

# STATISTICAL PHYSICS AND THERMODYNAMICS

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## EQUILIBRIUM GIBBS ENSEMBLES

### 1. BOLTZMANN STATISTICS

#### a. Overview and Boltzmann factors

In the micro-canonical ensemble all micro states are equal likely,

$$P(\Gamma) = \frac{1}{\Omega(N, V, U)} \quad (1)$$

because it applies for when the system is isolated and does not interact with the outside world, and is used for process where we control the exact values of  $N$ ,  $V$ , and  $U$ .

In the Canonical ensemble the micro states are not equally likely

$$P(\Gamma) = \frac{1}{Z} e^{-U(\Gamma)/k_B T} \quad (2)$$

This applies to processes where we control  $T$ ,  $N$ , and  $V$ . System  $S$  is not completely isolated, but typically in contact with thermal bath  $R$ . The system and reservoir,  $S$  and  $R$ , exchange energy in the form of heat. The number of micro states of  $S$  is much larger in the canonical ensemble than the micro-canonical set-up; all  $U$  are allowed now, only  $N$  and  $V$  are fixed. The temperature of the thermal bath sets the average energy carried by the object.  $S$  can lend and borrow energy to and from the thermal bath compared to this average.

$S$  and  $R$  combined are in the state of maximum entropy, but  $S$  by itself is not in a state of maximum entropy.  $S$  is in the state of minimum Helmholtz free energy.

The normalization factor  $Z$  is called the partition function.

$$Z = \sum_{\Gamma(N, V)} e^{-U(\Gamma)/k_B T} \quad \leftrightarrow \quad \sum_{\Gamma(N, V)} P(\Gamma) = 1 \quad (3)$$

$\Gamma$  runs overall micro states of  $S$  only, all states with a specific  $V$  and  $N$ , but the summation runs over all possible energies  $U$ .  $Z$  turns out to be equal to the Helmholtz free energy; in total analogy with the relation between entropy and the normalization factor  $\Omega(N, V, U)$  in the micro-canonical set-up.

$$Z(N, V, T) = e^{-F(N, V, T)/k_B T} \quad \leftrightarrow \quad \Omega(N, V, U) = e^{S(N, V, U)/k_B} \quad (4)$$

All micro states  $\Gamma$  with the same energy  $U(\Gamma)$  have the same probability.

Micro states with low energy have a higher probability than states with high energy. This seems strange, i.e., that the state with zero energy has the largest probability (largest Boltzmann factor). How can that be consistent with the statement that the thermal bath (via temperature and thermal equilibrium) maintains on average a specific energy; as in  $U = \frac{q}{2} k_B N T$  in the dilute gas? You probably anticipated that the micro states with energy  $U(\Gamma) = \frac{q}{2} k_B N T$  have the largest probability. Individually they do not, but together they do, because we need to take the multiplicity of states with the same  $U$  into account and they are at the macroscopic scale indistinguishable,

$$P(U) \sim \Omega(N, V, U) e^{-\beta U} = \left[ e^{s(u, v)/k_B} e^{-\beta u} \right]^N = \left[ (e^{-\beta(u - T s(u, v))}) \right]^N \quad (5)$$

The multiplicity  $\Omega(N, V, U)$  increases with  $U$  while the Boltzmann factor decreases. This creates a maximum. Moreover this function maximum becomes very narrow in the same sense as in the Gamma function representation of  $N!$  in the Stirling formula since  $U$  is proportional to the number of particles  $N$  (write it as  $U = u/N$ ), while entropy at fixed  $U$  is also proportional to  $N$ ,  $\Omega(N, V, U) = e^{S(N, V, U)/k_B} = e^{Ns(u, v)/k_B}$ .

Note that the argument in the exponential in eq.(5) becomes the Helmholtz free energy in the large  $N$  limit where we can replace the partition function by the maximum term.

**b. maximum entropy when in contact with an heat bath**

Consider two systems  $S$  and  $R$ , isolated from the rest of the universe, but with energy exchanges between the two of them. being allowed. The total energy  $U = U_S + U_R$  is constant, but  $U_S = U - U_R$  is allowed to fluctuate.

Object  $S$ , although large itself, is very small with respect to  $R$ .  $R$  acts as thermal reservoir. The definition of thermal bath implies that it does not change its temperature, irrespective of how much energy  $S$  sucks out of it. It's slope  $(\partial S_R / \partial U)_{N_R, V_R} = 1/T_R$  is thus independent of  $U_R$ . Assume for the sake of argument that  $N_R$  and  $V_R$  of the thermal bath are strictly constant, such that

$$S_R(U) = S_R(U_0) + (U - U_0)/T_R \quad (6)$$

is strictly linear (and increasing). In terms of the number of micro-states this reads

$$\Omega_R(U_R) = \Omega_R(U_0) e^{(U - U_0)/k_B T_R} \quad (7)$$

In thermal equilibrium the system as a whole is in the state of maximum entropy; such that all its micro states (of  $S$  and  $R$  combined) are equally likely and the total entropy is equal to  $S = k_B \log(\Omega_{tot})$  with

$$\begin{aligned} \Omega_{tot} &= \int_0^{U_0} dU_S \Omega_A(N_S, V_S, U_S) \Omega_R(N_R, V_R, U_0 - U_S) \\ \frac{\Omega_{tot}}{\Omega_R(N_R, V_R, U_0)} &= \int_0^{U_0} dU_S \Omega_A(N_S, V_S, U_S) e^{-U_S/k_B T_R} \\ &= \sum_{\Gamma(V, N)} e^{-U_S(\Gamma)/k_B T_R} = Z(N, V, T) \end{aligned} \quad (8)$$

The system as a whole obeys the maximum entropy principle, and therefore every specific micro state of the total system has the same probability but we are going to ask a different question here: What is the probability of finding object  $S$  in a specific sub-system micro-state  $\Gamma_S$ , irrespective (ignoring) what micro-state  $\Gamma_R$  the reservoir is in? This probability is proportional to the remaining degeneracy of the reservoir, i.e., to the number of micro-states the reservoir can be in under this condition in  $S$ . First, let's illustrate this with a simple example, one in which energy comes in discrete quanta  $u$  and where the reservoir is still small.

Let  $S$  be a single 2-level system  $n_0 = 0, 1$  occupied or empty with one energy quantum. Let  $R$  be a set of four 2-level systems, i.e., one with micro states  $(n_1, n_1, n_3, n_4)$  each with only 2 values  $n_i = 0, 1$  and  $i = 1, 2, 3, 4$ .

Assume there are 3 energy quanta in the combined  $R + S$  system. This mean there are  $\Omega_t = \Omega(4|5) = 5!/(3!2!) = 10$  micro states in the combined system. Each one is equally likely in thermal equilibrium, i.e.,  $P(n_0|n_1, n_2, n_3, n_4) = 1/10$  for  $\sum_0^4 n_i = 3$ , and zero otherwise. The question we ask in the above is analogous to: What is the probability  $P_S(n_0)$  that  $S$  is occupied/unoccupied?

When occupied,  $n_0 = 1$ , there are 2 quanta left in  $R$ , with  $\Omega(2|4) = 4!/(2!2!) = 6$  micro states inside  $R$ . When empty,  $n_0 = 0$ , there are 3 quanta left in  $R$ , with  $\Omega(3|4) = 4!/(3!1!) = 4$  micro states inside  $R$ . This means that

$$\frac{P_S(1)}{P_S(0)} = \frac{\Omega(3|4)/\Omega_t}{\Omega(2|4)/\Omega_t} = \frac{\Omega(3|4)}{\Omega(2|4)} = \frac{6}{4} \quad (9)$$

So the probability for one specific micro state  $\Gamma_S$  in  $S$  is proportional to the number of micro states in  $R$  that are still allowed for this given  $\Gamma_S$ .

Now replace  $S$  by a system with many internal degrees  $\Gamma$  and  $R$  by an even larger system with many-many more internal degree of freedom, such that its  $T_R$  does not change for any possible amount of energy quanta's possibly going in to  $S$ . In that case, the number of reservoir micro-states inside  $R$  under this condition is according to eq.(7) proportional to

$$\Omega_R \sim e^{-U_S/k_B T_R} \quad (10)$$

such that eq.(9), the probability ratio for finding  $S$  in specific micro state  $\Gamma_1$  compared  $\Gamma_2$ , turns into

$$\frac{P_S(\Gamma_1)}{P_S(\Gamma_2)} = \frac{\Omega_R(U_{tot} - U_{\Gamma_1})}{\Omega_R(U_{tot} - U_{\Gamma_2})} = e^{(U(\Gamma_2) - U(\Gamma_1))/k_B T} \quad (11)$$

with  $U_S(\Gamma_S)$  the energy associated with that micro state  $\Gamma_S$ . This probability needs to be properly normalized

$$P_S(\Gamma) = \frac{1}{Z} e^{-U_S(\Gamma)/k_B T_R} \quad (12)$$

with the partition function  $Z$  (the normalization factor) equal to

$$Z = \sum_{\Gamma_S} e^{-U_S(\Gamma_S)/k_B T_R} \quad (13)$$

So the Boltzmann factor represents the change in entropy of the thermal bath when it lends an amount of energy  $U_R$  to the object who's temperature it controls.

### c. Integral representations of Legendre transforms

To complete the story, we need to derive that

$$F(N, V, T) = -k_B T \log(Z) \quad (14)$$

There are several ways to show this. Note that

$$\begin{aligned} Z &= \int dU_A \Omega_A(N_A, V_A, U_A) e^{-U_A(\Gamma_A)/k_B T_R} \\ &= \int dU_A e^{S_A(N_A, V_A, U_A)/k_B} e^{-U_A(\Gamma_A)/k_B T_R} \\ &= \int dU_A e^{-\tilde{F}(N_A, V_A, T_R|U_A)/k_B T_R} \end{aligned} \quad (15)$$

with  $\tilde{F}(N_A, V_A, T_R|U_A) = U_A - T_R S_A(N_A, V_A, U_A)$  resembling the Helmholtz free energy.

$\tilde{F}$  is not quite equal to the Helmholtz free energy  $F(N_A, V_A, T_A)$  yet, because it has one too many variables, i.e., depends on  $U_A$ ; and also because it carries  $T_R$  instead of  $T_A$ . The integral over all  $U_A$  takes care of that. Like earlier integrals before, this integrant is extremely sharply peaked for large  $N$ ,

$$Z = \int du_A \left[ e^{-\tilde{f}(v_A, T_R|u_A)/k_B T_R} \right]^{N_A} \quad (16)$$

with  $v_A = V_A/N_A$ ,  $u_A = U_A/N_A$ ,  $s_A = S_A/N_A$ , and  $f(v_A, T_R|u_A) = \tilde{F}/N_A = u_A - T_R s_A(v_A, u_A)$ . This allows us to replace the integral by the value of its integrant at its maximum with respect to  $u_A$ . That eliminates  $u_A$  as independent variable. Moreover,  $\tilde{f}$  has its minimum at this value  $u_A^{(m)}$

$$\tilde{f}(v_A, T_R|u_A^{(m)}) = f(v_A, T_R) \quad (17)$$

and  $T_R = T_A$  because we are in thermal equilibrium. Therefore

$$Z = e^{-F(N_A, V_A, T_R)/k_B T_A} \quad (18)$$

Notice that this is closely linked to the Legendre transforms from thermodynamics. The partition function is a clever way to perform the Legendre transform. The Pluecker line geometry interpretation of the Legendre transform taught us that it can be interpreted geometrically as the inner (or outer) envelope of a set of tangents and that this in itself is a variational representation of the Legendre transform. The partition function performs this minimization.

The above identification relies on the large  $N$  limit. The identification of the canonical partition function with the Helmholtz free energy follows rigorously for all  $N$  from the general structure of entropy in statistics

$$S = -k_B \sum_{\Gamma} P(\Gamma) \log[P(\Gamma)] \quad (19)$$

Insert the Boltzmann-Gibbs distribution into this

$$\begin{aligned} S(N, V, T)/k_B &= - \sum_{\Gamma} \frac{1}{Z} e^{-\frac{1}{k_B T} U(\Gamma)} \log\left[\frac{1}{Z} e^{-\frac{1}{k_B T} U(\Gamma)}\right] \\ &= - \sum_{\Gamma} P(\Gamma) \log\left[\frac{1}{Z} e^{-\frac{1}{k_B T} U(\Gamma)}\right] \\ &= - \sum_{\Gamma} P(\Gamma) \left[ -\log(Z) - \frac{1}{k_B T} U(\Gamma) \right] \\ &= \log(Z) \sum_{\Gamma} P(\Gamma) + \frac{1}{k_B T} \sum_{\Gamma} P(\Gamma) U(\Gamma) \\ &= \log(Z) + \frac{1}{k_B T} \langle U \rangle \\ k_B T \log(Z) &= TS - \langle U \rangle = F(N, V, T) \end{aligned} \quad (20)$$

#### d. resume of the Canonical ensemble

The identification  $F = -k_B T \log(Z)$  allows us to calculate all thermodynamic properties as derivatives of the Helmholtz free energy, as we did in thermodynamics

$$\begin{aligned} dU &= TdS - pdV + \mu dN \quad \rightarrow \quad ds = \frac{1}{T} du - \frac{p}{T} dv \\ dF &= d(U - TS) \quad \rightarrow \quad df = -sdT - pdv \end{aligned} \quad (21)$$

in other words

$$\left(\frac{\partial f}{\partial T}\right)_v = -s \quad \text{and} \quad \left(\frac{\partial f}{\partial v}\right)_T = -p \quad (22)$$

and also the response parameters, e.g.,

$$c_v = T \left(\frac{\partial s}{\partial T}\right)_v = -T \left(\frac{\partial^2 f}{\partial T^2}\right)_v \quad (23)$$

## 2. FLUCTUATIONS

### a. statistical averages

For some of those thermodynamic properties, the ones related to internal energy, the variable that fluctuates because of thermal contact with the thermal bath, we can use the statistical averages approach as alternative:

$$\langle U \rangle = \sum_{\Gamma} E(\Gamma) P(\Gamma) = \frac{1}{Z} \sum_{\Gamma} E(\Gamma) e^{-\beta E(\Gamma)} \quad (24)$$

where we introduced  $\beta \equiv 1/k_B T$ . Note that this can be rewritten as a logarithmic derivative of  $Z$

$$\langle U \rangle = \frac{1}{Z} \sum_{\Gamma} E(\Gamma) e^{-\beta E(\Gamma)} = - \left( \frac{\partial}{\partial \beta} \log Z \right)_{V,N} \quad (25)$$

Moreover, the heat capacity  $C_V$  (at constant  $N$  and  $V$ ) is proportional to the second derivative of  $\log(Z)$

$$C_V = \left( \frac{\partial}{\partial T} \langle U \rangle \right)_{V,N} = - \frac{1}{k_B T^2} \left( \frac{\partial}{\partial \beta} \langle U \rangle \right)_{V,N} = \frac{1}{k_B T^2} \left( \frac{\partial^2}{\partial \beta^2} \log Z \right)_{V,N} \quad (26)$$

and also equal to

$$\begin{aligned} k_B T^2 C_V &= - \left( \frac{\partial}{\partial \beta} \langle U \rangle \right)_{V,N} = - \left( \frac{\partial}{\partial \beta} \frac{1}{Z} \sum_{\Gamma} E(\Gamma) e^{-\beta E(\Gamma)} \right)_{V,N} \\ &= \left( \langle E^2 \rangle - \langle E \rangle^2 \right) = \langle (E - \langle E \rangle)^2 \rangle = (\Delta U)^2 \end{aligned} \quad (27)$$

This means that  $C_V$  is a measure of the fluctuations in the energy. The heat capacity is proportional to the number of particles, and therefore the fluctuations (the standard deviation) in the total energy scales as  $\Delta U \sim \sqrt{N}$ . As seen from the per particle perspective, the fluctuations in the energy (per particle) vanish in the thermodynamic limit as  $\Delta u = \Delta U/N \sim 1/\sqrt{N}$ .

### b. central limit theorem

There is no mystery here. The above simply reflects once more the extreme sharpness of the distribution with respect to energy.

$$\begin{aligned} \langle U \rangle &= \sum_{\Gamma} E(\Gamma) \frac{1}{Z} e^{-E(\Gamma)/k_B T} = \frac{1}{Z} \int dU \ U \ \Omega(N, V, U) e^{-U/k_B T} \\ &= \frac{1}{Z} \int dU \ U \ e^{(TS(N, V, U) - U)/k_B T} \end{aligned} \quad (28)$$

Compare this with the similar expression for the partition function. The factor in the exponential is again the Helmholtz free energy like function  $\tilde{F}$

$$\langle U \rangle = \frac{1}{Z} \int dU \ U \ e^{-\tilde{F}(N, V, U)/k_B T} \quad (29)$$

Switch (just as in eq.(19) to the free energy per particle,  $\tilde{f}(u, v) = \tilde{F}(N, V, U)/N$ , with  $u$  and  $v$  the energy and volume per particle.

$$\langle U \rangle = \frac{1}{Z} \int dU \ U \ \left[ e^{-\tilde{f}(v, u)/k_B T} \right]^N \quad (30)$$

This integral becomes extremely sharp with increasing  $N$ , and can be replaced by the maximum term. In that limit, the maximum, where  $f(u, v)$  is at a minimum, becomes equal to the true Helmholtz free energy  $f(T, v)$ . The same happens in the denominator. so they cancel and leave us with

$$\langle U \rangle = U^{(m)} \quad (31)$$

The maximum entropy principle of closed system thermodynamics is replaced now by a minimum Helmholtz free energy principle for systems in contact with a heat bath.

At small  $N$ , the average  $u$  and the value at the maximum do not coincide, but in the large  $N$  limit they do. Moreover, the width of the distribution (in terms of  $u$  becomes increasingly narrow, such that fluctuations about the average (maximum) value become increasingly rare. They die out as  $1/\sqrt{N}$ . Also note, that this square-root is similar to the Gaussian integral  $\sqrt{N}$  in the derivation of Stirling's formula.

This explains why in macroscopic thermodynamics we never observe a spontaneous cooling/heating of a gas by flow of heat to/from the surroundings. The process where the object heats spontaneously is allowed, but has zero statistical weight. This is the statistical explanation of the validity of the second law of thermodynamics. In small systems (small  $N$  - as in, e.g., Brownian motion), such fluctuations are statistically possible. Small systems become increasingly important in current technology. For example, the molecular sized engines walking over macromolecules, the ones that make your muscles move and transport stuff inside your cells are fundamentally stochastic (and make use of that).

### 3. GRAND CANONICAL AND OTHER ENSEMBLES

#### a. generalized forces and densities

We can generalize the above to more general statistical ensembles. The so-called Grand canonical ensemble is one of those.

Consider a system characterized by a set of extensive variables  $X_\alpha$  (like volume, energy, and particle number). One of them can be set aside, let's call it  $X_0$ , to define densities  $x_\alpha = X_\alpha/X_0$ . According to Boltzmann the entropy in a closed system like that is equal to

$$S(X_\alpha) = X_0 s(x_\alpha) = \log \left( \Omega(X_\alpha) \right) \quad (32)$$

with  $\Omega$  the number of micro states of the system for those prescribed values  $X_\alpha$ .

The second law is represented by the differential of the entropy

$$ds(x_\alpha) = \sum_{\alpha} p_{\alpha} dx_{\alpha} \quad (33)$$

with the generalized forces defines as

$$p_{\alpha} = \left( \frac{\partial S}{\partial x_{\alpha}} \right)_{x_{\beta}} \quad (34)$$

The free energies are defined as the Legendre transforms of  $s(x_\alpha)$  with respect to subsets  $\beta$  of the density variables  $x_\alpha$

$$f(p_{\beta}, x_{\gamma}) = s(x_{\alpha}) - \sum_{\beta} x_{\beta} p_{\beta} \quad (35)$$

with  $\gamma = \alpha - \beta$  the remaining densities.

### b. Generalized Boltzmann factors

Consider a large system  $R$  (playing the role of reservoir) coupled to a much smaller object  $A$ , but both macroscopically large. Assume the densities  $x_\gamma$  are frozen in  $A$ , but that all  $x_\beta$  can fluctuate by various exchange mechanism between  $R \leftrightarrow S$ . The combined entropy of  $R$  and  $A$  obeys again the maximum entropy principle, i.e., all micro states of  $R + A$  are equally likely.

The probability ratio for finding  $A$  in specific micro state  $\Gamma_1$  versus  $\Gamma_2$ , is equal to

$$\frac{P_A(\Gamma_1)}{P_A(\Gamma_2)} = \frac{e^{-\sum_\beta \lambda_\beta X_\beta(\Gamma_1)}}{e^{-\sum_\beta \lambda_\beta X_\beta(\Gamma_2)}} \quad (36)$$

with  $\lambda_\beta$  the values of the generalized forces in the reservoir. The generalized partition function  $Z$  (the normalization factor) is equal to

$$Z = \sum_{\Gamma(\{x_\gamma\})} e^{-\sum_\beta \lambda_\beta X_\beta(\Gamma)} \quad (37)$$

with  $\Gamma$  the set of all micro states of system  $S$  at fixed  $x_\gamma$  and arbitrary  $X_\beta$ .

### c. generating functions

Alternatively, the partition function can be interpreted as an abstract generating function in which the  $\lambda_\beta$  as yet unidentified parameters. All micro states with the same values of the  $X_\beta$  have the same weight. Rearrange, the summation accordingly

$$Z = \sum_{X_\beta} \Omega(X_\beta, X_\alpha) e^{-\sum_\beta \lambda_\beta X_\beta} = \sum_{X_\beta} e^{S(X_\beta, X_\alpha) - \sum_\beta \lambda_\beta X_\beta} \quad (38)$$

with  $\Omega(X_\beta, X_\alpha)$  the microscopic degeneracy for each of these subsets and Boltzmann entropy  $S(X_\beta, X_\alpha) = \log(\Omega(X_\beta, X_\alpha))$ .

Select one of the fixed extensive variables  $X_\alpha$  for the role of  $X_0$ ,

$$Z = \sum_{X_\beta} e^{X_0 [s(x_\beta, x_\alpha) - \sum_\beta \lambda_\beta x_\beta]} \quad (39)$$

This form exposes clearly that the summation is sharply peaked, and in the thermodynamic limit can be replaced by keeping only the maximum term (saddle point method).

$$Z = \exp \left[ X_0 \max_{x_\beta} \left[ s(x_\beta, x_\alpha) - \sum_\beta \lambda_\beta x_\beta \right] \right] \quad (40)$$

The maximum is located at the point where

$$\delta s(x_\beta, x_\alpha) - \sum_\beta \lambda_\beta \delta x_\beta = 0 \quad (41)$$

with respect to variations in all  $x_\beta$ , i.e., at

$$\left( \frac{\partial s}{\partial x_\beta} \right)_{x_{\tilde{\beta}}} = \lambda_\beta \quad (42)$$

This identifies the lambda's with the forces  $\lambda_\beta = p_\beta$ .

We recognize the generating function as an integration trick to perform Legendre transforms (in its variational formulation) and we identifies the generating function with the generalized “free energy” of eq.(32) as

$$\mathcal{Z} = e^{-X_0} f(p_\beta, x_\gamma) = \sum_{\Gamma} e^{-\sum_{\beta} \lambda_{\beta} X_{\beta}(\Gamma)} \quad (43)$$

#### d. summary of the grand canonical ensemble

We know now how to get-up any type of generalized statistical ensemble. The most common one is the so-called grand canonical ensemble. It represents the case where both the energy and particle number fluctuate, i.e., it evaluates the Legendre transform of  $S(U, V, N)$  where  $U$  and  $N$  are replaced by their conjugate forces  $1/T$  and  $\mu/T$ . The Gibbs-Duhem relation,  $\mu N = U - TS + pV \rightarrow \mu\rho = u - Ts + p$ , with  $\rho = N/V$  and  $u = U/V$  the density and energy per unit volume, identifies this thermodynamic potential as the pressure  $p(\mu, T)$ . Since  $-pV/k_B T = S/k_B + \mu N/k_B T - U/k_B T$ , the recipe yields

$$\mathcal{Z}_{GC} = e^{p(N, V, T)V/k_B T} = \sum_{\Gamma(V)} e^{\mu N/k_B T - U(\Gamma)/k_B T} \quad (44)$$

The second law takes here the form

$$\begin{aligned} dU &= TdS - pdV + \mu dN \rightarrow du = Tds + \mu d\rho \\ dp &= d(sT - u + \mu\rho) \rightarrow dp = -\rho d\mu - u dT \end{aligned} \quad (45)$$

in other words

$$\left(\frac{\partial p}{\partial T}\right)_{\mu} = s \quad \text{and} \quad \left(\frac{\partial p}{\partial \mu}\right)_T = \rho \quad (46)$$

The advantage of all these alternative equivalent formulations of evaluating the thermodynamic properties is that typically one of these partition functions is much easier to handle than the others.

Next, we will find out that for a classical ideal gas the canonical ensemble is the best choice, while for quantum gases the preferred formulation will turn out to be the grand canonical ensemble.

### 4. THE IDEAL GAS MERRY-GO-ROUND

#### a. Micro-canonically

As example of the above machinery, and to illustrate it is true that the calculation simplifies in specific ensembles, consider once more the monoatomic ideal gas.

Recall the micro canonical ensemble

$$e^{S(N, V, U)/k_B} = \Omega(N, V, U) = \sum_{\Gamma(V, N, U)} 1 \quad (47)$$

result

$$\Omega = \frac{1}{\Delta^{3N}} \frac{V^N}{N!} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} (\sqrt{2mU})^{3N-1} \quad (48)$$

with  $\Delta$  short hand for the counting cutoff  $\Delta x \Delta p$ . This reduces for large  $N$  to

$$S(N, V, U) = Ns(v, u) = Ns_0 + k_B N \log(vu^{3/2}) \quad (49)$$

with

$$s_0 = k_B \left[ \frac{3}{2} \log\left(\frac{4m\pi}{3\Delta^2}\right) + \frac{5}{2} \right] + \mathcal{O}\left(\frac{\log(N)}{N}\right) \quad (50)$$



The  $\log(N)/N$  correction comes into play for  $N$  smaller than a few hundred. The major contribution to those corrections originate from the Stirling's formula approximation.

Recall the saddle point derivation for  $\log(N!)$  using the gamma function integral. The simplest Stirling formula  $\log(N!) \simeq N \log(N) - N$ . represents only the maximum term of that integral. The improved Stirling formula

$$\log(N!) \simeq N \log(N) - N + \frac{1}{2} \log(2\pi N) \quad (51)$$

includes the finite width of the integral, approximated by a Gaussian integral. It is important to keep an eye on these corrections. You will see that our ensembles are equivalent and give identical results up to this same maximum term type level, but differ at  $N$  where the  $\frac{1}{2} \log(2\pi N)$  corrections come into play. Moreover, the statistical fluctuations discussed above are directly linked to those same finite gaussian width corrections.

The equations of state follow from  $ds = \frac{1}{T} du + \frac{p}{T} dv$  as:

$$\begin{aligned} \frac{1}{T} &= \left( \frac{\partial s}{\partial u} \right)_v = \frac{3}{2} k_B \frac{1}{u} \rightarrow u = \frac{3}{2} k_B T \\ \frac{p}{T} &= \left( \frac{\partial s}{\partial v} \right)_u = k_B \frac{1}{p} \rightarrow pv = k_B T \end{aligned} \quad (52)$$

We can do the same in more conventional thermodynamics language by switching lead variable,

$$u(s, v) = v^{-\frac{2}{3}} e^{\frac{2}{3} \frac{s-s_0}{k_B}} \quad ; \quad du = T ds - p dv \quad (53)$$

$$\begin{aligned} T &= \left( \frac{\partial u}{\partial s} \right)_v = \frac{2}{3 k_B} u \rightarrow u = \frac{3}{2} k_B T \\ -p &= \left( \frac{\partial u}{\partial v} \right)_s = -\frac{2}{3} \frac{u}{v} \rightarrow pv = \frac{2}{3} u \end{aligned} \quad (54)$$

The second derivatives are adiabatic type response functions. In the  $u(s, v)$  formulation they take familiar forms. The second derivative of  $u(v, s)$  with respect to  $v$  is the adiabatic compressibility (which determines the sound velocity)

$$\kappa_s^{-1} = B_s = -v \left( \frac{\partial p}{\partial v} \right)_s = v \left( \frac{\partial^2 u}{\partial v^2} \right)_s \quad (55)$$

For the monoatomic gas this gives the familiar result  $\kappa_s^{-1} = \gamma p$  (with  $\gamma = c_p/c_v = 5/3$ ). The second derivative of  $u(v, s)$  with respect to  $s$  is the isochoric specific heat

$$c_v = \left( \frac{\partial Q}{\partial T} \right)_v = T \left( \frac{\partial s}{\partial T} \right)_v \rightarrow c_v^{-1} = T^{-1} \left( \frac{\partial T}{\partial s} \right)_v = -T \left( \frac{\partial^2 u}{\partial s^2} \right)_v \quad (56)$$

For the monoatomic gas this gives the familiar result  $c_v = \frac{3}{2} k_B$ .

A curve with a positive curvature (second derivative) is called convex.  $u(v, s)$  is convex in both variables, because  $c_v$  and  $\kappa_T$  must both be positive for thermodynamic and mechanical stability reasons.

### b. Helmholtz free energy as a Legendre Transform.

Let's first evaluate  $f(v, T)$  as the Legendre transform of  $s(v, u)$  and then check whether the canonical ensemble yields the same result

$$\begin{aligned} f(v, T) &= u - Ts = \frac{3}{2}k_B T - T(s_0 + k_B N \log(vu^{3/2})) \\ &= -k_B T \left[ 1 + \frac{3}{2} \log\left(\frac{2\pi m k_B}{\Delta^2}\right) + \log(vT^{3/2}) \right] + \mathcal{O}\left(\frac{\log(N)}{N}\right) \end{aligned} \quad (57)$$

### c. Helmholtz free energy from the canonical ensemble.

The canonical ensemble generating function is very easy to evaluate

$$\begin{aligned} e^{F(N, V, T)/k_B T} &= \mathcal{Z}(N, V, T) = \sum_{\Gamma(V, N)} e^{-U(\Gamma)/k_B T} \\ &= \frac{1}{N!} \frac{1}{\Delta^{3N}} \left[ \left( \prod_i \int d\vec{r}_i \int d\vec{p}_i \right) e^{-\sum_i \vec{p}_i^2 / 2mk_B T} \right] \\ &= \frac{1}{N!} \frac{1}{\Delta^{3N}} V^N \left[ \int_{-\infty}^{\infty} dp e^{-\vec{p}^2 / 2mk_B T} \right]^{3N} \\ &= \frac{1}{N!} \frac{1}{\Delta^{3N}} V^N \left[ \sqrt{2m\pi k_B T} \right]^{3N} \end{aligned} \quad (58)$$

with as constraint that all particles must be inside the box,  $\vec{r}_i \in V$ .

The result is the same as in eq.(57), except that the  $\log(N)/N$  corrections are different; we need only use Stirling formula in the evaluation of the positional entropy factor, instead of in both the position and momentum sectors.

The canonical ensemble calculation is easier than the micro canonical one, because the momentum integrations factorize. The total energy constraint is gone, the amount of energy of each particle is independent of the others. Each one is in thermal equilibrium with the heat bath independently. The fluctuations decouple. In the microcanonical ensemble, energy is conserved and the fluctuations couple.

The amusing circularity aspect of all of this is, that in our derivation of the area of an hypersphere we used Gaussian integrals. The canonical ensemble was hiding in the back ground already. We are simply more comfortable with integrals (Newton and Leibnitz) than pure geometry (Euclid, Pythagoras, and Aristotle).

The second law  $dU = TdS - pdV + \mu dN$  and the Gibbs-Duhem relation,  $U = ST - pV + \mu N$ , in per particle representation,  $du = Tds - pdv$  and  $u = sT - pv + \mu$ , yield  $df = d(u - Ts) = -sdT - pdv$ , such that

$$p(v, T) = -\left(\frac{\partial f}{\partial v}\right)_T = k_B T \frac{1}{v} \rightarrow pv = k_B T \quad (59)$$

$$s(v, T) = -\left(\frac{\partial f}{\partial T}\right)_v = -\frac{f(v, T)}{T} + \frac{3}{2}k_B \rightarrow u = f + Ts = \frac{3}{2}k_B T \quad (60)$$

The second derivatives of  $f(v, T)$  represent two conventional response functions: The isochoric specific heat

$$c_v = \left(\frac{\partial Q}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v = -T \left(\frac{\partial^2 f}{\partial T^2}\right)_v \quad (61)$$

and the isothermal compressibility

$$\kappa_T^{-1} = B_T = -v \left(\frac{\partial p}{\partial v}\right)_T = v \left(\frac{\partial^2 f}{\partial v^2}\right)_T \quad (62)$$

For the monoatomic gas,  $c_v = \frac{3}{2}k_B$  and  $\kappa_T = 1/p$ .

A curve with a negative (positive) curvature is called concave (convex). Since both  $c_v$  and  $\kappa_T$  must be positive for thermodynamic and mechanical stability reasons,  $f(v, T)$  is convex in  $v$  and concave in  $T$  (for any substance).

#### d. The Gibbs free energy as a Legendre transform.

The logarithm of the grand canonical ensemble partition function yields the pressure as function of chemical potential and temperature. Note that  $p(\mu, T)$  is a thermodynamic potential. We want to check the grand canonical result against what we get by Legendre transforming the micro canonical thermodynamic potential  $s(u, v)$  directly.

This procedure looks more familiar when we flip lead variable,  $p(\mu, T) \rightarrow \mu(p, T)$ . The Gibbs-Duhem relation  $U = ST - pV + \mu N$ , in per particle representation,  $u = sT - pv + \mu$ , implies that the Gibbs free energy per particle is the chemical potential,  $G = U - TS + pV = \mu N$ , and that  $\mu = u - Ts + pv$  is the Legendre transform of the micro canonical potential  $u(s, v)$  (rewritten with  $u$  as lead variable instead of  $s$ ) with respect to both  $v$  and  $s$ . From eqs.(48)-(51) it follows that

$$\begin{aligned}\mu &= u + pv - Ts = \frac{3}{2}k_B T + k_B T - T[s_0 + k_B \log(vu^{3/2})] \\ &= \frac{5}{2}k_B T - k_B T \left[ \frac{5}{2} + \frac{3}{2} \log\left(\frac{4m\pi}{3\Delta^2}\right) + \log(vu^{3/2}) \right] + \mathcal{O}\left(\frac{\log(N)}{N}\right) \\ &= -k_B T \log \left[ \left( \frac{2\pi m}{\Delta^2} \right)^{\frac{3}{2}} \frac{1}{p} (k_B T)^{\frac{5}{2}} \right] + \mathcal{O}\left(\frac{\log(N)}{N}\right)\end{aligned}\quad (63)$$

and by switching lead variable

$$p = \left( \frac{2\pi m}{\Delta^2} \right)^{\frac{3}{2}} (k_B T)^{\frac{5}{2}} e^{\mu/k_B T} + \mathcal{O}\left(\frac{\log(N)}{N}\right) \quad (64)$$

In the representation with  $\mu$  as lead variable, the second law takes the form  $d\mu = d(u + pv - sT) = +vdp - sdT$  (Gibbs-Duhem relation) and the first derivatives yield the equations of state as

$$v = \left( \frac{\partial \mu}{\partial p} \right)_T = k_B T \frac{1}{p} \rightarrow pv = k_B T \quad (65)$$

$$s = - \left( \frac{\partial \mu}{\partial T} \right)_p = - \frac{\mu(p, T)}{T} + \frac{5}{2}k_B \rightarrow u = sT - pv + \mu = \frac{3}{2}k_B T \quad (66)$$

The second derivatives of  $\mu(p, T)$  represent again two conventional response functions: The isobaric specific heat

$$c_p = \left( \frac{\partial Q}{\partial T} \right)_p = T \left( \frac{\partial s}{\partial T} \right)_p = -T \left( \frac{\partial^2 \mu}{\partial T^2} \right)_p \quad (67)$$

and (once more) the isothermal compressibility

$$\kappa_T = \frac{1}{B_T} = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = -\frac{1}{v} \left( \frac{\partial^2 \mu}{\partial p^2} \right)_T \quad (68)$$

For the monoatomic gas,  $c_p = \frac{5}{2}k_B$  and  $\kappa_T = 1/p$ .  $\mu(p, T)$  is concave in both  $p$  and  $T$  (for any substance), because  $c_\mu$  and  $\kappa_T$  must be positive to assure thermodynamic and mechanical stability.

#### e. The pressure from the grand canonical ensemble.

The grand canonical partition function

$$e^{p(\mu, T)V/k_B T} = \mathcal{Z}_{GC}(V, \mu, T) = \sum_{\Gamma(V)} e^{[\mu N(\Gamma) - U(\Gamma)]/k_B T} \quad (69)$$

is most easily evaluated for the classical monoatomic gas as a trace over the canonical one:

$$\begin{aligned}
\mathcal{Z}_{GC}(V, \mu, T) &= \sum_{N=0}^{\infty} e^{\mu N/k_B T} \frac{1}{N!} \frac{1}{\Delta^{3N}} \left[ \left( \prod_i \int d\vec{r}_i \int d\vec{p}_i \right) e^{-\sum_i \vec{p}_i^2 / 2mk_B T} \right] \\
&= \sum_{N=0}^{\infty} e^{\mu N/k_B T} \mathcal{Z}_C(N, V, T) \\
&= \sum_{N=0}^{\infty} e^{\mu N/k_B T} \frac{1}{N!} \frac{1}{\Delta^{3N}} V^N \left( \sqrt{2m\pi k_B T} \right)^{3N} \\
&= \sum_{N=0}^{\infty} \frac{1}{N!} \left[ e^{\mu/k_B T} \frac{1}{\Delta^3} V \left( 2m\pi k_B T \right)^{3/2} \right]^N \\
&= \exp \left[ e^{\mu/k_B T} \frac{1}{\Delta^3} V \left( 2m\pi k_B T \right)^{3/2} \right]
\end{aligned} \tag{70}$$

In the last step we used the Taylor series expansion  $\exp(x) = \sum x^n/n!$ . Eq.(70) yields eq.(64), but now without any corrections of order  $\log(N)/N$ . Stirling's formula is not needed anymore. This illustrates once more that the ensembles are only equivalent in the thermodynamic limit.

With pressure as lead variable,  $p(\mu, T)$ , the thermodynamic landscape of section (d) is viewed from a slightly different perspective. The Gibbs-Duhem relation, takes the form  $p = sT - u + \mu\rho$  in per unit volume variables, (with  $s$  and  $u$  the entropy and energy per unit volume and  $\rho$  the density), and the second law reads  $dp = d(sT - u + \mu\rho) = +\rho d\mu + sdT$ , such that the equations of state are evaluated (using eq.(64)) as

$$\rho = \left( \frac{\partial p}{\partial \mu} \right)_T = \frac{p(\mu, T)}{k_B T} \rightarrow p = \rho k_B T \tag{71}$$

$$s = \left( \frac{\partial p}{\partial T} \right)_\mu = \left[ \frac{5}{2} - \frac{\mu}{k_B T} \right] \frac{p(\mu, T)}{T} \rightarrow u = sT - p + \mu\rho = \frac{3}{2} k_B T \tag{72}$$

The second derivatives of  $p(\mu, T)$  represent again response functions, but less familiar ones:

$$\left( \frac{\partial^2 p}{\partial \mu^2} \right)_T = \left( \frac{\partial \rho}{\partial \mu} \right)_T \tag{73}$$

tells us how the density of the system responds to a change in chemical potential at constant temperature. Consider, e.g., a cup of water in coexistence with a gas mixture containing air and water vapor. Suppose we change the humidity of the gas at constant the temperature. The chemical potential of the water vapor changes and by chemical equilibrium also the chemical potential of the water. An (in this case extremely) small change in water density is the response.

The second derivative with respect to temperature gives the specific heat at constant chemical potential

$$c_\mu = \left( \frac{\partial Q}{\partial T} \right)_\mu = T \left( \frac{\partial s}{\partial T} \right)_\mu = T \left( \frac{\partial^2 p}{\partial T^2} \right)_\mu \tag{74}$$

$c_\mu$  for the ideal gas depends explicitly on the value of the chemical potential,

$$c_\mu = \rho k_B \left[ \frac{15}{4} - 3 \frac{\mu}{k_B T} + \left( \frac{\mu}{k_B T} \right)^2 \right] \tag{75}$$

(per unit volume) and not as simple as, e.g.,

$$c_p = T \left( \frac{\partial s}{\partial T} \right)_p = -T \left( \frac{\partial^2 \mu}{\partial T^2} \right)_p = \frac{5}{2} k_B \tag{76}$$

(per particle) using  $\mu$  instead of  $p$  as lead variable,  $\mu(p, T)$ ; such that the second law takes the form  $d\mu = vdp - sdT$ .

Isobaric heating is what you do with water in an open pot on your kitchen stove.  $p$  and  $T$  are the control variables. The confusing part in this is that typically you see water evaporating, except when you cap the pot with a freely movable piston. During the entire process, the pressure remains constant inside the water by mechanical equilibrium imposed by the outside air.  $\mu$  is not constrained in this set-up and varies with temperature. The air can absorb water vapor (a change in humidity) but is typically not in chemical equilibrium with the water. A glass of water left alone empties out eventually by evaporation unless the humidity is 100%.

$c_\mu$  represents heating at constant  $\mu$ , i.e., while in chemical equilibrium with a particle reservoir instead of a pressure bath; particles are added and removed from the system during the heating in a manner such that  $\mu$  does not change;  $p$  now varies. Absorbed monolayers on surface in coexistence with a three dimensional gas above it, are an example of such a set-up, and will be discussed later (Langmuir absorption isotherms).

Finally, the third choice of lead variable for the grand canonical thermodynamic potential,  $T(\mu, p)$ , tells us that a system held in mechanical and chemical equilibrium with respectively a pressure and particle reservoir has a unique temperature.