Physics 7230: Statistical Mechanics

Lecture set 4: Grandcanonical Ensemble

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Abstract

In this set of lectures, we will introduce and discuss the *grandcanonical* ensemble description of quantum and classical statistical mechanics, deriving it by considering a small grandcanonical subsystem of a closed microcanonical one, with the complement of the system acting like a particle and energy reservor. We will apply it to a study of some example grandcanonical systems, including Boltzmann, lattice, and bosonic gases, with details worked out on the homework, and will compare our findings with those derived in the microcanonical and canonical ensembles in previous two lectures.

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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 $E, V, N \to S(E, V, N) \longleftrightarrow E(S, V, N)$

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

  \- Grandcanonical ensemble: fixed $T, V, \mu \to \Pi(T, V, \mu) \equiv \mathcal{F} = E - TS - \mu N$ (I will use Π and $\mathcal{F}$ interchangibly with $\mathcal{F}$ reminding us that it is just a free energy in the T, μ ensemble.)

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

II. GRANDCANONICAL 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 then generalized to a canonical ensemble where a system is open to exchange of energy with its bath (thermal equilibrium) though not the particles nor change in volume, thus having T, N and V fixed.

Here we further generalize our treatment to systems that are in contact with the environment that acts like thermal and particle reservor, i.e., a large bath at temperature T and chemical potential μ that set the average energy and particle number of our system - think of a tea pot (system) with an permeable top, cooling and exchanged molecues with the air in the kitchen (bath).

A. Fundamentals of grandcanonical ensemble

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

$$P_q = \frac{1}{\mathcal{Z}} e^{-H_q/k_B T + \mu N_q/k_B T} \tag{1}$$

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

$$\mathcal{Z}(T,\mu) = \sum_{\{q_i\}} e^{-\beta(H_q - \mu N_q)} \equiv e^{-\mathcal{F}/k_B T} \tag{2}$$

is the *grandcanonical partition function* (using the same notation as for the canonical ensemble to keep it simple), that is the normalization of $P[\{q_i\}]$, and is the grandcanonical ensemble analog of the multiplicity $\Omega(E)$ of the microcanonical ensemble from last lecture. Crucially, with the partition function $\mathcal{Z}(T,\mu)$ 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,

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

where $\mathcal{F} \equiv \Pi(T,\mu,V)$ is the grandcanonical free energy $\mathcal{F} = E - TS - \mu N = F - \mu N$.

In the rest of these lectures we will derive and elaborate on these relations and utilize them to compute thermodynamics of some standard pedagogical systems, Boltzmann, lattice and bosonic gases.

B. Derivation of Grandcanonical Ensemble

1. *From Microcanonical to Grandcanonical Ensemble*

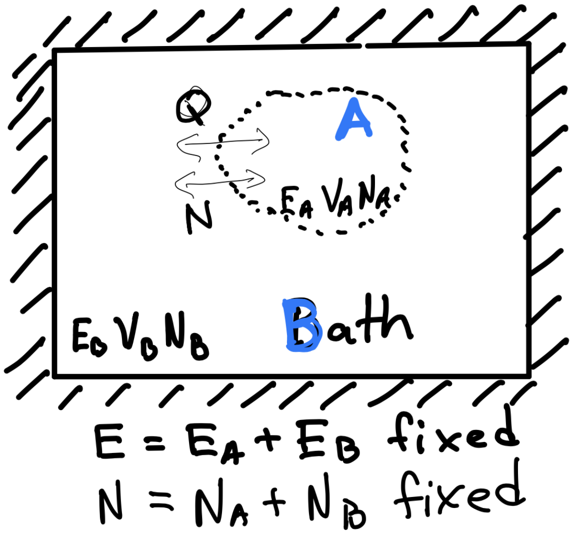

FIG. 1: An illustration of a *grandcanonical* system A, thought of as a small part of a total *microcanonical closed* system $A+B$, with complementary component B the bath/environment to A. While the total energy $E = E_A + E_B$ and particle number $N = N_A + N_B$ are fixed, heat and particles can freely exhange between the system A and bath B (at fixed volumes V_A, V_B, and in equilibrium will respectively settle to average values set by equality of temperatures $T_A = T_B = T$ and chemical potential $\mu_A = \mu_B = \mu$.

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

To answer this key question, as illustrated in Fig.1 we proceed in direct extention of the previous lecture, where we went from microcanonical to canonical ensemble. Namely, 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 $E = E_A + E_B$ and particle number $N = N_A + N_B$ are fixed, heat and particles (but for simplicity keeping volumes V_A, V_B fixed) 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 $T_A = T_B = T$ and chemical potential $\mu_A = \mu_B = \mu$.

To derive the E, N dependences of the Gibb's grandcanonical probability distribution (1), we extend the previous treatment to allow for N_A, N_B variation. Namely we note that microcanonical probability distribution for total system $A + B$ is given by

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

where $\Omega(E, N) = \sum_{N_A=0}^{N} \int_0^E dE_A \Omega_A(E_A, N_A)\Omega_B(E - E_A, N - N_A)$, which, by definition we call $P_A(E_A, N_A) \equiv P(E_A, N_A, E - E_A, N - N_A)$. We then consider $\ln P_A(E_A, N_A)$ and Taylor expand it to lowest order in small E_A and N_A,

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

which, using $\frac{\partial \ln \Omega_B}{\partial E_B} = 1/k_B T \equiv \beta$, $\frac{\partial \ln \Omega_B}{\partial N_B} = -\mu/k_B T \equiv \alpha$ leads to the sought after result,

$$P_A(E_A, N_A) = \frac{g_A(E_A, N_A)}{\mathcal{Z}} e^{-\beta(E_A - \mu N_A)} \sim e^{-\beta E_A - \alpha N_A}, \tag{5}$$

namely a form of the Gibbs distribution in (1), with a prefactor the density of states, $g_A(E_A, N_A)$, that ensures its normalization when integrated over E_A, N_A, that can be fixed after the fact and is by definition the grand partition function $\mathcal{Z}$.

2. *Statistics of Grandcanonical Ensemble via Lagrange multipliers*

We can analyze the derivation of the above Boltzmann-Gibbs factor for the grandcanonical ensemble in greater detail by considering an ensemble of $\mathcal{N} \gg 1$ systems labelled by microstates q, with the ensemble set $\{n_q\}$ characterizing the number n_q of them that are in each of the microstate q with energy E_q and number of particles N_q.

We then impose three constraints,

$$\sum_q n_q = \mathcal{N}, \ \sum_q n_q E_q = E\mathcal{N}, \ \sum_q n_q N_q = N\mathcal{N}, \tag{6}$$

via Lagrange multipliers γ, β, α, with E and N the average energy and particle number in the ensemble.

The number of configurations for a given $\mathcal{N}$ and set $\{n_q\}$ is given by the usual combinatorial factor

$$W[\{n_q\}] = \frac{\mathcal{N}!}{n_1!n_2!n_3!\ldots}. \tag{7}$$

Maximizing $W[\{n_q\}]$ with above constraints over set $\{n_q\}$ (with details left as a homework exercise), we find the most probable set n_q^*.

Since this distribution can be shown to be vanishingly narrow in the thermodynamic limit $\mathcal{N} \to \infty$, above $n_q^* = \langle n_q \rangle$. This then gives the sought after grandcanonical probability distribution $P_q \equiv n_q^*/\mathcal{N}$ given in (1)

$$P_q = \frac{1}{\mathcal{Z}} e^{-\alpha E_q - \beta N_q}. \tag{8}$$

As we will see below, matching the predictions from statistical mechanics with those in thermodynamics allows us to identify $\alpha = -\mu/k_B T$ and $\beta = 1/k_B T$.

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, with $H_q = E[\{q_i\}] \equiv E_q$ and N_q the corresponding energies and particle numbers for microstate q.

  For **quantum** system, above statements must be understood as operators, with $\hat{H}$ the Hamiltonian operator and $\hat{N}$ the total number operator. Equivalently, we can define a grandcanonical Hamiltonian, $\hat{H}_\mu = \hat{H} - \mu \hat{N}$, with everything going through the same way as for canonical ensemble . We work with the *density matrix*

  $$\hat{\rho} = \frac{1}{\mathcal{Z}} e^{-(\hat{H} - \mu \hat{N})/k_B T}.$$

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

$$\rho_{nm} = \frac{1}{\mathcal{Z}} e^{-(E_n - \mu N_n)/k_B T} \delta_{nm}, \quad \mathcal{Z} = \sum_n e^{-E_n^\mu/k_B T}, \quad \langle \hat{O} \rangle = \frac{1}{\mathcal{Z}} \sum_n O_{nn} e^{-E_n^\mu/k_B T}. \quad (9)$$

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

$$\hat{\rho} = \frac{1}{\mathcal{Z}} e^{-\hat{H}_\mu/k_B T}, \quad \mathcal{Z} = \mathrm{Tr}\left[e^{-\hat{H}_\mu/k_B T}\right], \quad \langle \hat{O} \rangle = \mathrm{Tr}\left[\hat{O}\hat{\rho}\right]. \quad (10)$$

that reduce to (9) in the Hamiltonian basis.

- Grandcanonical, Canonical and Microcanonical ensemble relations
  - **Correspondence** between two ensembles is quite clear:

    It is convenient to express the correspondence in terms of α, β Lagrange multipliers, which of course are related to temperature and chemical potential, as given above and demanded by thermodynamics correspondence. Utilizing the definitions, (3), (8), we have,

$$\begin{aligned} \Omega(E,N) &\longleftrightarrow Z(\beta,\alpha) \\ S(E,N) = k_B \ln \Omega &\longleftrightarrow \mathcal{F}((\beta,\mu) = -\beta^{-1} \ln \mathcal{Z} \\ \beta = \frac{\partial \ln \Omega}{\partial E} &\longleftrightarrow E = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \\ \beta\mu = -\frac{\partial \ln \Omega}{\partial N} &\longleftrightarrow N = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} \end{aligned}$$

  - **Density of states and Laplace transform** $E \to \beta$: As with our discussion of the canonical ensemble, here too, the β dependence of the grandcanonical partition function $\mathcal{Z}(\beta, \alpha)$ enters as the Laplace transform of $\Omega(E, N)$ (the density of states) from E to β.
  - **Discrete Laplace transform from** $N \to \alpha$:

    We note that grandcanonical partition function is given by (2), where we sum over all microstates q corresponds to all energies E_q and numbers N_q. In fact this is the convenience of the grandcanonical ensemble as performing sums that are not constrained to a particular E and N is much easier, and is the way we utilize grandcanonical ensemble. However, conceptually it is useful to think of this summation to be done in two steps: (i) first we sum over all the microstates q for a fixed N, which is nothing more than the canonical partition function $Z(N,\beta)$ and then (ii) follow this with a sum over all N to obtain $\mathcal{Z}(\alpha,\beta)$.

To make this explicit, we consider the grandcanonical partition function $\mathcal{Z}(\alpha,\beta)$, rewriting its standard form (2), as

$$\begin{aligned}\mathcal{Z}(\alpha,\beta) &= \sum_{\{q_i\}} e^{-\beta E_q-\alpha N_q} = \sum_{N=0}^{\infty}\left[\sum_{\{q_i\}}\delta_{N,N_q}e^{-\beta E_q-\alpha N_q}\right] = \sum_{N=0}^{\infty}e^{-\alpha N}\left[\sum_{\{q_i\}}\delta_{N,N_q}e^{-\beta E_q}\right], \\ &= \sum_{N=0}^{\infty} z^N Z(T,N) \equiv LT_d[Z(T,N)], \qquad (11)\end{aligned}$$

where we defined *fugacity* $z \equiv e^{-\alpha}$. We now see that $\mathcal{Z}(\alpha,\beta)$ is a discrete Laplace transform (sometimes also called the z-transform) of $Z(N,\beta)$ from N to α (or equivalently to fugacity z).

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

- **Equivalence of ensembles**:

  Our analysis for the canonical ensemble directly generalizes to the grandcanonical one, where one can show, that despite summation over all N, in the thermodynamic limit it is equivalent to the canonical and microcanonical ensemble, because fractional fluctuations in N vanish as $1/sqrt(N)$ in the thermodynamic limit.

  To see this we note that fractional mean-squared fluctuations in N is given by,

$$\begin{aligned}n_{rms}^2 &= \frac{\overline{(\Delta N)^2}}{\overline{N}^2} = \frac{1}{\overline{N}^2}\left(\overline{N^2}-\overline{N}^2\right) = -\frac{1}{\overline{N}^2}\frac{\partial \overline{N}}{\partial\alpha}|_{T,V}, \\ &= -\frac{1}{\overline{N}^2}\left(\frac{\partial\mu}{\partial\alpha}\right)\left(\frac{\partial\overline{N}}{\partial\mu}\right)_{T,V} = -\frac{k_BT}{V}\left[\frac{1}{v}\frac{\partial v}{\partial P}|_T\right], \\ &= \frac{k_BT}{V}\kappa_T \to 0, \qquad (12)\end{aligned}$$

where $\kappa_T = -\frac{1}{v}\frac{\partial v}{\partial P}|_T$ is the isothermal compressibility.

Thus, in the $\overline{N} \to \infty$ thermodynamic limit, this analysis demonstrates the equivalence of the grandcanonical and the microcanonical and canonical ensembles

- Relation to thermodynamics

In addition to the key expression for the Helmholtz free energy, $\mathcal{F}(T, \mu, V) = -k_B T \ln \mathcal{Z} \equiv -k_B T q(\alpha, \beta, V)$ (where we defined function $q(\alpha, \beta, V)$), here we establish other connections to thermodynamics and thereby identify the thermodynamic meaning of α, β, that we already anticipated in the beginning of these lectures.

We first note very useful relations,

$$N = \sum_q N_q P_q = -\frac{\partial}{\partial \alpha}[\ln \mathcal{Z}] = -\frac{\partial q}{\partial \alpha}, \tag{13}$$

$$E = \sum_q E_q P_q = -\frac{\partial}{\partial \beta}[\ln \mathcal{Z}] = -\frac{\partial q}{\partial \beta}, \tag{14}$$

$$\tag{15}$$

Hence we observe that $dq = -N d\alpha - E d\beta + \beta P dV$, where pressure is given by,

$$P = -\frac{\partial E}{\partial V}|_{\alpha,\beta} = -\frac{\sum_q \partial E_q/\partial V e^{-\alpha N_q - \beta E_q}}{\mathcal{Z}}. \tag{16}$$

This implies that

$$d(q + \alpha N + \beta E) = \alpha dN + \beta dE + \beta P dV,$$

which is of the same form as $dS = 1/T dE + P/T dV - \mu/T dN$ giving $\beta = 1/k_B T, \alpha = -\mu/k_B T$, as asserted in earlier section. Thus, this also connects q to thermodynamic potentials, $q = S/k_B - \alpha N - \beta E$ and using $-k_B T q = \mathcal{F}$, gives,

$$\mathcal{F} = E - TS - G = F - \mu N = -PV,$$

i.e., grandcanonical free energy density gives us the negative of the pressure P. Above we used Gibbs free energy, that is given by $G(T, N, P) = E - TS + PV = \mu N$. We also note $d\mathcal{F} = -SdT - PdV - Nd\mu$.

> As an aside we recall the following calculation of Gibbs free energy. Namely, because it is extensive and only extensive variable is N, it must be the case that $G(T, P, N) = Ng(T, P)$. We also note that $\mu = (\partial G/\partial N)_{T,P} = \mu$, finding that $g(T, P) = \mu$. Thus, indeed $G = \mu N$, i.e., chemical potential is Gibbs free energy per particle. Similar analysis (independent of the derivation in the preceeding paragraph) gives that $\mathcal{F}(T, \mu, V) = Vf(T, \mu)$, which implies that $f = -P$, and thus indeed $\mathcal{F} = -PV$, i.e., grand canonical free energy density is $-P$. The rest of thermodynamics follows from above expressions.
>
> We reiterate that $\mathcal{F}$ is easier to calculate because it is free of E and N constraints and also is closer to real physical systems and thus experiements that are typically done (at least in condensed matter systems) at fixed T, μ rather than fixed E, N.

Thus, with grandcanonical partition function $\mathcal{Z}(T, \mu, V)$ and the corresponding grand free energy $\mathcal{F}(T, \mu, V) = -k_B T \ln \mathcal{Z}$ 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 $\mathcal{Z}(T, \mu, V)$. Below we will sketch out such computations for a few canonical examples, relegating the details of the derivation to homework 3.

III. APPLICATIONS OF GRANDCANONICAL STATISTICAL MECHANICS

Having established the foundation of grandcanonical ensemble statistical mechanics, we now discuss the associated thermodynamics for a few pedagogical examples with details relegated to the homework.

A. Boltzmann gas

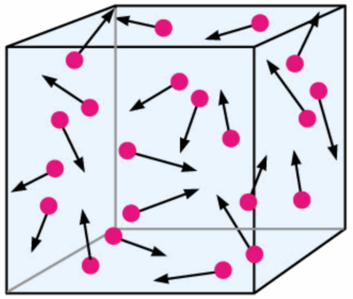

FIG. 2: An illustration of a Boltzmann (noninteracting, classical) gas of N particles, confined to a closed box of volume V and in contact with a surrounding bath at temperature T.

We now revisit statistical mechanics of a Boltzmann gas of N identical noninteracting (low density) classical particles, confined to a 3-dimensional box of linear size L. To make it a bit more interesting, we consider the particles to be diatomic molecules (e.g., O_2 in the air), which can translate, rotate and vibrate. The corresponding Hamiltonian is given by $H = \sum_{i=1}^{N}\left[H_{tr} + H_{rot} + H_{vib}\right]$, with single particle Hamiltonians

$$\begin{aligned} H_{tr} &= \mathbf{p}^2/2m, && (17)\\ H_{rot} &= \frac{p_\theta^2}{2I_\theta} + \frac{p_\phi^2}{2I_\phi}, && (18)\\ H_{vib} &= p_r^2/2m + \frac{1}{2}m\omega_0^2 r_r^2, && (19) \end{aligned}$$

with $I_\theta = mr^2, I_\phi = mr^2\sin^2\theta$, and it is crucial to note that in the vibrational part of the energy, only the radial component is involved. To get this from a more microscopic description of two atoms, one can start out with a single diatomic molecule Hamiltonian, $H = \mathbf{p}_1^2/2m + \mathbf{p}_1^2/2m + V(|\mathbf{r}_1 - \mathbf{r}_2|)$, where the potential has a minimum at a nonzero value of the average bond length ℓ, with $V(|\mathbf{r}|) \approx \frac{1}{2}m\omega_0^2(r-\ell)^2 = \frac{1}{2}m\omega_0^2(\sqrt{x^2+y^2+z^2}-\ell)^2$, and so only quadratic in radial coordinates. The corresponding integration measure keeps track of the 3d nature of the integral $\int r^2 dr \ldots$, but because of a nonzero bond length ℓ at low T, such that $r_{rms} \ll \ell$ reduces to an effective 1d integral $\approx \int \ell^2 dr \ldots$, and (as discussed below) giving 7 rather than 9 quadratic degrees of freedom of a diatomic molecule[12]. However, at high T such that $r_{rms} \gg \ell$, the result crosses over to a 3d integral and one again recovers 9 quadratic degrees of freedom, as for a spring where ℓ is neglected and analysis can be done using Cartesian coordinates, where it is just 9 Gaussian integrals. Of course physically, the molecule will likely dissociate thermally long before this limit is reached.

From our discussion above, the grandcanonical partition functon is given by

$$\begin{aligned}\mathcal{Z}(z, V, T) &= \sum_{N=0}^{\infty} z^N Z(N, V, T) = \sum_{N=0}^{\infty} \frac{[zZ(1, V, T)]^N}{N!}, \\ &= e^{zZ(1,V,T)}, \end{aligned} \tag{20}$$

where we used the fact that for N noninteracting degrees of freedom, the canonical partition function is Nth power of the single particle partition function, $Z(N) = Z_1^N/N!$. This gives us $\mathcal{F} = -k_B T \ln \mathcal{Z} = -k_B T z Z_1 \equiv -k_B T q$, and the rest of thermodynamics follows by differentiation with respect to dependent variables. In particular, with $N = -(\partial q/\partial\alpha)_{\beta,V}$ and $E = -(\partial q/\partial\beta)_{\alpha,V} = \frac{1}{2} N_{dof} k_B T$, we immediately recover the ideal gas law and equipartition. While the former does not depend on any details, the latter requires a calculation of $Z(1, T)$. A detailed Gaussian integrals calculation verifies that $N_{dof} = 7N$ corresponding to 3 center-of-mass translational kinetic (p_x, p_y, p_z), 2 rotational (p_θ, p_ϕ), and 2 vibrational (p_r, r_r) quadratic degrees of freedom per molecule.

B. Lattice gas

We now consider (what's commonly called) a "lattice gas", where there are N_0 noninteracting absorption sites in the presence of a noninteracting Boltzmann gas, with 2d schematic illustrated in Fig.(3). This toy model can be a good representation of a chemical vapor deposition and adhesion, or even oxygen O_2 attachment to Fe^{2+} in hemoglobin of the blood.

Physically we would like to calculate the coverage, i.e., occupation of N_0 possible absorption sites by the atoms.

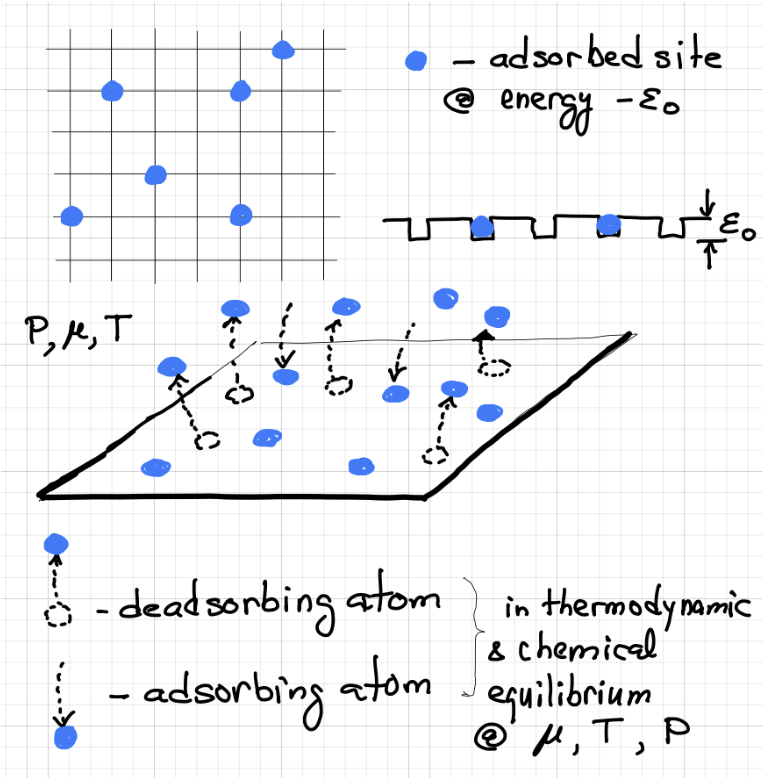

FIG. 3: An illustration of a lattice gas with N atoms occupying N_0 absorption sites at temperature T.

We first focus on the simplest case of only single occupancy, where each site can only at most accomodate one atom inside its single state of attractive energy $-\varepsilon_0$. Thus there are two states at each site 0 (unoccupied) and $-\varepsilon_0$ (occupied by one atom), as illustrated in Fig. (3). One can think of this as a "fermionic" version of lattice gas. Although this is a classical problem, because of the descreteness of the states on each absorption site, much of the analysis and results resembles closely a quantum problem of spins and of harmonic oscillators.

1. "Fermionic"

The thermodynamics can be computed using the canonical or the grandcanonical ensemble, latter being significantly simpler. In the former case the partition function is a constrained sum, with the occupations $\sum_{i=1}^{N_0} n_i = N$ constrained to N, namely we have,

$$Z(N,T) = \sum_{\{n_i=0,1\}}' e^{-\beta\sum_i(-\varepsilon_0)n_i} = \frac{N_0!}{N!(N_0-N)!}e^{-\beta N\varepsilon_0}, \tag{21}$$

where we recognized that all fixed-N occupations have identical energy $-N\varepsilon_0$, with degeneracy given by the familiar binomial coefficient. To connect to the more physical grandcanonical treatment, we can compute the chemical potential $\overline{\mu} = (\partial F/\partial N)_{T,V}$.

Alternatively, but equivalently, we can compute the grandcanonical partition function,

$$\begin{aligned} \mathcal{Z}(\mu,T) &= \sum_{N=0}^{N_0} z^N \sum_{\{n_i=0,1\}}' e^{-\beta\sum_i(-\varepsilon_0)n_i} = \sum_{N=0}^{N_0} z^N Z(N), & (22)\\ &= \prod_{i=1}^{N_0}\left[\sum_{n_i=0,1} e^{\beta(\varepsilon_0+\mu)n_i}\right] = \left[\sum_{n_i=0,1} e^{\beta(\varepsilon_0+\mu)n_i}\right]^{N_0}, & (23)\end{aligned}$$

where in the second line, we were able to transform to a much simpler unconstrained sum (discussed above), which reduces to a product of N_0 of identical sums over $n_i = 0,1$ giving the final result. Simple analysis then gives $\mathcal{Z}(\mu,T)$, from which we can obtain the grandcanonical free energy, which gives us pressure $P(\mu,T) = \mathcal{F}/V$, entropy $S(\mu,T) = -(\partial\mathcal{F}/\partial T)_{\mu,V}$, and coverage

$$\overline{N}(\mu,T) = -(\partial\mathcal{F}/\partial\mu)_{T,V} = \frac{N_0}{1+e^{-(\varepsilon_0+\mu)/k_BT}}. \tag{24}$$

We observe that for the chemical potential ranging from large negative $\mu < 0$ to large positive $\mu > 0$ the coverage $\overline{N}$ ranges from zero and N_0, respectively, as expected. Furthermore, consistent with intuition increasing the absorption energy ε_0 increases coverage. Indeed $\overline{N}(\mu,T)$ looks like the Fermi function that we will discuss later in the course on Fermi gas - this connection here is purely of a mathematical origin. We also note that the expression for $\mathcal{Z}$ above can be equivalently obtained by performing the N summation in the first line of (23) using (21).

Finally we note that the adsorbed atoms are in thermal and chemical equilibrium with the Boltzmann vapor above it, with a common temperature T and chemical potential μ. Thus, to get the more useful physical result, this allows us to express the chemical potential of the adsorbed lattice gas in terms of the pressure P of the Boltzmann vapor above it, giving us pressure and temperature dependent coverage $\overline{N}(P,T)$, with the details of this interesting and technologically relevant problem left for the homework.

2. **"Bosonic"**

As another example, one can consider a "bosonic" version, where atoms don't interacting and thus each site can accomodate arbitrary number of absorbed atoms all at same energy $-\varepsilon_0$. A simple generalizaton of this, which crudely accounts for interactions (sites can get full) is allowing a site filling of only up to a maximum number of m. As we will see on the homework, such bosonic model exhibits a "catastrophy" of sorts when its coverage discontinuously jumps to infinity.

With this lecture discussion, amplified by your detailed homeowork analysis we are now experts in micro-, canonical and grand statistical mechanics. In the next lecture we will turn to some important applications.

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