Physics 7230: Statistical Mechanics

Lecture set 3: Canonical Ensemble

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Abstract

In this set of lectures, we will introduce and discuss the *canonical* ensemble description of quantum and classical statistical mechanics, deriving it by considering a small subsystem of a closed microcanonical one, with the complement of the system acting like a bath. 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 on the homework, and will compare our findings with those derived in the microcanonical ensemble in previous lecture.

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I. REMINDER OF FUNDAMENTALS

Let's begin with a review of 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,…)
- $\langle O\rangle = \sum_{\{q_i\}} O(\{q_i\})P(\{q_i\}) = \mathrm{Tr}[\hat{O}\hat{\rho}]$
- $P(\{q_i\}) = f[H(\{q_i\})]$, dictated by Liouville's theorem, so that probability distribution is stationary (time independent)

  - Microcanonical ensemble: fixed $E, V, N \to S(E, V, N)$

  - Canonical ensemble: fixed $T, V, N \to F(T, V, N) = E - TS$

  - Grandcanonical ensemble: fixed $T, V, \mu \to \Pi(T, V, \mu) = E - TS - \mu N$

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

II. CANONICAL ENSEMBLE

In the last set of lectures we studied isolated systems closed to exchange of energy E, particle number N and change in volume V. These were appropriately described by the most basic microcanonical ensemble. We now want to generalize our treatment to systems that are in contact with the environment, i.e., a large bath at temperature T - think of a tea pot (system) cooling in a kitchen (bath).

A. Fundamentals of canonical ensemble

As we will derive below, the most important key result is that a canonical system with a Hamiltonian $H_q \equiv H[\{q_i\}]$, in contact with the environment (bath) at temperature T

is described by the Boltzmann-Gibbs probability distribution $P_q \equiv P[\{q_i\}]$ (equivalently density matrix $\rho = P_q$, to be discussed in detail later in the course),

$$P_q = \frac{e^{-H_q/k_B T}}{Z}, \tag{1}$$

where T is the common equilibrium temperature between the bath and the system, and

$$Z(T) = \sum_{\{q_i\}} e^{-H_q/k_B T} \tag{2}$$

is the *partition function*, that is the normalization of $P[\{q_i\}]$, and is the canonical ensemble analog of the multiplicity $\Omega(E)$ of the microcanonical ensemble from last lecture. Crucially, with the partition function $Z(T)$ in hand (which can be challenging to compute), at least in principle we can calculate any and all thermodynamic properties of the system. Z's key connection to thermodynamics is through,

$$F(T) = -k_B T \ln Z, \tag{3}$$

where F is the Helmholtz free energy $F = E - TS$.

In the rest of these lectures we will derive and elaborate on these relations and utilize them to compute thermodynamics of our standard pedagogical systems, Boltzmann gas, Einstein phonons (harmonic oscillators) and paramagnet (spins in a magnetic field).

B. From Microcanonical to Canonical Ensemble

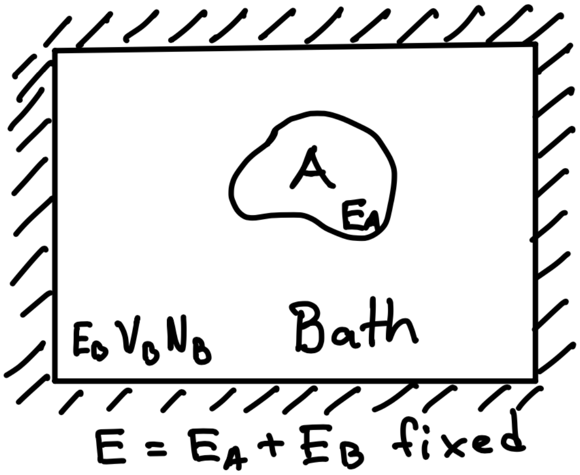

FIG. 1: An illustration of a *canonical* system A, thought of as a small part of a total *microcanonical closed* system $A + B$, with complementary component B the bath/environment to A. While the total energy $E = E_A + E_B$ is fixed, heat can freely exhange between the system A and bath B, and in equilibrium will settle to an average value set by equality of temperatures $T_A = T_B = T$.

So how do we obtain the above claimed Boltzmann-Gibbs probability distribution $P(\{q_i\})$ for the canonical ensemble?

To answer this key question, as illustrated in Fig.1 we consider a *microcanonical* (i.e., closed and isolated with fixed energy E, and other conserved quantities like N and V) system $A+B$, with its small part as our system of interest A, and a large complementary part B that will act like a bath/environment to A. While the total energy $E = E_A + E_B$ is fixed, heat can freely exhange between the system A and bath B, and as we learned in previous lectures, in equilibrium will settle to an average value set by equality of temperatures $T_A = T_B = T$.

To derive the Gibb's canonical probability distribution (1), we note that microcanonical probability distribution for total system $A + B$ is given by

$$P(E_A, E_B) = \frac{\Omega_A(E_A)\Omega_B(E_B)}{\Omega(E)},$$

where $\Omega(E) = \int_0^E dE_A \Omega_A(E_A)\Omega_B(E-E_A)$, which, by definition we call $P_A(E_A) \equiv P(E_A, E-$

E_A). We then consider $\ln P_A(E_A)$ and Taylor expand it to lowest order in small E_A,

$$\ln P_A(E_A) \;\approx\; \ln\left(\frac{\Omega_A(E_A)}{\Omega(E)}\right) + \ln\Omega_B(E) - E_A\frac{\partial\ln\Omega_B}{\partial E_B}|_{E_A=0}, \tag{4}$$

which, using $\frac{\partial\ln\Omega_B}{\partial E_B} = 1/k_BT$ leads to the sought after result,

$$P_A(E_A) \;\approx\; \left(\frac{\Omega_A(E_A)\Omega_B(E)}{\Omega(E)}\right)e^{-E_A/k_BT} = \frac{g_A(E_A)}{Z}e^{-E_A/k_BT}, \tag{5}$$

namely a form of the Gibbs distribution in (1), with a prefactor the density of states, $g_A(E_A)$ that ensures its normalization when integrated over E_A (for details, see below).

C. Properties and connection to thermodynamics

- Quantum vs Classical systems

  For **classical** systems formulation of the previous section, e.g., (1) applies directly as microstates are labelled by real numbers, and $H_q = E[\{q_i\}]$ is are the corresponding energies.

  For **quantum** system, above statements must be understood as operators, with $\hat{H}$ the Hamiltonian operator. In fact in quantum context, P_q is referred to as the *density matrix* (I will use the two terms interchangibly),

  $$\hat{\rho} = \frac{1}{Z}e^{-\hat{H}/k_BT}.$$

  So, to apply the canonical formulation one must first diagonalize $\hat{H}$, i.e., solve the time-independent Schrodinger equation $\hat{H}|E_n\rangle = E_n|E_n\rangle$. The microstates are then labelled by quantum numbers n and $H_q \to E_n$. In this basis, the density matrix is then diagonal

  $$\rho_{nm} = \frac{1}{Z}e^{-E_n/k_BT}\delta_{nm}, \quad Z = \sum_n e^{-E_n/k_BT}, \quad \langle\hat{O}\rangle = \frac{1}{Z}\sum_n O_{nn}e^{-E_n/k_BT}. \tag{6}$$

Equivalently, we can work in basis-independent formulation, namely

$$\hat{\rho} = \frac{1}{Z} e^{-\hat{H}/k_B T}, \quad Z = \mathrm{Tr}\left[e^{-\hat{H}/k_B T}\right], \quad \langle \hat{O} \rangle = \mathrm{Tr}\left[\hat{O}\hat{\rho}\right]. \tag{7}$$

that reduce to (6) in the Hamiltonian basis.

- Canonical - Microcanonical relations

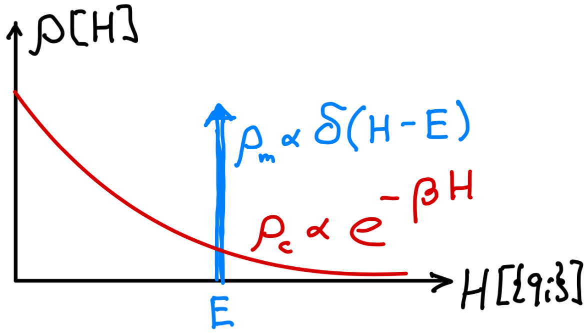

FIG. 2: A comparison between microcanonical (controlled by E) and canonical (controlled by Lagrange multiplier $\beta = 1/k_B T$) ensembles probability distributions (density matrix), appearing to be drastically different.

Although as illustrated in Fig.(2), the two ensembles, described by density matrices $\hat{\rho}_{mc}(E) = \Omega^{-1}\delta(\hat{H} - E)$ and $\hat{\rho}_c(\beta) = Z^{-1}e^{-\beta\hat{H}}$ appear to be drastically different, this is deceiving and in fact, in thermodynamic limit the two ensembles are equivalent, as we discuss below.

  - **Correspondence** between two ensembles is quite clear:

$$\begin{aligned} \Omega(E) &\longleftrightarrow Z(\beta) \\ S(E) = k_B \ln\Omega &\longleftrightarrow F(\beta) = -k_B T \ln Z \\ k_B\beta = \frac{\partial S}{\partial E} &\longleftrightarrow E = \frac{\partial(\beta F)}{\partial \beta} \end{aligned}$$

  - **Density of states**: It is crucial to distinguish the summation over microstates $\{q_i\}$ and over energies E, often a point of confusion in canonical ensemble. The connection, of course, is the degeneracy $g(E)dE$ at E counting a number of microstates $\{q_i\}$ between energy E and $E + dE$, as we are familiar with in e.g., quantum mechanics.

To make this explicit, we consider the partition function Z, rewriting its standard form (2), as an integration over energies,

$$\begin{aligned} Z(\beta) &= \sum_{\{q_i\}} e^{-\beta H_q} = \int dE \sum_{\{q_i\}} \delta(E - H_q) e^{-\beta E}, \\ &= \int dE g(E) e^{-\beta E}, \end{aligned} \tag{8}$$

where $g(E) = \sum_{\{q_i\}} \delta(E - H_q)$ is the density of states, related to multiplicity of the microcanonical ensemble, $\Omega(E) = \Delta g(E)$.

– **Laplace transform**:

From above we observe that in fact the partition function $Z(\beta)$ is a Laplace transform of the multiplicity $\Omega(E)$ (up to factor Δ), namely

$$Z(\beta) = \Delta^{-1} \mathrm{LT}[\Omega(E)].$$

Similarly, (up to normalization) canonical density matrix is a Laplace transform of the microcanonical one, namely,

$$\begin{aligned} \hat{\rho}_c(\beta) &\sim \int dE \hat{\rho}_{mc}(E) e^{-\beta E} \sim \int dE \delta(\hat{H} - E) e^{-\beta E} \\ &\sim e^{-\beta \hat{H}}. \end{aligned} \tag{9}$$

Concomitantly with this relation, the corresponding thermodynamic potentials, entropy $S(E)$ and Helmholts free energy $F(\beta)$ are related by a Legendre transform from E to β as is already clear in correspondence above and will be elaborated on below.

– **Equivalence of ensembles**:

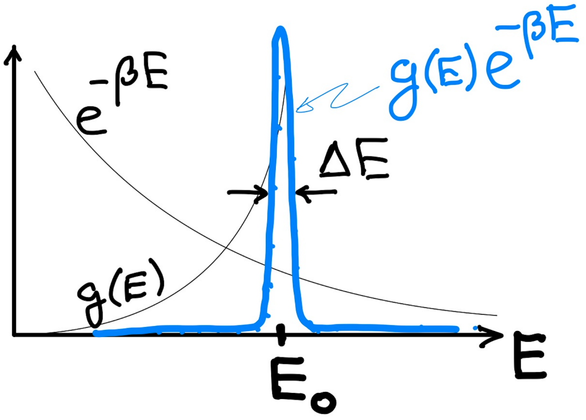

FIG. 3: An illustration of the peak form of the canonical ensemble $g(E)e^{-\beta E}$, with peak located at energy $E_0 = E(\beta)$ and a width Δ vanishingly small in the thermodynamic limit. This thereby demonstrates the equivalence to the microcanonical ensemble, with $Z(\beta) = \Omega(E(\beta))e^{-\beta E(\beta)}$.

We now look in more detail at the equivalence between the canonical (fixed β) and microcanical (fixed E) ensembles. To this end, we examine $Z(\beta)$ in Eq. (8). We note that $g(E)$ extremely strongly increasing function of E, in fact growing exponentially with system size (e.g., in a Boltzmann gas $\Omega(E) \sim E^{dN/2-1}$), exponent of order Avagadro number! On the other hand $e^{-\beta E}$ is a strongly decreasing function of E, with the rate of increase set by β. Thus, as illustrated in Fig.3 the integrand $g(E)e^{-\beta E}$ is an extremely strongly peaked function (becoming a δ-function of E in thermodynamic limit), with the location of the peak $E_0 = E_0(\beta)$ controlled by Laplace transform variable (Lagrange multiplier) β. So if the peak is sufficiently narrow, with width ΔE vanishing relative to E_0, i.e., $\Delta E/E_0 \to 0$ in the thermodynamic limit (as you will demonstrate on the homework), integrating over E (canonical) via saddle point approximation is equivalent to just setting $E = \langle E\rangle = E_0$ (microcanonical).

Such analysis thereby demonstrates the equivalence to the microcanonical ensemble, and derives $Z = e^{-\beta F}$, claimed above in Eq. (3).

- Relation to thermodynamics

In addition to the key expression for the Helmholtz free energy, $F = -k_BT \ln Z$, here we establish other connections to thermodynamics.

We recall from thermodynamics that $dS = 1/TdE + P/TdV - \mu/TdN$, which is equivalent to the 1st law of thermodynamics,

$$dE = TdS - PdV + \mu dN. \tag{10}$$

We then observe that average energy can be directly obtained from the partition function,

$$\begin{aligned} E &= \mathrm{Tr}[\hat{H}\hat{\rho}] = \frac{1}{Z}\sum_q E_q\, e^{-E_q/k_BT}, \\ &= -\frac{\partial \ln Z}{\partial \beta}. \end{aligned} \tag{11}$$

By reexpressing above relation in terms of F, we also obtain the thermodynamic relation $E = F + TS$, where $S = -\partial F/\partial T|_{V,N}$. This allows to view $F = E - TS$ as the Legendre transform from $E(S)$ to $F(T)$, with,

$$dF = -SdT - PdV + \mu dN. \tag{12}$$

which gives us the thermodynamic quantities,

$$S = -\frac{\partial F}{\partial T}|_{V,N}, \quad P = -\frac{\partial F}{\partial V}|_{T,N}, \quad \mu = \frac{\partial F}{\partial N}|_{T,V},$$

but in contrast to thermodynamics, canonical statistical mechanics gives us F in (3).

As we noted in the last lecture, 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 $C_v = T\left(\frac{\partial S}{\partial T}\right)|_{V,N} = \left(\frac{\partial E}{\partial T}\right)|_{V,N}$ and $C_p = T\left(\frac{\partial S}{\partial T}\right)|_{P,N} = \left(\frac{\partial H}{\partial T}\right)|_{P,N}$, where $H = E + PV$ is the Enthalpy thermodynamic potential. Using the expression for S in terms of F, we can then express these in terms of Helmholtz free energy,

$$C_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)|_{V,N} \tag{13}$$

We note in passing that Shannon's entropy (1948), quantifying the amount of information carried by a signal characterized by probability distribution P_q,

$$\begin{aligned} S_{\text{Shannon}} &= -\sum_q P_q \ln P_q = -\langle \ln P_q \rangle, \\ &= \ln Z + \beta \langle E_q \rangle = \beta(E - F) = S/k_B, \end{aligned} \tag{14}$$

is proportional to the thermodynamic entropy we have been discussing.

Thus, with partition function $Z(T)$ and the corresponding Helmholtz free energy $F(T) = -k_B T \ln Z$ in hand, we can compute any thermodynamic property! (at least in principle, though it may be difficult.)

The problem thus reduces to a computation of the partition function $Z(T)$. Below we will sketch out such computations for a few canonical examples, relegating the details of the derivation to homework 2.

III. 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. Gaussian integral calculus

one degree of freedom:

Let us start out slowly with standard, scalar, one-dimension Gaussian integrals

$$Z_0(a) = \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}ax^2} = \sqrt{\frac{2\pi}{a}}, \tag{15}$$

$$Z_1(a) = \int_{-\infty}^{\infty} dx x^2 e^{-\frac{1}{2}ax^2} = -2\frac{\partial}{\partial a} Z_0(a) = \frac{1}{a}\sqrt{\frac{2\pi}{a}} = \frac{1}{a} Z_0, \tag{16}$$

$$Z_n(a) = \int_{-\infty}^{\infty} dx x^{2n} e^{-\frac{1}{2}ax^2} = \frac{(2n-1)!!}{a^n} Z_0, \tag{17}$$

that can be deduced from dimensional analysis, relation to the first basic integral $Z_0(a)$ (that can in turn be computed by a standard trick of squaring it and integrating in polar coordinates) or another generating function and Γ-functions

$$Z(a,h) = \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}ax^2+hx} = \int_{-\infty}^{\infty} dx e^{-\frac{1}{2}a(x-h/a)^2} e^{\frac{1}{2}h^2/a} = e^{\frac{1}{2}h^2/a} Z_0(a), \tag{18}$$

$$= \sum_{n=0} \frac{h^{2n}}{(2n)!} Z_n(a). \tag{19}$$

Quite clearly, odd powers of x vanish by symmetry, and even powers give the $2n$-point correlation function,

$$C_{2n} \equiv \frac{Z_n(a)}{Z_0(a)} = \langle x^{2n} \rangle, \tag{20}$$

$$= \frac{1}{Z_0(a)} \frac{\partial^{2n}}{\partial h^{2n}} Z(a,h)|_{h=0} = (2n-1)!!(C_2)^n, \tag{21}$$

where $C_2 = G_0$ is a 2-point correlation function, that is also referred to as the propagator, G_0 of the harmonic theory (subscript 0 denotes the harmonic nature of the propagator).

N degrees of freedom:

This calculus can be straightforwardly generalized to multi-variable coupled Gaussian integrals characterized by an $N \times N$ symmetric matrix $(\mathbf{A})_{ij}$, as would appear in a Hamiltonian for N coupled harmonic oscillators,

$$Z_0(\mathbf{A}) = \int_{-\infty}^{\infty} [d\mathbf{x}] e^{-\frac{1}{2}\mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{x}} = \prod_{i=1}^{N} \sqrt{\frac{2\pi}{a_i}} = \sqrt{\frac{(2\pi)^N}{\det \mathbf{A}}}, \tag{22}$$

$$Z_1^{ij}(\mathbf{A}) = \int_{-\infty}^{\infty} [d\mathbf{x}] x_i x_j e^{-\frac{1}{2}\mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{x}} = \mathbf{A}_{ij}^{-1} Z_0, \tag{23}$$

$$Z(\mathbf{A}, \mathbf{h}) = \int_{-\infty}^{\infty} [d\mathbf{x}] e^{-\frac{1}{2}\mathbf{x}^T \cdot \mathbf{A} \cdot \mathbf{x} + \mathbf{h}^T \cdot \mathbf{x}} = e^{\frac{1}{2}\mathbf{h}^T \cdot \mathbf{A}^{-1} \cdot \mathbf{h}} Z_0, \tag{24}$$

computed by diagonalizing the symmetric matrix $\mathbf{A}$ and thereby decoupling the N-dimensional integral into a product of N independent scalar Gaussian integrals (17), each characterized by eigenvalue a_i, and then converting back into representation-independent form. In above we also defined a common multi-integral notation $\int_{-\infty}^{\infty} [d\mathbf{x}] \equiv \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} dx_1 \ldots dx_N = \prod_i^N \left[\int_{-\infty}^{\infty} dx_i \right]$.

As a corollary of these Gaussian integral identities we have two more key results for a

Gaussian random variable $\mathbf{x}$ (obeying Gaussian statistics), with variance $\mathbf{A}^{-1}_{ij}$,

$$Z[\mathbf{h}] \equiv \langle e^{\mathbf{h}^T\cdot\mathbf{x}}\rangle Z_0 = e^{\frac{1}{2}\langle(\mathbf{h}^T\cdot\mathbf{x})^2\rangle} Z_0 = e^{\frac{1}{2}\mathbf{h}^T\cdot\mathbf{G}\cdot\mathbf{h}} Z_0, \tag{25}$$

$$\langle \mathbf{x}_i\mathbf{x}_j\rangle \equiv G^0_{ij} = \frac{1}{Z_0}\int_{-\infty}^{\infty}[d\mathbf{x}]x_i x_j e^{-\frac{1}{2}\mathbf{x}^T\cdot\mathbf{A}\cdot\mathbf{x}} = \mathbf{A}^{-1}_{ij}, \tag{26}$$

$$= \frac{1}{Z_0}\frac{\partial^2}{\partial h_i\partial h_j}Z[\mathbf{h}]|_{\mathbf{h}=0} = \frac{\partial^2}{\partial h_i\partial h_j}\ln Z[\mathbf{h}]|_{\mathbf{h}=0} \tag{27}$$

with the first identity the relative of the Wick's theorem, which will be extremely important for computation of Gaussian correlation functions. $Z[\mathbf{h}]$ is called the generating function for correlators of $\mathbf{x}$, because its n-th derivative with respect to h_i gives n-point correlation function of x_i.

As we will see in later, application of these identities to physical harmonic oscillator systems, they immediately reproduce the equipartition theorem ($\frac{1}{2}k_BT$ per classical quadratic degree of freedom), as in e.g., phonons in a solid.

B. N noninteracting particles: Boltzmann gas

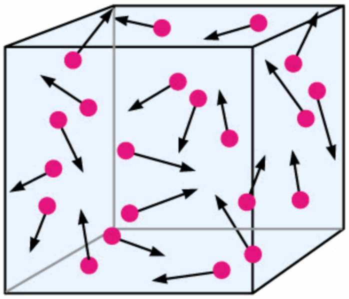

FIG. 4: An illustration of a Boltzmann (noninteracting, classical) gas of N particles, confined to a closed box of volume V and in contact with a surrounding bath at temperature T.

We now revisit statistical mechanics of a Boltzmann gas of N identical noninteracting (low density) classical particles, confined to a d-dimensional box of linear size L, described by a Hamiltonian

$$H(\{\mathbf{p}_i\}) = \sum_i^N \mathbf{p}_i^2/2m, \tag{28}$$

which for classical system is the energy $E[\{\mathbf{r}_i, \mathbf{p}_i\}] = H(\{\mathbf{p}_i\})$, and,

Microstates: $2dN$ dimensional phase space with coordinates $\{\mathbf{r}_i, \mathbf{p}_i\}$.

This time we treat it within the canonical ensemble, considering the gas to be in contact with a bath at temperature T.

Using the fundamentals introduced and discussed above, we can now readily compute the partition function, given by

$$Z(T, V, N) \;=\; \frac{1}{N!}\prod_i^N \left[\int \frac{d^d\mathbf{r}_i d^d\mathbf{p}_i}{(2\pi\hbar)^d}\right] e^{-H(\{\mathbf{p}_i\})/k_B T}, \tag{29}$$

Leaving the detailed analysis to the homework, here we only highlight and outline the analysis.

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 $1/2\pi\hbar$ is required by dimensionless analysis (Ω is a dimensionless number), with its precise form enconding 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 key simplifying feature of this problem is the noninteracting nature of the particles with the Hamiltonian being a sum of dN (N particles in d dimensions) quadratic terms in p_α. As a result the total Gibbs weight factors into a product of dN one-dimensional Gaussian weights, that can be evaluated individually using the Gaussian integral calculus above. We note that this factoring immediately gives us extensive scaling of the free energy F (and by extension of all thermodynamics) with N. The Gibbs factor is still needed to convert V into V/N.

4. The Gibbs probability distribution immediately leads to the famous Maxwell velocity and speed distributions for the noninteracting Boltzmann gas.

5. Clearly, $Z(T,V,N) = \frac{V^N}{N!} f(N,E)$, from which we immediately obtain the celebrated ideal gas law $PV = Nk_BT$.

A straightforward computation of Z (relegated to homework) gives in 3d all the key thermodynamic quantities,

$$F(T,V,N) = Nk_BT\left[\ln(n\lambda_T^3) - 1\right], \tag{30}$$

$$S(T,V,N) = -Nk_B\left[\ln(n\lambda_T^3) - \frac{5}{2}\right], \tag{31}$$

$$E = \frac{3}{2}Nk_BT, \quad C_V = \frac{3}{2}Nk_B, \tag{32}$$

where n is the gas density, λ_T is the thermal deBroglie wavelength set by equality of the kinetic $p^2/2m$ and thermal k_BT energies, obtained the expected equipartition for the average energy E and heat capacity C_V, and we have recovered the Sackur-Tetrode form found in Lecture 1 using microcanonical ensemble. We again note that above expression are explicitly extensive as required on general physical grounds and Gibbs $N!$ factor was crucial to have this happen.

Observations:

- I note that the expression are explicitly extensive as required on general physical grounds, and are consistent with those we found via the microcanonical ensemble.

- Z has a nice physical interpretation in terms of quantum de Broglie wavepackets description. Namely, the partition function $Z \approx (V/(N\lambda_T^3))^N$ counts the number of configurations of N particles in volume V, each taking up de Broglie volume λ_T^3.

- Entropy $S(T,N)$ becomes unphysically negative for $n\lambda_T^3 > 1$, or equivalently $\lambda_T > d \equiv n^{-1/3}$, reminding us of the breakdown of above classical phase-space treatment of this fundamentally quantum system.

C. N harmonic oscillators: Einstein phonons in a solid

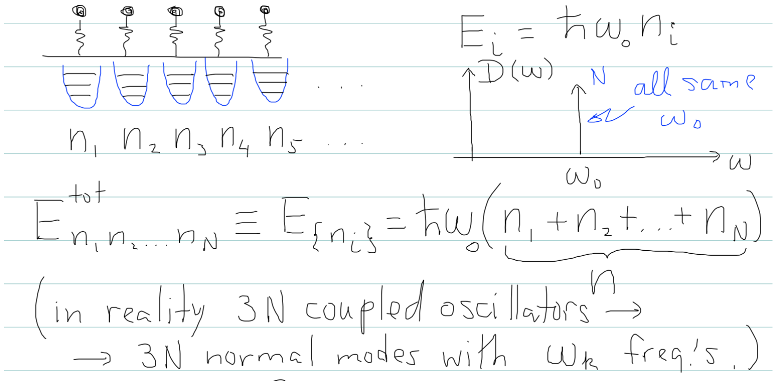

FIG. 5: An illustration of the Einstein phonon model in a solid of N independent harmonic oscillator.

1. *Classical*

We now revisit N noninteracting d-dimensional *classical* harmonic oscillators - Einstein phonon model - described by a familiar Hamiltonian

$$H = \sum_i^N \left[\mathbf{p}_i^2/2m + \frac{1}{2} m\omega_0^2 \mathbf{r}_i^2 \right], \tag{33}$$

with $\mathbf{r}_i, \mathbf{p}_i$ the classical phase-space coordinates, now treating it using the canonical ensemble. 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 $E[\{\mathbf{r}_i, \mathbf{p}_i\}] = H(\{\mathbf{r}_i, \mathbf{p}_i\})$.

Microstates: $2dN$ dimensional phase space with coordinates $\{\mathbf{r}_i, \mathbf{p}_i\}$.

Again, using the fundamentals introduced and discussed above, we can now readily compute the partition function, given by

$$Z(T, V, N) = \prod_i^N \left[\int \frac{d^d\mathbf{r}_i d^d\mathbf{p}_i}{(2\pi\hbar)^d} \right] e^{-H(\{\mathbf{p}_i\},\{\mathbf{r}_i\})/k_B T}, \tag{34}$$

Leaving the detailed analysis to the homework, here we only highlight and outline the analysis.

Comments:

1. There is no Gibbs "fudge" factor $1/N!$ since oscillators are fixed in a definite place and can thereby be distinguished by their location.

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. As we saw above for the Boltzmann gas, here too the key simplifying feature is the noninteracting nature of the particles with the Hamiltonian being a sum of dN oscillators. As a result the total Gibbs weight factors into a product of $2dN$ one-dimensional Gaussian weights, that can be evaluated individually using the Gaussian integral calculus above. We note that this factoring immediately gives us extensive scaling of the free energy F (and by extension of all thermodynamics) with N.

   We also observe that the kinetic and potential energies decouple in this classical treatment, giving $Z = Z_K Z_U$, something that does not happen in a quantum case, where K and U do not decouple due to their noncommutativity going back to $[x,p] = i\hbar$.

A straightforward computation of Z (relegated to homework) in d dimensions gives

$$Z(T,N) = \left(\frac{k_B T}{\hbar\omega_0}\right)^{dN},$$

which then leads to all the key thermodynamic quantities,

$$\begin{aligned} F(T,N) &= dNk_BT\ln(\hbar\omega_0/k_BT), && (35)\\ S(T,N) &= dNk_B\left[\ln(k_BT/\hbar\omega_0)+1\right], && (36)\\ E &= dNk_BT, \quad C_V = dNk_B, && (37) \end{aligned}$$

that I urge you to carefully compare to their microcanonical computation on homework 1 and lectures 2.

Observations:

- I note that the expression is explicitly extensive as required on general physical grounds, and are consistent with those we found via the microcanonical ensemble.

- Z has a nice physical interpretation in terms of quantum oscillators. Namely, for large extensive energy, $q \equiv k_B T/\hbar\omega_0$ measures the typical number of oscillator states that are excited per 1d oscillator with thermal energy $k_B T$. Thus our result is simply $Z = q^{dN}$ as the total number of possible microstates for dN 1d oscillators.

- Entropy $S(T, N)$ becomes unphysically negative for $k_B T < \hbar\omega_0$, reminding us of the breakdown of above classical phase-space treatment of this fundamentally quantum system.

2. Quantum

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

$$\hat{H} = \sum_i^N \left[\hat{\mathbf{p}}_i^2/2m + \frac{1}{2}m\omega_0^2\hat{\mathbf{r}}_i^2 - \frac{d}{2}\hbar\omega_0\right], \tag{38}$$

where for convenience I defined $\hat{H}$ with zero point energy subtracted off. We now treat it using canonical ensemble.

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

$$E[\{n_\alpha\}] = \hbar\omega_0 \sum_\alpha^{dN} n_\alpha, = \hbar\omega_0(n_{x1} + n_{y1} + n_{z1} + \ldots + n_{x2} + n_{y2} + n_{z2} + \ldots), \tag{39}$$

with α ranging over dN (coordinate and particle label) values.

Thus, by definition, the partition function for N d-dimensional quantum harmonic oscillators is given by,

$$Z(T) \;=\; \mathrm{Tr}[e^{-\beta\hat{H}}] = \sum_{\{n_\alpha\}} e^{-\beta\hbar\omega\sum_\alpha^{dN} n_\alpha} \tag{40}$$

A straightforward computation of Z (relegated to homework) in d dimensions then leads to thermodynamics,

$$\begin{aligned} F(T,N) &= dN\left[k_BT\ln\left(2\sinh(\hbar\omega_0/2k_BT)\right)-\frac{1}{2}\hbar\omega_0\right], &(41)\\ S(T,N) &= dNk_B\left[\frac{\hbar\omega_0}{2k_BT}\coth(\hbar\omega_0/2k_BT)-\ln\left(2\sinh(\hbar\omega_0/2k_BT)\right)\right], &(42)\\ E &= \frac{1}{2}dN\hbar\omega_0\left[\coth(\hbar\omega_0/2k_BT)-1\right], &(43)\end{aligned}$$

that I urge you to carefully compare to their microcanonical computation on homework 1 and lectures 2 and to explore carefully the classical and quantum limits, ensuring consistency with expectations.

Observations:

1. We note that at high temperature, these expressions recover the expected classical results and in particular the equipartition found above.

2. Note that in the 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 ε_α as continuous variables and computing the equipartition Z by integrating, rather than summing over ε_α to obtain as we did for the microcanonical treatment. I urge to verify this for yourself.

5. Note how much easier the computations are in the canonical ensemble, hence its promised utility.

D. N Spin-1/2: Langevin paramagnet

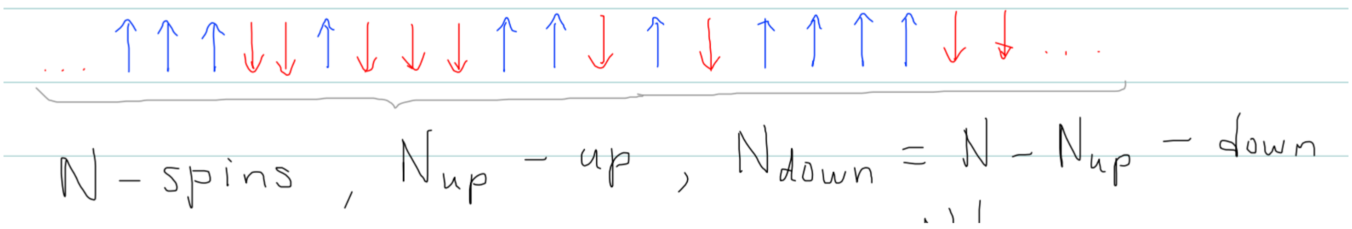

FIG. 6: An illustration of an Ising spin-1/2 quantum paramagnet in an external magnetic field B, consisting of N spins, that only have two quantum states each. Generalizaton to spin-s leads to $2s + 1$ states for each spin.

As a last basic example we revisit model of a paramagnet consisting of N noninteracting spin-s magnetic moments in an external magnetic field $\mathbf{B}$, with Hamiltonian given by Zeeman energy,

$$\hat{H} = -\sum_{i=1}^{N} \hat{\boldsymbol{\mu}}_i \cdot \mathbf{B} = -\sum_{i=1}^{N} g\mu_B B \hat{S}_i^z \tag{44}$$

where μ_B is Bohr magneton (carrying units of magnetic moment), g is the gyromagnetic ratio (between magnetic moment and spin) and S_z is the component of the spin along the external magnetic field $\mathbf{B}$. We now analyze this problem classically and then quantum mechanically.

E. Classical paramagnet

Let us first discuss the classical case, where $\mathbf{S}$ is a classical $3d$ vector of fixed magnitude s, characterized by points on a surface of a 3d sphere. Thus $S_i^z = s\cos\theta_i$ and the classical partition function is given by,

$$Z = \left[\int_0^{2\pi}\int_0^{\pi} d\phi d\theta \sin\theta e^{\beta\mu B\cos\theta}\right]^N, \tag{45}$$

where magnetic moment $\mu = g\mu_B s$. Straighforward analysis then leads to thermodynamics,

$$\begin{aligned} F(T) &= -Nk_BT\ln\left[\frac{4\pi k_BT}{\mu B}\sinh(\mu B/k_BT)\right], && (46)\\ M(T) &= N\mu\left[\coth\left(\frac{\mu B}{k_BT}\right)-\frac{k_BT}{\mu B}\right] \equiv N\mu L\left(\frac{\mu B}{k_BT}\right), && (47)\\ E &= -MB, && (48) \end{aligned}$$

where $L(x) = \coth(x) - 1/x$ is the Langevin function.

As you will explore in detail on the homework, we note that:

- At temperatures $T \ll T_2 \equiv g\mu_B sB/k_B$ the spin system exhibits equipartition with $2N$ degrees of freedom, characterized by heat capacity $C = Nk_B$. Why do we expect this behavior?

  Because these are classical spins, we don't expect a freeze-out in this treatment (but see the quantum treatment, below).

- In contrast at very high temperatures $T \gg T_2 \equiv g\mu_B sB/k_B$, above exact result reduces to the expected equal thermal distribution over all orientations of the spin, also with a vanishing heat capacity.

- At low field the linear magnetic susceptiblity $\chi_C = \partial M/\partial B|_{B\to 0} \sim 1/T$ is of Curie law form. Why?

F. Quantum paramagnet

We now analyze the quantum version of the problem, where quantum spins cannot assume arbitrary orientations relative to $\mathbf{B}$ – they are quantized with microstates as the eigenstates, $\hat{S}_i^z|s,m\rangle = \hbar m|s,m\rangle$, with $m = -s, -s+1, \ldots, s-1, s$ take on $2s+1$ eigenvalues, and $\hat{H}|s,m\rangle = E_m|s,m\rangle$, with $E_m = g\mu_B Bm \equiv \mu Bm$. For general angular momentum J, the gyromagnetic ratio is $g = \frac{3}{2} + \frac{s(s+1)-L(L+1)}{2J(J+1)}$ ($g = 2$ for pure spin and $g = 1$ for pure orbital angular momentum problems).

Since spins are noninteracting the N-spin partition function $Z = Z_1^N$ decouples into single spin partition function Z_1, given by

$$Z_1 = \sum_{m=-s}^{s} \exp\left(\beta\mu B m\right), \tag{49}$$

and after standard computation gives,

$$\begin{aligned} F(T) &= -Nk_BT\ln\left[\frac{\sinh(\beta\mu B(s+\frac{1}{2}))}{\sinh(\frac{\beta\mu B}{2})}\right], \quad (50)\\ M(T) &= N\mu s B_s[\mu s B/k_BT], \quad (51)\end{aligned}$$

where $B_s(x) = \left(1+\frac{1}{2s}\right)\coth\left[x(1+\frac{1}{2s})\right] - \frac{1}{2s}\coth\left[\frac{x}{2s}\right]$ is the Brillouin function.

As a simple example, we consider the so-called Ising case of $s = 1/2$, where there are only two states per spin and $g = 2$. The partition function and magnetization density then reduce to,

$$\begin{aligned} Z(B) &= = \left[e^{\mu_B B/k_BT} + e^{-\mu_B B/k_BT}\right]^N = \left[2\cosh(\mu_B B/k_BT)\right]^N, \quad (52)\\ m(B) &= \frac{\mu_B N}{VZ(B)}\left[e^{\mu_B B/k_BT} - e^{-\mu_B B/k_BT}\right] = -\frac{\partial F}{\partial B}, \quad (53)\\ &= n\mu_B\tanh(\mu B/k_BT), \quad (54)\end{aligned}$$

as can also be obtained directly from the general s Brillouin function above.

Observations:

1. We note that for large $s \gg 1$ the partition function Z_1 resembles that of a harmonic oscillator.

2. For ultra quantum spin limit of $s = 1/2$, the result reduces to a much simpler familiar form found within microcanonical ensemble in Lecture Set 2. $M = N\mu_B\tanh(\mu_B B/k_BT)$.

3. In the opposite $s \gg 1$ limit the results reduce to that of the classical spin, with a Langevin function for magnetization, as expected. Why?

4. At very low temperatures $T \ll T_1 \equiv g\mu_B B/k_B$ all spin degrees of freedom freeze out, as they fully align with the field B, giving a vanishing heat capacity.

5. In contrast at very high temperatures $T \gg T_2 \equiv g\mu_B sB/k_B$, above exact result reduces to the expected equal thermal distribution over all orientations of the spin, also with a vanishing heat capacity.

6. Interesting, at intermediate temperatures, $T_1 \ll T \ll T_2$, the spin system exhibits equipartition with $2N$ degrees of freedom, characterized by heat capacity $C = Nk_B$. Why do we expect this behavior?

7. At low field the linear magnetic susceptiblity $\chi_C = \partial m/\partial B|_{B\to 0} = \frac{1}{3}n\mu^2\frac{s(s+1)}{k_BT} \equiv \frac{c}{T}$ is of Curie law form, as can also be seen from lowest order perturbation theory. This $1/T$ linear susceptibility behavior is a generic experimental signature of independent local moments, with the amplitude c a measure of the size of the magnetic moment and the associated spin. At finite T the susceptibility is finite and paramagnetic (i.e., magnetization is along the applied magnetic field and vanishes with a vanishing field), only diverging at a vanishing temperature. This captures the fact that in a classical regime, as $T \to 0$ a nonzero magnetization is induced in response to an infinitesimal field, as disordering thermal fluctuations vanish. For sufficiently low T a quantum regime of large Zeeman gaps $\mu B \gg k_BT$ is reached, and magnetization density saturates at its maximum value of $n\mu s$, and susceptibility and heat capacity vanish exponentially. In the opposite limit of high temperature and low field, $s\mu B \ll k_BT$, all states are equally accessible, entropy dominates and the free energy approaches $-k_BT\ln(2s+1)$. These limits are illustrated in Figs.(7) and (8). As I discuss in an advanced course on statistical mechanics (Phys7240), interactions between local moments lead to a far richer behavior.

8. Finally we can also straightforwardly compute the heat capacity (specific heat), $C_v(T) = T\frac{\partial S}{\partial T}|_{V,N}$, and extract its low and high temperatures asymptotics, with the crossover temperature to freeze-out set by the Zeeman gap, displaying a Schottky form, as always is the case of a gapped quantum systems.

With this lecture discussion, amplified by your detailed homeowork analysis we are now experts in both micro- and canonical statistical mechanics. In the next lecture we will turn to the grand-canonical ensemble and rework above exampls in the grand-canonical statistical

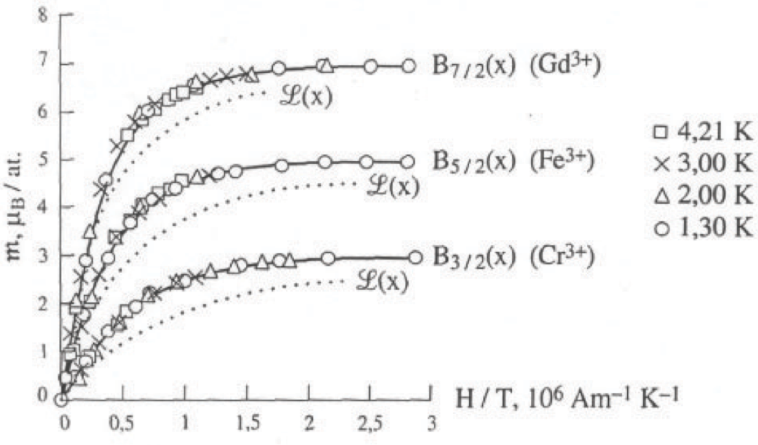

FIG. 7: Reduced magnetization curves for three paramagnetic salts and comparison with Brillouin theory prediction, from Ref.11.

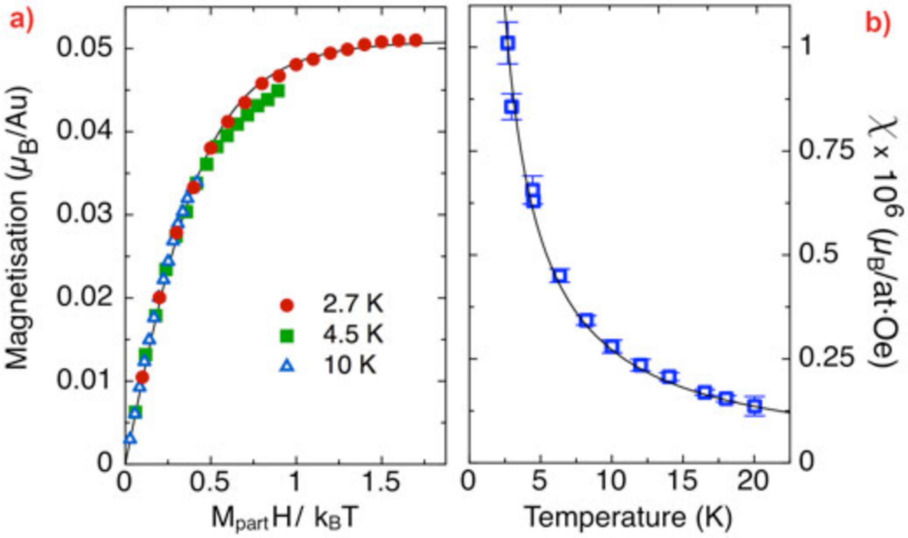

FIG. 8: Magnetization and corresponding Curie susceptibility in gold (Au) nanoparticles, measured at several temperatures up to $H = 17$ Tesla. Reduced magnetization curves for three paramagnetic salts and comparison with Brillouin theory prediction, from Ref.10.

mechanics, confirming that the ensembles agree in the thermodynamic limit.

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