

## School of Physics & Astronomy

### PHS4200/4021 Statistical Mechanics

#### Lecture 3: The Canonical and Grand Canonical Ensembles

##### 3.1 Introduction

The microcanonical ensemble, which was introduced in Lecture 2, is appropriate for closed systems, where the energy, volume and particle number are fixed. In principle the microcanonical ensemble can describe all statistical mechanical systems, since any system can be enlarged to include its surroundings (e.g., the heat bath can be included in the total closed system). However, it can be a non-trivial exercise to perform calculations with the microcanonical ensemble, since they often involve high dimensional volumes in phase space (see Example 2.2). By relaxing the constraints on fixed energy and particle number, we arrive at the canonical ensemble and grand canonical ensemble, respectively. As we shall see, these ensembles are better suited for practical calculations of a system's thermodynamics.

##### 3.2 The Canonical Ensemble

To establish the canonical ensemble we consider a system  $A$  at a fixed temperature  $T$ , volume  $V$ , and particle number  $N_A$ , which is able to exchange energy (but not particles) with a heat bath. The heat bath is considered to be a second system, with a large number of degrees of freedom ( $N_{Bath} \gg N_A$ ) that provides an infinitely large energy reservoir. Ultimately we are not interested in the heat bath; however, let us first consider the microcanonical ensemble of a isolated composite system, comprising the system of interest  $A$ , with energy  $E_A$ , and the heat bath having energy  $E_{Bath}$ . The total energy  $E$  of the combined system is:

$$E = E_A + E_{Bath} \quad (E_{Bath} \gg E_A). \quad (3.1)$$

The temperature  $T$  of system  $A$  is fixed by the much larger heat bath; however, the energy of system  $A$  is no longer fixed. The possible microstates with different energies are determined by a probability distribution, with those microstates having large energies being improbable. Since system  $A$  has a fixed  $V$  and  $N_A$ , the probability  $\mathcal{P}_i$  that it is in a certain microstate  $i$  with energy  $E_i$  is:

$$\mathcal{P}_i \propto \Omega_A(E_i). \quad (3.2)$$

Likewise the probability  $\mathcal{P}_i$  is determined by the number of microstates in the total system (comprising system  $A$  and the heat bath), for which  $A$  is in microstate  $i$  with energy  $E_i$ . This probability will also be equivalent to:

$$\mathcal{P}_i \propto \Omega_{Bath}(E_{Bath}) = \Omega_{Bath}(E - E_i) \quad \text{where} \quad E = E_i + E_{Bath}. \quad (3.3)$$

The entropy is defined as:

$$S_{Bath}(E_{Bath}, V, N) = k_B \ln \Omega_{Bath}(E_{Bath}) = k_B \ln \Omega_{Bath}(E - E_i). \quad (3.4)$$

Since  $E_i \ll E$ , we can expand Eq. (3.4) in a Taylor series:

$$\begin{aligned} S_{Bath}(E-E_i, V, N) &= k_B \ln \Omega_{Bath}(E - E_i) \\ &= k_B \ln \Omega_{Bath}(E) + \left( \frac{\partial (k_B \ln \Omega_{Bath})}{\partial E} \right)_{V, N} (-E_i) + O(E_i^2) \\ &\approx S_{Bath}(E) - \left( \frac{\partial S_{Bath}}{\partial E} \right)_{V, N} E_i. \end{aligned} \quad (3.5)$$

From Eq. (2.33) we have:

$$\left( \frac{\partial S_{Bath}}{\partial E} \right)_{N, V} = \frac{1}{T}. \quad (3.6)$$

Hence Eq. (3.5) can be written as:

$$k_B \ln \Omega_{Bath}(E - E_i) \approx k_B \ln \Omega_{Bath}(E) - \frac{E_i}{T} \Rightarrow \Omega_{Bath}(E - E_i) \approx \Omega_{Bath}(E) e^{-E_i/k_B T}. \quad (3.7)$$

Notice how the number of microstates decreases exponentially with  $E_i$  as one would expect! Using Eq. (3.3) allows us to write the probability  $\mathcal{P}_i$  for system  $A$  to be in microstate  $i$  with energy  $E_i$  as:

$$\mathcal{P}_i \propto \Omega_{Bath}(E - E_i) \propto e^{-E_i/k_B T} \quad \text{or} \quad \mathcal{P}_i = C e^{-E_i/k_B T}, \quad (3.8)$$

where  $C$  is the normalisation constant determined from insisting that  $\sum_i \mathcal{P}_i = 1$ . Imposing this normalisation condition we obtain:

$$\sum_i \mathcal{P}_i = \sum_i C e^{-E_i/k_B T} = 1 \Rightarrow C = \frac{1}{\sum_i e^{-E_i/k_B T}}, \quad (3.9)$$

so that the correctly normalised probability is:

$$\mathcal{P}_i \equiv \mathcal{P}(E_i) = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}. \quad (3.10)$$

For a continuous probability distribution in  $\Gamma$ -space, we replace  $\mathcal{P}_i$  with the canonical phase space density. For indistinguishable particles this is given by:

$$\rho(\mathbf{q}, \mathbf{p}) = \frac{e^{-H(\mathbf{q}, \mathbf{p})/k_B T}}{\frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{-H(\mathbf{q}, \mathbf{p})/k_B T} d^{3N} q d^{3N} p}. \quad (3.11)$$

At this point we introduce one of the central concepts in statistical mechanics; namely the partition function. The canonical partition function<sup>1</sup> corresponding to Eqs. (3.10) and (3.11) are denoted by:

$$Z(\beta, V, N) = \sum_i e^{-\beta E_i}, \quad (3.12)$$

and

$$Z(\beta, V, N) = \frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N} q d^{3N} p. \quad (3.13)$$

where  $\beta = 1/k_B T$  and we have set  $H(\mathbf{q}, \mathbf{p}) = E$ .

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<sup>1</sup> The symbol  $Z$  is chosen to denote the canonical partition function, since it is the first letter of the German word *Zustandsumme*, referring to the “state sum” or sum over the microstates of the system.

Equations (3.10) - (3.13) are of sufficient importance that we now rederive them based on the fundamental definition of entropy in Eq. (2.54). We will do this for the continuous canonical phase space density, with the discrete case left as an exercise. We start with the definition of entropy in terms of an ensemble average:

$$S = -\langle k_B \ln \rho(\mathbf{q}, \mathbf{p}) \rangle = \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) (-k_B \ln \rho(\mathbf{q}, \mathbf{p})) d^{3N} \mathbf{q} d^{3N} \mathbf{p}. \quad (3.14)$$

We now impose the following constraints on the system, i.e.,

$$\frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) d^{3N} \mathbf{q} d^{3N} \mathbf{p} = 1, \quad (3.15)$$

and

$$\langle H(\mathbf{q}, \mathbf{p}) \rangle = \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) H(\mathbf{q}, \mathbf{p}) d^{3N} \mathbf{q} d^{3N} \mathbf{p} = \langle E \rangle \equiv U. \quad (3.16)$$

From Eq. (3.16) we see that the internal energy  $U$  is just the ensemble average of  $H(\mathbf{q}, \mathbf{p}) = E$ . We want to extremise Eq. (3.14) subject to the constraints (3.15) and (3.16). This is a problem suited to the method of Lagrange multipliers (see Appendix A). To proceed, we form an auxiliary function:

$$\begin{aligned} \mathcal{f}(\rho, \lambda_1, \lambda_2) &= -\langle k_B \ln \rho(\mathbf{q}, \mathbf{p}) \rangle + \lambda_1 \left( \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) d^{3N} \mathbf{q} d^{3N} \mathbf{p} \right) + \lambda_2 \langle H(\mathbf{q}, \mathbf{p}) \rangle \\ &= \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) (-k_B \ln \rho(\mathbf{q}, \mathbf{p})) d^{3N} \mathbf{q} d^{3N} \mathbf{p} + \lambda_1 \left( \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) d^{3N} \mathbf{q} d^{3N} \mathbf{p} \right) \\ &\quad + \lambda_2 \left( \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) H(\mathbf{q}, \mathbf{p}) d^{3N} \mathbf{q} d^{3N} \mathbf{p} \right), \end{aligned} \quad (3.17)$$

where  $\lambda_1$  and  $\lambda_2$  are Lagrange multipliers, which are to be determined. The extremum of the auxiliary function  $\mathcal{f}(\rho, \lambda_1, \lambda_2)$  is given by:

$$\frac{\partial \mathcal{f}(\rho, \lambda_1, \lambda_2)}{\partial \rho} = 0, \quad (3.18)$$

from which we obtain:

$$\frac{1}{N! h^{3N}} \int_{\Gamma(E)} [-k_B (\ln \rho(\mathbf{q}, \mathbf{p}) + 1) + \lambda_1 + \lambda_2 H(\mathbf{q}, \mathbf{p})] d^{3N} \mathbf{q} d^{3N} \mathbf{p} = 0. \quad (3.19)$$

Equation (3.19) is satisfied by a suitable choice of the Lagrange multipliers, i.e., we require:

$$-k_B (\ln \rho(\mathbf{q}, \mathbf{p}) + 1) + \lambda_1 + \lambda_2 H(\mathbf{q}, \mathbf{p}) = 0, \quad (3.20)$$

or

$$\ln \rho(\mathbf{q}, \mathbf{p}) = -1 + \frac{\lambda_1}{k_B} + \frac{\lambda_2 H(\mathbf{q}, \mathbf{p})}{k_B}. \quad (3.21)$$

We could choose to absorb Boltzmann's constant  $k_B$  into the Lagrange multipliers; however, in what follows we will make  $k_B$  explicit. From Eq. (3.21) we see that:

$$\rho(\mathbf{q}, \mathbf{p}) = e^{-1 + \lambda_1/k_B} e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} = C e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B}. \quad (3.22)$$

The constant  $C$  is determined from the normalisation condition (3.15), i.e.,

$$\begin{aligned} \frac{1}{N!h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) d^{3N}q d^{3N}p &= \frac{C}{N!h^{3N}} \int_{\Gamma(E)} e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N}q d^{3N}p = 1 \\ \Rightarrow C &= \frac{1}{\frac{1}{N!h^{3N}} \int_{\Gamma(E)} e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N}q d^{3N}p}. \end{aligned} \quad (3.23)$$

Hence the correctly normalised density function is:

$$\rho(\mathbf{q}, \mathbf{p}) = C e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} = \frac{e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B}}{\frac{1}{N!h^{3N}} \int_{\Gamma(E)} e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N}q d^{3N}p}. \quad (3.24)$$

The second Lagrange multiplier  $\lambda_2$  can be determined from Eq. (3.16). In Example 3.1 we will prove that  $\lambda_2 = -1/T$ , in which case:

$$\frac{\lambda_2}{k_B} = -\frac{1}{k_B T} = -\beta. \quad (3.25)$$

Remarkably this shows that the Lagrange multiplier is related to the usual  $\beta$ -factor, which was introduced earlier simply for notational convenience. In fact we could have defined the second Lagrange multiplier as  $\beta = -\lambda_2/k_B$ , in which case this Lagrange multiplier is really  $\beta = 1/k_B T$ . We can now write Eq. (3.24) in the conventional form, i.e.,

$$\rho(\mathbf{q}, \mathbf{p}) = C e^{-\beta H(\mathbf{q}, \mathbf{p})} = \frac{e^{-\beta H(\mathbf{q}, \mathbf{p})}}{\frac{1}{N!h^{3N}} \int_{\Gamma(E)} e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N}q d^{3N}p} \quad (\beta = 1/k_B T). \quad (3.26)$$

We also note that the partition function is “just” the inverse of the normalisation constant  $C$ , i.e.,

$$Z(\beta, V, N) = \frac{1}{N!h^{3N}} \int_{\Gamma(E)} e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N}q d^{3N}p = \frac{1}{C}. \quad (3.27)$$

so that we can also write the normalised probability density as:

$$\rho(\mathbf{q}, \mathbf{p}) = C e^{-\beta H(\mathbf{q}, \mathbf{p})} = \frac{1}{Z(\beta, V, N)} e^{-\beta H(\mathbf{q}, \mathbf{p})}. \quad (3.28)$$

**Example 3.1:** Using the constraint given by Eq. (3.16) prove that the Lagrange multiplier  $\lambda_2 = -1/T$ , and hence  $\beta = 1/k_B T$ .

### Solution

We start with the canonical partition function, defined in terms of the Lagrange multiplier  $\lambda_2$ , i.e.,

$$Z(\lambda_2, V, N) = \frac{1}{N!h^{3N}} \int_{\Gamma(E)} e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N}q d^{3N}p.$$

Differentiating with respect to  $\lambda_2$  we obtain:

$$Z'(\lambda_2) = \frac{\partial Z(\lambda_2, V, N)}{\partial \lambda_2} = \frac{1}{N! h^{3N}} \int \frac{1}{k_B} H(\mathbf{q}, \mathbf{p}) e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N} q d^{3N} p.$$

The internal energy is defined by Eq. (3.16), where the probability density  $\rho(\mathbf{q}, \mathbf{p})$  given by Eq. (3.24), i.e.,

$$\begin{aligned} U = \langle H(\mathbf{q}, \mathbf{p}) \rangle &= \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) H(\mathbf{q}, \mathbf{p}) d^{3N} q d^{3N} p \\ &= \frac{\frac{1}{N! h^{3N}} \int_{\Gamma(E)} H(\mathbf{q}, \mathbf{p}) e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N} q d^{3N} p}{\frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N} q d^{3N} p}. \end{aligned}$$

Using the preceding results we can now express the condition for the determination of  $\lambda_2$  as:

$$\langle H(\mathbf{q}, \mathbf{p}) \rangle = \frac{k_B Z'(\lambda_2)}{Z(\lambda_2)} = U.$$

To proceed we exploit the definition of entropy (3.14), which we write in terms of the partition function as:

$$\begin{aligned} S &= -\langle k_B \ln \rho(\mathbf{q}, \mathbf{p}) \rangle \\ &= \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}) (-k_B \ln \rho(\mathbf{q}, \mathbf{p})) d^{3N} q d^{3N} p. \\ &= -k_B \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \frac{e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B}}{Z(\lambda_2)} \ln \left( \frac{e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B}}{Z(\lambda_2)} \right) d^{3N} q d^{3N} p \\ &= -k_B \frac{1}{Z(\lambda_2)} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} \left[ \frac{\lambda_2}{k_B} H(\mathbf{q}, \mathbf{p}) - \ln Z(\lambda_2) \right] d^{3N} q d^{3N} p \\ &= -\lambda_2 \frac{1}{Z(\lambda_2)} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} H(\mathbf{q}, \mathbf{p}) e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N} q d^{3N} p + k_B \frac{\ln Z(\lambda_2)}{Z(\lambda_2)} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{\lambda_2 H(\mathbf{q}, \mathbf{p})/k_B} d^{3N} q d^{3N} p \\ &= -\lambda_2 \langle H(\mathbf{q}, \mathbf{p}) \rangle + k_B \ln Z(\lambda_2). \end{aligned}$$

In arriving at this result we have utilised the definition of the normalisation condition and ensemble average [see Eqs. (3.15) and (3.16)]. The entropy can therefore be written as:

$$S = -\lambda_2 \langle H(\mathbf{q}, \mathbf{p}) \rangle + k_B \ln Z(\lambda_2) = -\lambda_2 k_B \frac{Z'(\lambda_2)}{Z(\lambda_2)} + k_B \ln Z(\lambda_2) = k_B \left( -\lambda_2 \frac{Z'(\lambda_2)}{Z(\lambda_2)} + \ln Z(\lambda_2) \right).$$

Finally, we make the connection with thermodynamics by using the definition of temperature. From Eq. (2.33) we have:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V, N} = \left( \frac{\partial S}{\partial \lambda_2} \right)_{V, N} \left( \frac{\partial \lambda_2}{\partial U} \right)_{V, N} = \frac{\left( \frac{\partial S}{\partial \lambda_2} \right)_{V, N}}{\left( \frac{\partial U}{\partial \lambda_2} \right)_{V, N}}.$$

The derivatives are given by:

$$\left( \frac{\partial S}{\partial \lambda_2} \right)_{V, N} = -k_B \frac{Z'(\lambda_2)}{Z(\lambda_2)} - k_B \lambda_2 \frac{\partial}{\partial \lambda_2} \left( \frac{Z'(\lambda_2)}{Z(\lambda_2)} \right) + k_B \frac{Z'(\lambda_2)}{Z(\lambda_2)} = -k_B \lambda_2 \frac{\partial}{\partial \lambda_2} \left( \frac{Z'(\lambda_2)}{Z(\lambda_2)} \right),$$

and

$$\left( \frac{\partial U}{\partial \lambda_2} \right)_{V,N} = k_B \frac{\partial}{\partial \lambda_2} \left( \frac{Z'(\lambda_2)}{Z(\lambda_2)} \right).$$

Combining these results we obtain:

$$\frac{1}{T} = \frac{\left( \frac{\partial S}{\partial \lambda_2} \right)_{V,N}}{\left( \frac{\partial U}{\partial \lambda_2} \right)_{V,N}} = \frac{-k_B \lambda_2 \frac{\partial}{\partial \lambda_2} \left( \frac{Z'(\lambda_2)}{Z(\lambda_2)} \right)}{k_B \frac{\partial}{\partial \lambda_2} \left( \frac{Z'(\lambda_2)}{Z(\lambda_2)} \right)} = -\lambda_2.$$

Hence the Lagrange multiplier is:

$$\lambda_2 = -\frac{1}{T} \quad \Rightarrow \quad \frac{\lambda_2}{k_B} = -\frac{1}{k_B T} = -\beta \quad \text{or} \quad \beta = \frac{1}{k_B T}.$$

**Exercise 3.1:** Repeat the calculation leading to Eqs. (3.26) - (3.28) for the case of a discrete probability function  $\mathcal{P}_i$ .

### 3.2.1 Helmholtz Free Energy

In the microcanonical ensemble the state of the system has a fixed energy  $E = E(S, V, N)$ , with the temperature  $T$ , pressure  $p$ , and chemical potential  $\mu$  all being derived quantities (see Sec. 2.3.1). However, in the canonical ensemble the temperature is fixed and the energy is allowed to vary. In this case the change of independent variable from  $S$  to  $T$  is achieved by a Legendre transformation (see Sec. 1.3), in which energy, as the independent variable, is replaced with the Helmholtz free energy  $F$ , where:

$$F = F(T, V, N) = U - TS \quad (U = \langle H \rangle). \quad (3.29)$$

From Example 3.1 we also have the relationship between entropy, the internal energy and the partition function, i.e.,

$$S = k_B \beta \langle H(\mathbf{q}, \mathbf{p}) \rangle + k_B \ln Z(\beta, V, N) = \frac{U}{T} + k_B \ln Z(\beta, V, N). \quad (3.30)$$

Rearranging Eq. (3.30) and comparing with Eq. (3.29), we see that the free energy is given by:

$$S = \frac{U}{T} + k_B \ln Z(\beta, V, N) \quad \Rightarrow \quad -k_B T \ln Z(T, V, N) = U - TS, \quad (3.31)$$

or

$$F(T, V, N) = -k_B T \ln Z(T, V, N). \quad (3.32)$$

Equation (3.32) is central to our treatment of statistical mechanics, since all other thermodynamic properties are derived from the Helmholtz free energy, e.g.,

$$p = - \left( \frac{\partial F}{\partial V} \right)_{T,N}, \quad S = - \left( \frac{\partial F}{\partial T} \right)_{V,N}, \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}, \quad (3.33)$$

with

$$U = \langle H \rangle = F + TS \quad \text{and} \quad G = F + pV. \quad (3.34)$$

The canonical ensemble is often more convenient for calculating the thermodynamic properties

of a system. To illustrate this point, we repeat the calculation of the equation of state for an ideal gas, which was carried out in Examples 2.2 and 2.3 for the microcanonical ensemble.

**Example 3.2:** Calculate the thermodynamic properties of an ideal monatomic gas in the canonical ensemble.

### Solution

The Hamiltonian for  $N$  non-interacting indistinguishable monoatomic gas atoms, each of mass  $m$ , confined to a volume  $V$  in 3-space is:

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}.$$

The corresponding partition function (3.13) is:

$$Z(\beta, V, N) = \frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N}q d^{3N}p.$$

Since the Hamiltonian does not depend on  $\{q_i\}$  ( $i = 1, 2, \dots, 3N$ ), we can immediately integrate over the coordinates to get:

$$Z(\beta, V, N) = \frac{V^N}{N! h^{3N}} \int_{\Gamma(E)} e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N}p = \frac{V^N}{N! h^{3N}} \prod_{i=1}^{3N} \int_{-\infty}^{+\infty} e^{-\beta p_i^2 / 2m} dp_i.$$

The remaining integrals are real-valued Gaussian integrals, which are evaluated using:

$$\int_{-\infty}^{+\infty} e^{-\frac{1}{2}\alpha x^2} dx = \sqrt{\frac{2\pi}{\alpha}}.$$

Hence the partition function is:

$$Z(\beta, V, N) = \frac{V^N}{N! h^{3N}} \prod_{i=1}^{3N} \int_{-\infty}^{+\infty} e^{-\beta p_i^2 / 2m} dp_i = \frac{V^N}{N! h^{3N}} \prod_{i=1}^{3N} \left( \frac{2\pi}{\beta/m} \right)^{1/2} = \frac{V^N}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2}.$$

The Helmholtz free energy is given by:

$$F(T, V, N) = -k_B T \ln Z(T, V, N) = -k_B T \left[ N \ln V - \ln N! + N \ln \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right].$$

Using Stirling's approximation (see Appendix B, Lecture 1),  $\ln N! \approx N \ln N - N$ , we obtain:

$$\begin{aligned} F(T, V, N) &= -k_B T \left[ N \ln V - \ln N! + N \ln \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \\ &= -k_B T \left[ N \ln V - N \ln N + N + N \ln \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \\ &= -N k_B T \left[ 1 + \ln \left\{ \left( \frac{V}{N} \right) \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \right]. \end{aligned}$$

The thermodynamic functions are calculated from Eqs. (3.33) and (3.34), e.g.,

and

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_B T}{V} \Rightarrow pV = Nk_B T = nRT.$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B \left[ \frac{5}{2} + \ln \left\{ \left( \frac{V}{N} \right) \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \right].$$

The entropy calculated using the canonical ensemble is identical to Eq. (2.44), which was arrived at using the microcanonical ensemble, where the constant in Eq. (2.44) is  $\sigma = h^3$ .

**Exercise 3.2:** Calculate the chemical potential  $\mu$  of an ideal gas using the Helmholtz free energy and Eq. (3.33).

**Exercise 3.3:** Repeat the calculation in Example 3.2 for an ultrarelativistic ideal gas, whose Hamiltonian is given by:

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^N E_i \quad \text{where} \quad E_i = \sqrt{|\mathbf{p}_i|^2 c^2 + m_0^2 c^4} \rightarrow |\mathbf{p}_i| c \quad (|\mathbf{p}_i| c \gg m_0 c^2).$$

### 3.2.2 Energy Fluctuations in the Canonical Ensemble

The spread in energy about the mean value is determined by the second moment:

$$\sigma_H^2 = \langle (H - \langle H \rangle)^2 \rangle = \langle H^2 \rangle - \langle H \rangle^2, \quad \text{with} \quad \langle H(\mathbf{q}, \mathbf{p}) \rangle = \langle E \rangle = U, \quad (3.35)$$

where

$$U = \langle H(\mathbf{q}, \mathbf{p}) \rangle = \frac{1}{Z(\beta)} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} H(\mathbf{q}, \mathbf{p}) e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N} q d^{3N} p = -\frac{1}{Z(\beta)} \frac{\partial Z(\beta)}{\partial \beta} = -\frac{\partial \ln Z(\beta)}{\partial \beta}. \quad (3.36)$$

We also note that:

$$\begin{aligned} \frac{\partial U}{\partial \beta} &= \frac{\partial \langle H(\mathbf{q}, \mathbf{p}) \rangle}{\partial \beta} = \frac{\partial}{\partial \beta} \left( \frac{1}{Z(\beta)} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} H(\mathbf{q}, \mathbf{p}) e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N} q d^{3N} p \right) \\ &= -\frac{1}{Z(\beta)} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} H^2(\mathbf{q}, \mathbf{p}) e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N} q d^{3N} p \\ &\quad + \left( \frac{1}{Z(\beta)} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} H(\mathbf{q}, \mathbf{p}) e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N} q d^{3N} p \right)^2 \\ &= -\langle H^2 \rangle + \langle H \rangle^2. \end{aligned} \quad (3.37)$$

Equation (3.37) is rearranged to give:

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = -\frac{\partial U}{\partial \beta} = \frac{\partial^2 \ln Z(\beta)}{\partial \beta^2}. \quad (3.38)$$

We can also express Eq. (3.38) in terms of the heat capacity of the system (at constant  $V$ ), since:

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = -\left( \frac{\partial U}{\partial \beta} \right)_V = -\left( \frac{\partial U}{\partial T} \right)_V \left( \frac{\partial \beta}{\partial T} \right)^{-1} = k_B T^2 \left( \frac{\partial U}{\partial T} \right)_V = k_B T^2 C_V, \quad (3.39)$$



where the heat capacity measures the change in internal energy with temperature. Equation (3.39) shows that the fluctuations in energy are directly related to the heat capacity; this important result is an example of the fluctuation-dissipation theorem<sup>2</sup>, which relates the fluctuations (in this case the energy fluctuations) to the response of the system. We can also quantify the magnitude of the energy fluctuations in the canonical ensemble. The relative energy fluctuations are determined by the ratio

$$\frac{\sigma_H}{\langle H \rangle} = \frac{\sqrt{\langle H^2 \rangle - \langle H \rangle^2}}{\langle H \rangle} = \frac{1}{U} \sqrt{k_B T^2 C_V} \quad (3.40)$$

Since both the internal energy and heat capacity are extensive thermodynamic parameters, we have  $U \propto N$  and  $C_V \propto N$ , and Eq. (3.40) is expressed in terms of the particle number as:

$$\frac{\sigma_H}{\langle H \rangle} = \frac{1}{U} \sqrt{k_B T^2 C_V} \propto \frac{1}{N} \sqrt{k_B T^2 N} \propto \frac{1}{\sqrt{N}}. \quad (3.41)$$

Since  $N \sim 10^{24}$ , the relative fluctuations  $N^{-1/2} \sim 10^{-12}$  are tiny, and not observable in general. As  $N \rightarrow \infty$  only the mean energy is relevant in the canonical ensemble. Indeed in this thermodynamic limit the canonical ensemble approaches the  $\delta$ -function energy distribution of the microcanonical ensemble. In Sec. 3.3 we will explore this relationship in more detail.

### 3.3 Relationship between the Canonical and Microcanonical Ensembles

As we have seen in Example 3.2 the canonical ensemble gives the same results as the microcanonical ensemble. This is a general result, whence the two ensembles are indeed equivalent.

The probability of finding a system in the state  $(\mathbf{q}, \mathbf{p})$  is:

$$d\mathcal{P} = \frac{1}{N! h^{3N}} \rho(\mathbf{q}, \mathbf{p}) d^{3N}q d^{3N}p = \frac{1}{N! h^{3N}} \frac{e^{-\beta H(\mathbf{q}, \mathbf{p})}}{Z(\beta, V, N)} d^{3N}q d^{3N}p. \quad (3.42)$$

On the energy hypersurface  $H(\mathbf{q}, \mathbf{p}) = E$ , the probability is a constant; hence the probability of finding the system with energy between  $E$  and  $E + \Delta E$  is given by:

$$d\mathcal{P}(E) = \frac{1}{Z(\beta, V, N)} e^{-\beta E} \frac{1}{N! h^{3N}} \int_{E \leq H(\mathbf{q}, \mathbf{p}) \leq E + \Delta E} d^{3N}q d^{3N}p. \quad (3.43)$$

The integral in Eq. (3.43) was evaluated in Lecture 2 [see Eqs. (2.26) and (2.27)]; it is just the volume between two energy hypersurfaces with energy  $E$  and  $E + \Delta E$ , i.e.,

$$\frac{1}{N! h^{3N}} \int_{E \leq H(\mathbf{q}, \mathbf{p}) \leq E + \Delta E} d^{3N}q d^{3N}p = \omega(E + \Delta E) - \omega(E) = \Delta\omega. \quad (3.44)$$

For  $\Delta E \ll E$ , Eq. (3.44) becomes:

$$\Delta\omega = \left( \frac{\partial \omega}{\partial E} \right)_{N, V} \Delta E = g(E) \Delta E \Rightarrow g(E) = \frac{\partial \omega(E)}{\partial E}. \quad (3.45)$$

where  $g(E)$  is the density of states at energy  $E$ . Note the change in notation from  $\sigma(E)$  in Eq.

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<sup>2</sup> For a general discussion of the fluctuation-dissipation theorem see e.g.,

[https://en.wikipedia.org/wiki/Fluctuation-dissipation\\_theorem](https://en.wikipedia.org/wiki/Fluctuation-dissipation_theorem)  
<http://www.mrc-lmb.cam.ac.uk/genomes/madanm/balaji/kubo.pdf>

(2.27) to  $g(E)$  in Eq. (3.45); this is in keeping with the conventional notation in quantum statistical mechanics, where  $g$  is used to denote the degeneracy of a quantum system. The probability of finding a macrostate between two energy hypersurfaces with energy  $E$  and  $E + \Delta E$  is:

$$d\mathcal{P}(E) = \frac{1}{Z(\beta, V, N)} e^{-\beta E} g(E) dE \quad (3.46)$$

The partition function (3.27) can be obtained from Eq. (3.46), since:

$$\int_0^\infty d\mathcal{P}(E) = 1 \quad \Rightarrow \quad Z(\beta, V, N) = \int_0^\infty g(E) e^{-\beta E} dE. \quad (3.47)$$

Equation (3.47) shows that the canonical partition function is the Laplace transform<sup>3</sup> of the density of states function  $g(E)$ . Formally, we can write the Laplace transform and its inverse as:

$$Z(\tilde{\beta}) = \mathcal{L}\{g(E)\} = \int_0^\infty g(E) e^{-\tilde{\beta} E} dE \quad \Leftrightarrow \quad g(E) = \mathcal{L}^{-1}\{Z(\tilde{\beta})\} = \frac{1}{2\pi i} \int_{\beta-i\infty}^{\beta+i\infty} Z(\tilde{\beta}) e^{\beta E} d\tilde{\beta}, \quad (3.48)$$

where we treat  $\beta$  as a complex variable, and  $g(E)$  is calculated by evaluating a contour integral in the complex  $\tilde{\beta}$ -plane, whence we employ the analytic continuation  $\beta \rightarrow \tilde{\beta} = \beta + i\alpha$ .

We can use Eq. (3.48) to show the formal equivalence of the microcanonical and canonical ensembles. We start with the density of states for the microcanonical ensemble, which we write as:

$$\Omega(E) = \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \delta(H(\mathbf{q}, \mathbf{p}) - E) d^{3N}q d^{3N}p \quad (3.49)$$

Using Eq. (3.47) or (3.48) we have:

$$\begin{aligned} Z(\beta, V, N) &= \int_0^\infty \Omega(E) e^{-\beta E} dE \\ &= \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \left( \int_0^\infty \delta(H(\mathbf{q}, \mathbf{p}) - E) e^{-\beta E} dE \right) d^{3N}q d^{3N}p \\ &= \frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{-\beta H(\mathbf{q}, \mathbf{p})} d^{3N}q d^{3N}p, \end{aligned} \quad (3.50)$$

where we have used the sifting property of the Dirac delta function (see Appendix B, Lecture 2). This demonstrates that the canonical partition function is the Laplace transform of the density of states of the microcanonical ensemble.

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<sup>3</sup> The unilateral Laplace transform of a function  $f(t)$  is defined as:

$$F(s) = \mathcal{L}\{f(t)\} = \int_0^\infty f(t) e^{-st} dt \quad (s = \sigma + i\omega)$$

The corresponding inverse Laplace transform is defined via a complex contour integral, i.e.,

$$f(t) = \mathcal{L}^{-1}\{F(s)\} = \frac{1}{2\pi i} \lim_{T \rightarrow \infty} \int_{\gamma-iT}^{\gamma+iT} f(t) e^{st} ds.$$

The Laplace transform may be considered as a generalisation of the Fourier transform, see e.g.,

### 3.4 The Grand Canonical Ensemble

The canonical ensemble can be further generalised to the grand canonical ensemble (also known as the macrocanonical ensemble), which accounts for both energy and particle fluctuations, i.e., both heat and particles are exchanged with a heat bath and particle reservoir. In the grand canonical ensemble the relevant thermodynamic parameters are the temperature  $T$ , volume  $V$ , and chemical potential  $\mu$  of the system. The grand canonical ensemble can be derived via a route similar to that employed for the canonical ensemble (see Sec. 3.2). We consider a system  $A$  with a given temperature  $T$ , volume  $V$ , and chemical potential  $\mu$ , which is able to exchange both energy and particles with a heat bath and particle reservoir. The heat bath and particle reservoir, henceforth referred to collectively as the “reservoir” (and denoted by  $R$ ) is considered to be a second system, with a large number of degrees of freedom that provides an infinitely large energy and particle reservoir. As with the canonical ensemble, we are not particularly interested in the reservoir. The microcanonical ensemble can be applied to the composite system comprising the system of interest  $A$ , with energy  $E_A$ , and particle number  $N_A$ , interacting with the reservoir  $R$ . The total energy  $E$  and particle number  $N$  of the combined system is:

$$E = E_A + E_R \quad (E_R \gg E_A) \quad \text{and} \quad N = N_A + N_R \quad (N_R \gg N_A). \quad (3.51)$$

The temperature  $T$  and chemical potential  $\mu$  of system  $A$  is fixed by the much larger reservoir; however, the energy and particle number of system  $A$  is no longer fixed. The probability  $\mathcal{P}_i(N_A)$  of finding the system in the microstate with energy  $E_A = E_i$  and particle number  $N_A = 0, 1, 2, \dots, N$ , is determined by the number of microstates in the total system. This probability is also equivalent to:

$$\mathcal{P}_i(N_A) \propto \Omega_R(E_R, N_R) = \Omega_R(E - E_i, N - N_A), \quad (3.52)$$

where  $E = E_i + E_R$  and  $N = N_A + N_R$ . The entropy is defined as:

$$S_R(E_R, V, N_R) = k_B \ln \Omega_R(E_R, N_R) = k_B \ln \Omega_R(E - E_i, N - N_A). \quad (3.53)$$

Since  $E_i \ll E$  and  $N_A \ll N$  we can expand Eq. (3.53) in a Taylor series:

$$\begin{aligned} S_R(E - E_i, V, N - N_A) &= k_B \ln \Omega_R(E - E_i, N - N_A) \\ &= k_B \ln \Omega_R(E, N) + \left( \frac{\partial(k_B \ln \Omega_R)}{\partial E} \right)_{V, N} (-E_i) + \left( \frac{\partial(k_B \ln \Omega_R)}{\partial N} \right)_{E, V} (-N_A) + \dots \\ &\approx S_R(E, V, N) - \left( \frac{\partial S_R}{\partial E} \right)_{V, N} E_i - \left( \frac{\partial S_R}{\partial N} \right)_{E, V} N_A. \end{aligned} \quad (3.54)$$

From Eq. (2.33) we have:

$$\left( \frac{\partial S_R}{\partial E} \right)_{V, N} = \frac{1}{T} \quad \text{and} \quad \left( \frac{\partial S_R}{\partial N} \right)_{E, V} = -\frac{\mu}{T}. \quad (3.55)$$

Hence Eq. (3.54) can be written as:

$$\begin{aligned} k_B \ln \Omega_R(E - E_i, N - N_A) &\approx k_B \ln \Omega_R(E, N) - \frac{E_i}{T} + \frac{\mu N_A}{T} \\ \Rightarrow \Omega_R(E - E_i, N - N_A) &\approx \Omega_R(E, N) \exp \left( -\frac{1}{k_B T} (E_i - \mu N_A) \right). \end{aligned} \quad (3.56)$$

Using Eq. (3.52) allows us to express the probability  $\mathcal{P}_i(N_A)$  for system  $A$  to be in microstate  $i$  with energy  $E_i$  and particle number  $N_A$  as:

$$\mathcal{P}_i(N_A) \propto \Omega_R(E - E_i - N_A) \propto e^{-E_i/k_B T + \mu N_A/k_B T} \quad \text{or} \quad \mathcal{P}_i(N_A) = C e^{-\beta(E_i - \mu N_A)}, \quad (3.57)$$

where  $\beta = 1/k_B T$  and  $C$  is the normalisation constant determined from insisting that  $\sum_{N_A, i} \mathcal{P}_i(N_A) = 1$ . Imposing this normalisation condition we obtain:

$$\sum_{N_A, i} \mathcal{P}_i(N_A) = \sum_{N_A} \sum_i C e^{-\beta(E_i - \mu N_A)} = 1 \quad \Rightarrow \quad C = \frac{1}{\sum_{N_A} \sum_i e^{-\beta(E_i - \mu N_A)}}, \quad (3.58)$$

so that the correctly normalised probability is:

$$\mathcal{P}_i(N_A) \equiv \mathcal{P}(E_i, N_A) = \frac{e^{-\beta(E_i - \mu N_A)}}{\sum_{N_A} \sum_i e^{-\beta(E_i - \mu N_A)}}. \quad (3.59)$$

For a continuous probability distribution in  $\Gamma$ -space, we replace  $\mathcal{P}_i(N_A)$  with the grand canonical phase space density. For  $N$  indistinguishable particles this is given by:

$$\rho(\mathbf{q}, \mathbf{p}, N) = \frac{e^{-\beta(H(\mathbf{q}, \mathbf{p}) - \mu N)}}{\sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{-\beta(H(\mathbf{q}, \mathbf{p}) - \mu N)} d^{3N} q d^{3N} p}. \quad (3.60)$$

Note that there are no restrictions on the number of particles  $N$ . The grand canonical partition function corresponding to Eq. (3.59) and Eq. (3.60) is denoted by:

$$\Xi(\beta, V, \mu) = \sum_{N=0}^{\infty} \sum_i e^{-\beta(E_i - \mu N)}, \quad (3.61)$$

and

$$\Xi(\beta, V, \mu) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int_{\Gamma(E)} e^{-\beta(H(\mathbf{q}, \mathbf{p}) - \mu N)} d^{3N} q d^{3N} p. \quad (3.62)$$

It is common to define a fugacity<sup>4</sup> parameter  $\mathbf{z} = e^{\beta\mu}$ , so that, for example, Eq. (3.61) can be re-written as:

$$\Xi(\beta, V, \mathbf{z}) = \sum_{N=0}^{\infty} \sum_i \mathbf{z}^N e^{-\beta E_i} = \sum_{N=0}^{\infty} \mathbf{z}^N Z(\beta, V, N). \quad (3.63)$$

Equation (3.63) shows that the grand canonical ensemble is a weighted sum of canonical partition functions, with the weighting factor given by the fugacity. As with the canonical ensemble we can derive the relevant thermodynamics from the grand partition function. For example, the Helmholtz free energy  $F(T, V, N)$  is generalised to the grand potential  $\Phi(T, V, \mu)$ , defined by:

$$\Phi = \Phi(T, V, \mu) = F - \mu N = U - TS - \mu N \quad (U = \langle H \rangle). \quad (3.64)$$

and

$$\Phi = \Phi(T, V, \mu) = -k_B T \ln \Xi(T, V, \mu). \quad (3.65)$$

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<sup>4</sup> The concept of fugacity was first introduced in chemical thermodynamics to reconcile the behaviour of real gases with ideal gases. At low pressures the fugacity of a gas is equal to the gas pressure. Fugacity plays an important role in understanding chemical processes. The chemical potential is related to the fugacity parameter via  $\mu = k_B T \ln z$ , see e.g., <https://en.wikipedia.org/wiki/Fugacity>

Other thermodynamic quantities can be derived from the internal energy:

$$U = -\frac{\partial \ln \Xi(T, V, \mu)}{\partial \beta}. \quad (3.66)$$

**Example 3.3:** Calculate the thermodynamic properties of an ideal monatomic gas in the grand canonical ensemble.

**Solution**

We start with the canonical partition function derived in Example 3.2, i.e.,

$$Z(\beta, V, N) = \frac{V^N}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} = \frac{1}{N!} \left[ V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right]^N.$$

Hence the grand canonical partition function (3.63) is:

$$\Xi(\beta, V, z) = \sum_{N=0}^{\infty} z^N Z(\beta, V, N) = \sum_{N=0}^{\infty} \frac{1}{N!} \left[ e^{\beta \mu} V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right]^N = \exp \left( e^{\beta \mu} V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right),$$

where we have used the well known definition of the exponential function:

$$\sum_{N=0}^{\infty} \frac{1}{N!} \zeta^N = e^{\zeta} \quad \text{with} \quad \zeta = e^{\beta \mu} V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}.$$

The grand thermodynamic potential is given by Eq. (3.65):

$$\Phi(T, V, \mu) = -k_B T \ln \Xi(T, V, \mu) = -k_B T \ln \left[ \exp \left( e^{\beta \mu} V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right) \right] = -k_B T e^{\beta \mu} V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}.$$

The equations of state follow, i.e.,

$$\begin{aligned} S(T, V, \mu) &= - \left( \frac{\partial \Phi}{\partial T} \right)_{V, \mu} = k_B e^{\mu/k_B T} V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \left( \frac{5}{2} - \frac{\mu}{k_B T} \right), \\ p(T, V, \mu) &= - \left( \frac{\partial \Phi}{\partial V} \right)_{T, \mu} = k_B T e^{\mu/k_B T} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}, \\ N(T, V, \mu) &= - \left( \frac{\partial \Phi}{\partial \mu} \right)_{T, V} = e^{\mu/k_B T} V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}. \end{aligned}$$

The well known relationship between pressure, volume and temperature for an ideal gas is obtained by substituting  $N(T, V, \mu)$  into  $p(T, V, \mu)$ , i.e.,

$$p(T, V, \mu) = k_B T e^{\mu/k_B T} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} = k_B T \frac{N(T, V, \mu)}{V} \Rightarrow p(T, V, \mu) V = N(T, V, \mu) k_B T = nRT.$$

**Exercise 3.4:** Show that the entropy of an ideal gas calculated in Example 3.3 is in agreement with the entropy calculated in Sec. 2.3.2.

As with the canonical ensemble, we can derive the grand canonical ensemble from the entropy, defined as:

$$S = -\langle k_B \ln \rho(\mathbf{q}, \mathbf{p}, N) \rangle = \frac{1}{N! h^{3N}} \int_{\Gamma(E)} \rho(\mathbf{q}, \mathbf{p}, N) (-k_B \ln \rho(\mathbf{q}, \mathbf{p}, N)) d^{3N} \mathbf{q} d^{3N} \mathbf{p}. \quad (3.67)$$

It is left as an exercise to derive the grand canonical partition function from the entropy principle.

**Exercise 3.5:** Derive the grand canonical partition function from Eq. (3.67) subject to the normalisation condition and the definitions of the internal energy  $U$  and mean particle number  $\langle N \rangle$ . Show that in this case the Lagrange multipliers correspond to the Boltzmann factor  $\beta = 1/k_B T$  and  $\mu/k_B T$ . (Hint: See Example 3.1).

### 3.4.1 Fluctuations in the Grand Canonical Ensemble

Fluctuations in particle number about the mean value are defined in the grand canonical ensemble by the second moment:

$$\sigma_N^2 = \langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2, \quad (3.68)$$

where

$$\langle N \rangle = \frac{\sum_{N=0}^{\infty} N z^N Z(\beta, V, N)}{\sum_{N=0}^{\infty} z^N Z(\beta, V, N)} = \frac{1}{\Xi(\beta, V, N)} z \left( \frac{\partial}{\partial z} \Xi(\beta, V, N) \right) = z \left( \frac{\partial}{\partial z} \ln \Xi(\beta, V, N) \right) \quad (z = e^{\beta \mu}). \quad (3.69)$$

and

$$\langle N^2 \rangle = \frac{\sum_{N=0}^{\infty} N^2 z^N Z(\beta, V, N)}{\sum_{N=0}^{\infty} z^N Z(\beta, V, N)} = \frac{1}{\Xi(\beta, V, N)} \left( z \frac{\partial}{\partial z} \right) \left( z \frac{\partial}{\partial z} \right) \Xi(\beta, V, N). \quad (3.70)$$

Equations (3.69) and (3.70) allow us to express the second moment as:

$$\begin{aligned} \sigma_N^2 &= \langle N^2 \rangle - \langle N \rangle^2 \\ &= \frac{1}{\Xi(\beta, V, N)} \left( z \frac{\partial}{\partial z} \right) \left( z \frac{\partial}{\partial z} \right) \Xi(\beta, V, N) - \frac{1}{\Xi^2(\beta, V, N)} z^2 \left( \frac{\partial \Xi(\beta, V, N)}{\partial z} \right)^2 \\ &= \frac{1}{\Xi(\beta, V, N)} \left( z \frac{\partial}{\partial z} + z^2 \frac{\partial^2}{\partial z^2} \right) \Xi(\beta, V, N) - \frac{1}{\Xi^2(\beta, V, N)} z^2 \left( \frac{\partial \Xi(\beta, V, N)}{\partial z} \right)^2 \\ &= \left( z \frac{\partial}{\partial z} \right)^2 \ln \Xi(\beta, V, N). \end{aligned} \quad (3.71)$$

Combining Eq. (3.69) with Eq. (3.71), the fluctuations may be written as:

$$\sigma_N^2 = \left( z \frac{\partial}{\partial z} \right)^2 \ln \Xi(\beta, V, N) = z \frac{\partial \langle N \rangle}{\partial z} = e^{\beta \mu} \frac{\partial \langle N \rangle}{\partial \mu} \left( \frac{\partial z}{\partial \mu} \right)^{-1} = k_B T \frac{\partial \langle N \rangle}{\partial \mu}. \quad (3.72)$$

In the limit of large  $N$ , the expectation value  $\langle N \rangle$  can be replaced by the particle number  $N$ . It can be shown (see Ref. [1], pp. 152-153) that Eq. (3.72) may also be expressed as:

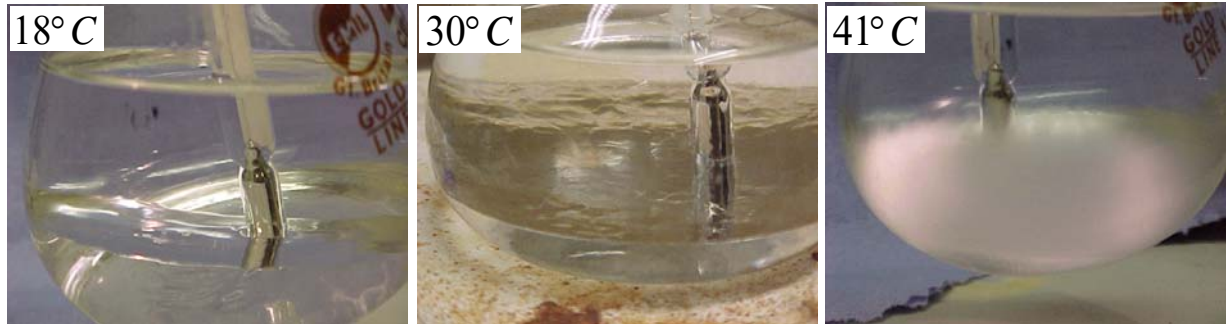
$$\sigma_N^2 = k_B T \frac{\partial \langle N \rangle}{\partial \mu} = -k_B T \frac{1}{\left( \frac{V^2}{N^2} \left( \frac{\partial p}{\partial V} \right)_T \right)}. \quad (3.73)$$

Defining the isothermal compressibility as  $\kappa = -1/V(\partial V/\partial p)_T$ , allows us to re-write Eq. (3.73) as:

$$\sigma_N^2 = k_B T N^2 \frac{\kappa}{V} \Rightarrow \frac{\sigma_N}{N} = \sqrt{\frac{k_B T}{V} \kappa}. \quad (3.74)$$

Equation (3.74) shows that the relative fluctuations in particle number vanish in the thermodynamic limit, where  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = \text{constant}$ . However, there is a caveat to this conclusion; namely, it assumes that the isothermal compressibility is finite. For a first order phase transition in a gas-liquid mixture,  $\partial p/\partial V$  can vanish, and there will be large fluctuations in particle number. This is observed in the phenomenon of critical opalescence<sup>5</sup> (see Fig. 3.1), first studied in 1869 by Andrews<sup>6</sup> in the  $p$ - $V$  diagram of  $\text{CO}_2$ .

**Exercise 3.6:** Reproduce the steps leading to Eqs. (3.72) - (3.74).



**Figure 3.1:** Critical opalescence in a mixture of hexane and methanol. At the critical temperature the density fluctuations in the mixture becomes comparable to the wavelength of light, which results in the light being strongly scattered, causing the cloudy appearance of the binary mixture. The images are from the website: <http://www.physicsofmatter.com/NotTheBook/CriticalOpal/OpalFrame.html>

<sup>5</sup> A video of critical opalescence in a mixture of methanol and cyclohexane is available on YouTube at: <https://www.youtube.com/watch?v=OgfxOl0eoJ0>

<sup>6</sup> See Thomas Andrews, “The Bakerian Lecture: On the Continuity of the Gaseous and Liquid States of Matter”, Philosophical Transactions of the Royal Society of London, Vol. 159 (1869), pp. 575-590. This paper can be accessed at: <http://rstl.royalsocietypublishing.org/content/159/575.full.pdf+html>

## Appendix A: The Method of Lagrange Multipliers

The method of Lagrange undetermined multipliers is used to find the extremum of a function subject to constraints. Consider a function  $f = f(x_1, x_2, \dots, x_n)$  whose maximum or minimum we wish to find, subject to the equation of constraint  $g = g(x_1, x_2, \dots, x_n) = 0$ . We introduce a parameter  $\lambda$ , known as the Lagrange multiplier, which is to be determined, so that:

$$d(f + \lambda g) = \left( \frac{\partial f}{\partial x_1} + \lambda \frac{\partial g}{\partial x_1} \right) dx_1 + \left( \frac{\partial f}{\partial x_2} + \lambda \frac{\partial g}{\partial x_2} \right) dx_2 + \dots + \left( \frac{\partial f}{\partial x_n} + \lambda \frac{\partial g}{\partial x_n} \right) dx_n = 0. \quad (\text{A3.1})$$

Since each of the differentials  $dx_1, dx_2, \dots, dx_n$  are to be independent and arbitrary, we can therefore choose  $\lambda$  such that:

$$\left( \frac{\partial f}{\partial x_i} + \lambda \frac{\partial g}{\partial x_i} \right) = 0 \quad (i = 1, 2, \dots, n). \quad (\text{A3.2})$$

After solving Eq. (A3.2), the solutions will be in terms of  $\lambda$ , which is to be determined. The method can be extended to find the extremum of a function of  $n$  variables subject to  $m$  equations of constraint, provided that the number of constraints is less than the number of variables, i.e.,  $m < n$ . In this latter case we introduce  $m$  Lagrange undetermined multipliers  $\{\lambda_k\}$  ( $k = 1, 2, \dots, m$ ). Example A3.1 shows how the method is applied in practice.

**Example A3.1:** A system contains  $N$  particles, each of which can be in  $M$  energy states, with energy  $E_i$  ( $i = 1, 2, \dots, M$ ). The number of particles in the  $i$ -th level is  $n_i$  and the total energy of the system is  $E$ . Find the distribution of the particles' energy levels that maximise the following multinomial probability function:

$$\mathcal{P} = \frac{N!}{n_1! n_2! \dots n_M!} = \frac{N!}{\prod_{i=1}^M n_i!}.$$

subject to the following constraints:

$$g = \sum_{i=1}^M n_i = N \quad \text{and} \quad h = \sum_{i=1}^M n_i E_i = E.$$

### Solution

We examined the simpler binomial probability function in Example 1.4; however, in that example we did not correctly account for the second constraint. Since  $N$  is fixed we will maximise  $\mathcal{P}$  by minimising  $n_1! n_2! \dots n_M!$  or equivalently by minimising its logarithm, i.e.,

$$f = f(n_1, n_2, \dots, n_M) = \ln \left( \prod_{i=1}^M n_i! \right) = \ln(n_1! n_2! \dots n_M!) = \ln n_1! + \ln n_2! + \dots + \ln n_M! = \sum_{i=1}^M \ln n_i!$$

Using Stirling's approximation  $\ln n_i! \approx n_i \ln n_i - n_i$ , we have:

$$f(n_1, n_2, \dots, n_M) = \sum_{i=1}^M \ln n_i! \approx \sum_{i=1}^M (n_i \ln n_i - n_i) = \sum_{i=1}^M n_i \ln n_i - N.$$

To find the extremum of  $f$  subject to the constraints  $g = N$  and  $h = E$ , we introduce two Lagrange undetermined multipliers,  $\lambda_1$  and  $\lambda_2$ , and solve the following equations:

$$\left( \frac{\partial f}{\partial n_i} + \lambda_1 \frac{\partial g}{\partial n_i} + \lambda_2 \frac{\partial h}{\partial n_i} \right) = 0 \quad (i = 1, 2, \dots, M).$$



Substituting for the relevant functions we obtain:

$$\left( \frac{\partial f}{\partial n_i} + \lambda_1 \frac{\partial g}{\partial n_i} + \lambda_2 \frac{\partial h}{\partial n_i} \right) = \ln n_i + \lambda_1 + \lambda_2 E_i = 0 \quad (i = 1, 2, \dots, M).$$

or

$$n_i = C e^{-\lambda_2 E_i} \quad (C = e^{-\lambda_1}).$$

The two constants  $C$  and  $\lambda_2$  are determined from:

$$\sum_{i=1}^M n_i = \sum_{i=1}^M C e^{-\lambda_2 E_i} = N \Rightarrow C = \frac{N}{\sum_{i=1}^M e^{-\lambda_2 E_i}},$$

and

$$\sum_{i=1}^M n_i E_i = \sum_{i=1}^M C E_i e^{-\lambda_2 E_i} = E \Rightarrow \frac{E}{N} = \frac{\sum_{i=1}^M E_i e^{-\lambda_2 E_i}}{\sum_{i=1}^M e^{-\lambda_2 E_i}}.$$

To explicitly determine  $\lambda_2$  we calculate the entropy:

$$S = k_B \ln \Omega \approx k_B \ln \mathcal{P}(n_i) = k_B \ln \left( \frac{N!}{n_1! n_2! \dots n_M!} \right)$$

Exploiting Stirling's approximation we have:

$$\begin{aligned} S &= k_B \ln \left( \frac{N!}{n_1! n_2! \dots n_M!} \right) \\ &\approx k_B (N \ln N - N) - k_B \left( \sum_{i=1}^M n_i \ln n_i - N \right) \\ &\approx k_B N \ln N - k_B \sum_{i=1}^M n_i \ln n_i, \end{aligned}$$

where we have used the value of  $\ln(n_1! n_2! \dots n_M!)$  that maximises  $\mathcal{P}$ , subject to the constraints. Substituting for  $n_i$  we obtain:

$$\begin{aligned} S &= k_B N \ln N - k_B \sum_{i=1}^M n_i \ln n_i \\ &= k_B N \ln N - k_B \sum_{i=1}^M n_i \ln (C e^{-\lambda_2 E_i}) \\ &= k_B N \ln N - k_B \sum_{i=1}^M n_i (\ln C - \lambda_2 E_i) \\ &= k_B N \ln N - k_B N \ln C + k_B \lambda_2 \sum_{i=1}^M n_i E_i \\ &= k_B N \ln N - k_B N \ln C + k_B \lambda_2 E. \end{aligned}$$

We make the connection with thermodynamics by using the definition of temperature. From Eq. (2.33) we have:

$$\left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T} \Rightarrow \frac{1}{T} = k_B \lambda_2 \quad \text{or} \quad \lambda_2 = \frac{1}{k_B T} = \beta.$$

Hence the Lagrange multiplier  $\lambda_2$  is just the  $\beta$ -factor (inverse temperature).

## References

- [1] Huang, K., *Statistical Mechanics* (2<sup>nd</sup> Edition, John Wiley and Sons, 1987). Chapter 7.
  - [2] Sethna, J. P., *Statistical Mechanics: Entropy, Order Parameters, and Complexity* (Oxford University Press, 2006). Chapter 6. A pdf of this textbook is available at:  
<http://pages.physics.cornell.edu/~sethna/StatMech/EntropyOrderParametersComplexity.pdf>
  - [3] Kardar, M., *Statistical Physics of Particles* (Cambridge University Press, 2007). Chapter 4. A pdf of this textbook is available at:  
[http://home.basu.ac.ir/~psu/Books/%5BMehran\\_Kardar%5D\\_Statistical\\_Physics\\_of\\_Particles\(BookFi.org\).pdf](http://home.basu.ac.ir/~psu/Books/%5BMehran_Kardar%5D_Statistical_Physics_of_Particles(BookFi.org).pdf)
  - [4] Chandler, D., *Introduction to Modern Statistical Mechanics* (Oxford University Press, 1987). Chapter 3.
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