $N$ noninteracting $d$-dimensional classical harmonic oscillators - Einstein phonon model - described by a familiar Hamiltonian

$$H = \sum_{i}^{N} \left[ \frac{p_i^2}{2m} + \frac{1}{2}m\omega_0^2 r_i^2 \right], \quad (21)$$

with $r_i, p_i$ the classical phase-space coordinates. Much of the analysis mirrors that of the Boltzmann gas of the previous section, above. Since the system is classical its energy is the Hamiltonian $E[\{r_i, p_i\}] = H(\{r_i, p_i\})$.

**Microstates**: $2dN$ dimensional phase space with coordinates $\{r_i, p_i\}$.

The multiplicity at energy $E$ - a number of states in a shell between $E$ and $E + \Delta$ - is then given by,

$$\Omega(E, V, N) = \sum_{\{r_i, p_i\}} \delta_{E, E[\{r_i, p_i\}]} = \sum_{\{r_i, p_i\}} \sum_{\{r_i, p_i\}} 1,$$

$$= \Delta \prod_{i}^{N} \left[ \int \frac{d^d r_i d^d p_i}{(2\pi \hbar)^d} \right] \delta(E - H(\{r_i, p_i\})), \quad (22)$$

**Comments:**
1. There is no Gibbs “fudge” factor $1/N$! Why not?

2. Phase space measure $1/2\pi\hbar$ is identical to that of the Boltzmann gas and for the same reason, that can ultimately only be determined by the classical limit of a quantum formulation below.

3. By considering the total number of states $\Omega_T(E_T)$ up to energy $E_T$, we see that it is now given by the phase-space volume of a $2dN$-dimensional sphere with radius set by $\sqrt{E}$ (up to phase-space coordinates rescaling), contrasting with that for the Boltzmann gas, above. We thus see that (up to rescaling of coordinates) $2E^{1/2}\Omega(E)/\Delta$ is the $2dN - 1$-dimensional “surface area” of the $2dN$-dimensional phase-space hypersphere.

4. This last observation makes the evaluation (left for homework 1) easy to carry out exact, as a surface area and volume of a $d$-dimensional unit hypersphere are given by $S_d = 2\pi^{d/2}/\Gamma(d/2)$ (with $S_2 = 2\pi, S_3 = 4\pi, \ldots$ and $V_d = \pi^{d/2}/\Gamma(d/2 + 1)$, respectively.

A straightforward computation (relegated to homework 1) gives in $d$ dimensions,

$$\Omega(E, N) = \left(\frac{E}{\hbar\omega_0}\right)^{dN} \frac{1}{(dN)!} \frac{\Delta}{E} \approx \left(\frac{E}{dN\hbar\omega_0}\right)^{dN} \frac{\Delta}{E}, \quad (23)$$

$$S(E, N) = k_BdN \ln \left(\frac{E}{dN\hbar\omega_0}\right), \quad (24)$$

where we used $S = k_B \ln \Omega$ and lowest order Stirling approximation for $N!$, valid in the thermodynamic limit, $N \gg 1$.

**Observations:**

- I note that the expression is explicitly extensive as required on general physical grounds.

- $\Omega$ has a nice physical interpretation in terms of quantum oscillators. Namely, for large extensive energy, $q \equiv E/(dN\hbar\omega_0)$ measures the typical number of oscillator states that can be excited per 1d oscillator. Thus our result is simply $\Omega = q^{dN}$ as the total number of possible microstates for $dN$ 1d oscillators.
2. Quantum

We now consider $N$ decoupled $d$-dimensional quantum harmonic oscillators as a model of atomic vibrations in a crystalline solid (Einstein phonons), described by familiar quantum Hamiltonian

\[ \hat{H} = \sum_i \left( \hat{p}_i^2 / 2m + \frac{1}{2} m \omega_0^2 \hat{r}_i^2 - \frac{d}{2} \hbar \omega_0 \right), \]  

(25)

where for convenience I defined $\hat{H}$ with zero point energy subtracted off.

**Microstates**: For a quantum system, the microstates are the eigenstates of the Hamiltonian, and thus we first need to solve $\hat{H} \ket{\psi_n} = E_n \ket{\psi_n}$. Standard analysis gives us Fock states $\ket{\{n_\alpha\}}$ as the eigenstates with harmonic oscillator eigenvalues

\[ E[\{n_\alpha\}] = \hbar \omega_0 \sum_\alpha n_\alpha, = \hbar \omega_0 (n_{x_1} + n_{y_1} + n_{z_1} + \ldots + n_{x_2} + n_{y_2} + n_{z_2} + \ldots), \]  

(26)

with $\alpha$ ranging over $dN$ (coordinate and particle label) values.

Thus, by definition, the multiplicity for $N$ $d$-dimensional quantum harmonic oscillators is given by,

\[ \Omega(E) = \sum_{\{n_\alpha\}} \delta_{E,E[\{n_\alpha\}]} \]  

(27)

**Comments**:

1. The result is only nonzero for energy $E = \hbar \omega_0 n$, ($n \in \mathbb{Z}$) i.e., integer multiple of excitation quantum $\hbar \omega_0$. So the answer is completely determined by the integer $n \equiv E / \hbar \omega_0$, the total number of excitation quanta.

2. A good warm up is a combinatorial computation of a degeneracy a single harmonic oscillator, $g(n) = \Omega(E = \hbar \omega_0 n)$ in 2d and 3d. The multiplicity for Einstein solid is clearly just a higher dimensional generalization of these.

3. Thinking about the combinatorics of distributing $n$ total quanta of excitations among $dN$ 1d oscillators, or equivalently performing $dN$ dimensional constrained sums, and
using the lowest Stirling formula approximation for $N \gg 1$ and $n \gg 1$, we obtain

$$\Omega(E) = \left(\frac{n + dN}{n}\right)^n \left(\frac{dN + n}{dN}\right)^{dN}.$$  \hspace{1cm} (28)

4. Classical limit of this expression recovers our result for multiplicity and the entropy, (24), above.

Having found $\Omega(E,N)$, we then can compute the entropy $S(E,N)$ and from it the temperature $T(E)$, thereby extracting energy $E(T)$ as a function of temperature $T$ (notice that in this microcanonical approach $T$ is a derived quantity). Relegating detailed analysis to the homework, from these we obtain,

$$E(T,N) = \frac{\hbar \omega_0 dN}{e^{\hbar \omega_0 / k_B T} - 1}$$  \hspace{1cm} (29)

**Observations:**

1. We note that at high temperature, this recovers the expected equipartition of classical description.

2. In the deep quantum limit of low temperature the result equipartition is violated, as excitations below the gap $\hbar \omega_0$ freeze out (i.e., are inactive), and occur with exponentially suppressed probability.

3. Heat capacity $C_v = dE/dT$ is now straightforwardly obtained, exhibiting high $T$ equipartition, low $T$ freeze-out, with two regimes separated by a characteristic peak at crossover temperature scale set by $\hbar \omega_0$.

4. The classical limit can also be obtained by treating oscillator eigenvalues $\epsilon_\alpha$ as continuous variables and integrating, rather than summing over them to obtain

$$\Omega(E) = \Delta \prod_{\alpha=1}^{dN} \int \frac{d\epsilon_\alpha}{\hbar \omega_0} \delta(E - E[\{\epsilon_\alpha\}]).$$

The above constrained hypervolume of an $M$-dimensional space is spanned by positive values of $x_i$ coordinates, limited by a hyperplane $x_1 + x_2 + \ldots + x_M = R$, can be shown
to be given by

\[ V(R) = \int_{\sum_{i=1}^{M} x_i \leq R} dx_1 dx_2 \ldots dx_M = \int_{0}^{R} dr S(r) = R^M/M!, \]  

where \( S(R) = R^{M-1}/(M - 1)! \) is the corresponding hyper-area at radius \( R \) needed for computation of the multiplicity \( \Omega(E) \).

C. N Spin-1/2: Langevin paramagnet

As a last basic example we study a toy model of a paramagnet consisting of \( N \) noninteracting spin-1/2 magnetic moments in an external magnetic field \( B \), with Hamiltonian given by Zeeman energy,

\[ H = - \sum_{i=1}^{N} \mathbf{\mu}_i \cdot \mathbf{B} = - \sum_{i=1}^{N} \mu_B B \sigma_i \]

\[ \equiv - \sum_{i=1}^{N} \hbar \sigma_i \]  

where \( \mu_B \) is Bohr magneton (carrying units of magnetic moment) and \( \sigma_i = \pm 1 \) labels the two Zeeman spin eigenstates states of \( i \)-th spin, with \( \hat{H}|s_z = \frac{1}{2} \hbar \sigma\rangle = E_\sigma |s_z = \frac{1}{2} \hbar \sigma\rangle \).

We note that the energy \( E = -\mu_B BM \) is uniquely determined by the dimensionless integer magnetization \( M = N_\uparrow - N_\downarrow \), with \( N_{\uparrow, \downarrow} \) is the number of spins up and down. Thus
\[ \Omega(E) = \sum_{\{\sigma_i\}} \delta_{E,E[\{\sigma_i\}]} \] (32)

is given by combinatorial counting of the number of spin microstates, \( \{\sigma_i\} \) for a fixed value of \( M \) and \( N \).

Standard analysis (relegated to the homework) gives \( \Omega(E, N) \) and from it, we can readily derive the entropy \( S(E) = k_B \ln \Omega \), from which all other thermodynamic quantities follow.

In particular using \( 1/T = \partial S/\partial E \) we find energy \( E(T) \) and magnetization \( m(T, B) = \mu_B \sum_{i=1}^{N} \sigma_i \),

\[ E(T) = -m(T)B = -N \mu_B B \tanh \left( \frac{\mu_B B}{k_B T} \right), \] (33)

**Observations:**

1. We note that at high temperature, \( \mu_B B / k_B T \ll 1 \) this expression gives the expected linear response form \( m \approx \chi_C B \), with linear susceptibility, \( \chi(T, B) = \partial m / \partial B_{B \to 0} \),

\[ \chi_C = a/T, \] (34)

where \( a \) is the constant that measures the size of the magnetic moment.

2. In the opposite quantum limit, \( \mu_B B / k_B T \gg 1 \), we obtain a saturated magnetization, \( m \approx \mu_B N \), understood as most spins are aligned with the external magnetic field, not having enough energy to excite across the Zeeman gap.

3. Finally we can also straightforwardly compute the heat capacity (specific heat), \( C_v(T) = T \frac{\partial S}{\partial T} \big|_{V,N} \), and extract its low and high temperatures asymptotics, with the crossover temperature set by the Zeeman gap, as always is the case for gapped quantum systems.

With this lecture discussion, amplified by your detailed homework analysis we are now experts on microcanonical statistical mechanics. In the next lecture we will turn to the canonical (and then grand-canonical) ensemble and rework above examples in the canonical
statistical mechanics, confirming that the ensembles agree in the thermodynamic limit.