

# Chapter 2

## Summary of Equilibrium Statistical Ensembles

In this chapter a summary of the main equilibrium ensembles is presented, essentially to fix part of the notation that will be needed later on. The phase-space probability density associated with each ensemble is derived by maximization of the Gibbs entropy under the appropriate constraints. For simplicity, most of this chapter is restricted to one-component systems, although the extension to mixtures is straightforward and is presented in the last section.

### 2.1 Phase Space

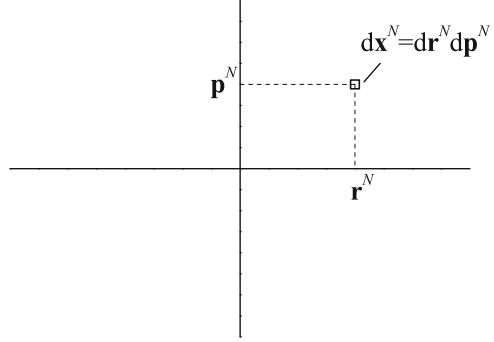
Let us consider a *classical* system made of  $N$  *identical* (and hence *indistinguishable*) point particles enclosed in a volume  $V$  in  $d$  dimensions. In classical mechanics, the dynamical state of the system is characterized by the  $N$  position vectors  $\{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$  and the  $N$  momentum vectors  $\{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N\}$ . In what follows, we will employ the following short-hand notation

$$\begin{aligned} \bullet \quad \mathbf{r}^N &= \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}, & d\mathbf{r}^N &= d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N, \\ \bullet \quad \mathbf{p}^N &= \{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N\}, & d\mathbf{p}^N &= d\mathbf{p}_1 d\mathbf{p}_2 \cdots d\mathbf{p}_N, \\ \bullet \quad \mathbf{x}^N &= \{\mathbf{r}^N, \mathbf{p}^N\}, & d\mathbf{x}^N &= d\mathbf{r}^N d\mathbf{p}^N. \end{aligned}$$

Thus, the whole *microscopic* state of the system (*microstate*) is represented by a single point  $\mathbf{x}^N$  in the  $(2d \times N)$ -dimensional *phase space* (see Fig. 2.1). The time evolution of the microstate  $\mathbf{x}^N$  is governed by the Hamiltonian of the system  $H_N(\mathbf{x}^N)$  through the classical Hamilton's equations [1].

Henceforth, and in order to make contact with thermodynamics, we will generally assume that the number of particles  $N$  and the volume  $V$  are so large that specific

**Fig. 2.1** Sketch of the phase space of a system of  $N$  identical particles. The *horizontal axis* represents the  $d \times N$  position variables ( $d$  components for each particle), while the *vertical axis* represents the  $d \times N$  momentum variables. A differential phase-space volume  $d\mathbf{x}^N$  around a point  $\mathbf{x}^N$  is represented



quantities (i.e., extensive quantities per particle or per unit volume) are independent of  $N$  or  $V$ . This is equivalent to formally taking the so-called *thermodynamic limit*, whereby

$$\left. \begin{array}{l} N \rightarrow \infty \\ V \rightarrow \infty \end{array} \right\} \text{with a finite ratio } N/V. \quad (2.1)$$

Given the practical impossibility of describing the system at a microscopic level, a statistical description is needed. Thus, we define the phase-space probability density  $\rho_N(\mathbf{x}^N)$  such that  $\rho_N(\mathbf{x}^N)d\mathbf{x}^N$  is the probability that the microstate of the system lies inside an infinitesimal (hyper)volume  $d\mathbf{x}^N$  around the phase-space point  $\mathbf{x}^N$ . The ensemble average of a certain dynamical variable  $A_N(\mathbf{x}^N)$  is

$$\langle A \rangle = \int d\mathbf{x}^N A_N(\mathbf{x}^N) \rho_N(\mathbf{x}^N). \quad (2.2)$$

Here, it is understood that the total number of particles ( $N$ ) is fixed and the position integral for each particle runs over a fixed volume ( $V$ ) of the system. Otherwise, the expression for the ensemble average may involve summation over the number of particles and/or integration over the system volume [see (2.30) and (2.44) below].

## 2.2 Gibbs Entropy Functional

The concept of a phase-space probability density is valid both out of equilibrium (where, in general, it changes with time according to the Liouville theorem [2, 3]) and in equilibrium (where it is stationary). In the latter case  $\rho_N(\mathbf{x}^N)$  can be obtained for isolated, closed, open, ... systems by following logical steps and starting from the *equal a priori probability postulate* for isolated systems [4]. Here we follow an alternative (but equivalent) method based on information-theory arguments [3, 5, 6].

Let us define the Gibbs entropy *functional*

$$\mathcal{S}[\rho_N] = -k_B \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) \ln [C_N \rho_N(\mathbf{x}^N)] , \quad (2.3)$$

where

$$C_N \equiv N! h^{dN} \quad (2.4)$$

is the quantum of phase-space volume. In (2.4)  $h$  is the Planck constant, the coefficient  $h^{dN}$  being introduced to comply with Heisenberg's uncertainty principle and also to preserve the non-dimensional character of the argument of the logarithm. Moreover, the factorial  $N!$  accounts for the fact that two apparently different microstates which only differ on the particle labels are physically the same microstate, thus avoiding the Gibbs paradox [7]. The factorial  $N!$  must be removed from  $C_N$  if the particles are *distinguishable*.

Equation (2.3) applies to systems with a fixed number of particles  $N$ . On the other hand, if the system is allowed to exchange particles with the environment, microstates with different  $N$  exist, so that one needs to define a phase-space probability density  $\rho_N(\mathbf{x}^N)$  for each  $N \geq 0$ . In that case, the entropy functional becomes

$$\mathcal{S}[\rho_N] = -k_B \sum_{N=0}^{\infty} \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) \ln [C_N \rho_N(\mathbf{x}^N)] . \quad (2.5)$$

Analogously, if the number of particles  $N$  is fixed but the volume  $V$  occupied by the particles can vary (formally) from zero to infinity, the phase-space probability density  $\rho_N(\mathbf{x}^N)$  depends on  $V$ . It is defined such that  $\rho_N(\mathbf{x}^N) d\mathbf{x}^N dV$  is the probability that the particles occupy a volume between  $V$  and  $V + dV$  and the microstate lies inside an infinitesimal (hyper)volume  $d\mathbf{x}^N$  around the phase-space point  $\mathbf{x}^N$ . The corresponding entropy functional is then

$$\mathcal{S}[\rho_N] = -k_B \int_0^{\infty} dV \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) \ln [C_N V_0 \rho_N(\mathbf{x}^N)] , \quad (2.6)$$

where  $V_0$  is an arbitrary volume scale factor (needed to keep the correct dimensions).

Now, the basic postulate consists in asserting that, out of all possible phase-space probability distribution functions  $\rho_N$  consistent with given *constraints* (which define the *ensemble* of accessible microstates), the *equilibrium* function  $\rho_N^{\text{eq}}$  is the one that *maximizes* the entropy functional  $\mathcal{S}[\rho_N]$ . Once  $\rho_N^{\text{eq}}$  is known, connection with thermodynamics is made through the identification of  $S = \mathcal{S}[\rho_N^{\text{eq}}]$  as the equilibrium entropy.

### 2.3 Microcanonical Ensemble: Isolated Systems

The microcanonical ensemble describes an isolated system and thus it is characterized by fixed values of  $V$ ,  $N$ ,  $E$  (the latter with a tolerance  $\Delta E$ , in accordance with the uncertainty principle). Therefore, the basic constraint is the normalization condition

$$\int_{E \leq H_N(\mathbf{x}^N) \leq E + \Delta E} d\mathbf{x}^N \rho_N(\mathbf{x}^N) = 1 . \quad (2.7)$$

Maximization of the entropy functional (2.3) just says that  $\rho_N(\mathbf{x}^N) = \text{const}$  for all the accessible microstates  $E \leq H_N(\mathbf{x}^N) \leq E + \Delta E$ . Thus,

$$\begin{aligned} \rho_N(\mathbf{x}^N) &= \begin{cases} [C_N \omega_{\Delta E}(E, V, N)]^{-1} , & E \leq H_N(\mathbf{x}^N) \leq E + \Delta E , \\ 0 , & \text{otherwise} , \end{cases} \\ &= \frac{\Pi_{E, E+\Delta E}(H_N(\mathbf{x}^N))}{C_N \omega_{\Delta E}(E, V, N)} , \end{aligned} \quad (2.8)$$

where  $\Pi_{a,b}(x)$  is the boxcar function, which is equal to 1 for  $a \leq x \leq b$  and 0 otherwise. The normalization function

$$\omega_{\Delta E}(E, V, N) = \frac{1}{C_N} \int_{E \leq H_N(\mathbf{x}^N) \leq E + \Delta E} d\mathbf{x}^N \quad (2.9)$$

is the phase-space volume comprised between the hyper-surfaces  $H_N(\mathbf{x}^N) = E$  and  $H_N(\mathbf{x}^N) = E + \Delta E$ , in units of  $C_N$ . We will refer to the dimensionless quantity  $\omega_{\Delta E}$  as the *microcanonical partition function*. It is interesting to note that, taking into account the representation

$$\delta(x - a) = \lim_{\Delta a \rightarrow 0} \frac{\Pi_{a, a+\Delta a}(x)}{\Delta a} \quad (2.10)$$

of the Dirac delta function, the microcanonical partition function can be rewritten as

$$\omega_{\Delta E}(E, V, N) \approx \frac{\Delta E}{C_N} \int d\mathbf{x}^N \delta(H_N(\mathbf{x}^N) - E) . \quad (2.11)$$

By insertion of (2.8) into (2.3) one immediately sees that  $\omega_{\Delta E}(E, V, N)$  is directly related to the equilibrium entropy as

$$S(E, V, N) = k_B \ln \omega_{\Delta E}(E, V, N) . \quad (2.12)$$

In this expression, the specific value of  $\Delta E$  becomes irrelevant in the thermodynamic limit (as long as  $\Delta E \ll E$ ).

Equation (2.12) means that entropy is proportional to the logarithm of the number of microstates with energy  $E$  (within an allowance  $\Delta E$ ). This is usually referred to as the Boltzmann entropy. An alternative definition of entropy in the microcanonical ensemble is [8]

$$S(E, V, N) = k_B \ln \bar{\omega}(E, V, N) , \quad (2.13a)$$

$$\bar{\omega}(E, V, N) \equiv \frac{1}{C_N} \int_{0 \leq H_N(\mathbf{x}^N) \leq E} d\mathbf{x}^N , \quad (2.13b)$$

where now the so-called Gibbs entropy is proportional to the logarithm of the number of microstates with an energy smaller than or equal to  $E$ . For “normal” systems, like classical liquids, energy does not have an upper bound and the function  $\omega_{\Delta E}(E)$  grows so rapidly with  $E$  that  $\ln \bar{\omega}(E) \approx \ln \omega_{\Delta E}(E)$  in the thermodynamic limit, and hence both definitions (2.12) and (2.13) become fully equivalent in that limit [8]. Such an equivalence, however, does not hold for *small* systems or for systems where energy has an upper bound  $E_{\max}$ . In the latter case, the function  $\omega_{\Delta E}(E)$  decreases with increasing energy as  $E_{\max}$  is approached from below, while the cumulative function  $\bar{\omega}(E)$  monotonically increases with  $E$ . As a consequence, the thermodynamic relation (1.4a) can give rise to *negative* absolute temperatures [9, 10] if the Boltzmann entropy is used, while the Gibbs entropy always predicts positive-definite temperatures. The question of which definition of entropy (Boltzmann’s versus Gibbs’s) is more adequate for small systems or when the energy is bounded is still open [11–17]. On the other hand, since we will always deal here with classical normal liquids in the thermodynamic limit, (2.12) can be safely adopted for the microcanonical entropy.

Making use of (1.4) (see also Table 1.1), the thermodynamic variables conjugate to  $E$ ,  $V$ , and  $N$  can be obtained from  $\omega_{\Delta E}$  as

$$\beta \equiv \frac{1}{k_B T} = \frac{\partial}{\partial E} \ln \omega_{\Delta E}(E, V, N) , \quad (2.14a)$$

$$\beta p = \frac{\partial}{\partial V} \ln \omega_{\Delta E}(E, V, N) , \quad (2.14b)$$

$$\alpha \equiv -\beta \mu = \frac{\partial}{\partial N} \ln \omega_{\Delta E}(E, V, N) . \quad (2.14c)$$

The inverse temperature parameter  $\beta$  has dimensions of inverse energy and is usually employed in statistical-mechanical formulas more frequently than the temperature  $T$  itself [see (1.35)]. Analogously,  $\alpha$  is a dimensionless parameter defined as the opposite of the chemical potential scaled with the thermal energy  $k_B T$ . The parameter  $\alpha$  is usually preferred over  $\mu$  in statistical-mechanical formal expressions. Its exponential defines the *fugacity*

$$z \equiv e^{-\alpha} \equiv e^{\beta \mu} . \quad (2.15)$$

## 2.4 Canonical Ensemble: Closed Systems

Now the system can have *any* value of the total energy  $E$ . However, we are free to prescribe a given value of the *average* energy  $\langle E \rangle = \langle H_N \rangle$ . Therefore, the constraints in the canonical ensemble are

$$\int d\mathbf{x}^N \rho_N(\mathbf{x}^N) = 1 , \quad (2.16a)$$

$$\int d\mathbf{x}^N H_N(\mathbf{x}^N) \rho_N(\mathbf{x}^N) = \langle E \rangle . \quad (2.16b)$$

The maximization of the entropy functional (2.3) subject to the constraints (2.16) can be carried out through the Lagrange multiplier method with the result

$$\rho_N(\mathbf{x}^N) = \frac{e^{-\beta H_N(\mathbf{x}^N)}}{C_N \mathcal{Z}_N(\beta, V)} , \quad (2.17)$$

where  $\beta$  is the Lagrange multiplier associated with the constraint on  $\langle E \rangle$  and the *canonical partition function*  $\mathcal{Z}_N$  is determined from the normalization condition as

$$\boxed{\mathcal{Z}_N(\beta, V) = \frac{1}{C_N} \int d\mathbf{x}^N e^{-\beta H_N(\mathbf{x}^N)} .} \quad (2.18)$$

Multiplying both sides of (2.18) by  $1 = \int dE \delta(H_N(\mathbf{x}^N) - E)$  and using (2.11), the partition function can alternatively be written as

$$\mathcal{Z}_N(\beta, V) = \frac{1}{\Delta E} \int dE e^{-\beta E} \omega_{\Delta E}(E, V, N) . \quad (2.19)$$

Substitution of (2.17) into (2.3) and use of (2.16) yields

$$S = k_B (\ln \mathcal{Z}_N + \beta \langle E \rangle) . \quad (2.20)$$

Comparison with (1.10) (where now the internal energy corresponds to  $\langle E \rangle$ ) allows one to identify  $\beta = 1/k_B T$  and

$$\boxed{F(T, V, N) = -k_B T \ln \mathcal{Z}_N(\beta, V) .} \quad (2.21)$$

Thus, the Lagrange multiplier  $\beta$  acquires a physical meaning as the inverse temperature parameter already defined in (1.35) and (2.14a). Besides, in the canonical ensemble the connection with thermodynamics is conveniently established via the Helmholtz free energy rather than via the entropy.

As an average of a phase-space dynamical variable, the internal energy can be directly obtained from  $\ln \mathcal{Z}_N$  as

$$\langle E \rangle = - \frac{\partial \ln \mathcal{Z}_N}{\partial \beta} . \quad (2.22)$$

More in general, the energy moments are

$$\langle E^k \rangle = \frac{(-1)^k}{\mathcal{Z}_N} \frac{\partial^k \mathcal{Z}_N}{\partial \beta^k} . \quad (2.23)$$

In particular, energy fluctuations in a closed system are measured by the variance

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln \mathcal{Z}_N}{\partial \beta^2} = k_B T^2 C_V , \quad (2.24)$$

where in the last step use has been made of (1.20a). Since both the internal energy  $\langle E \rangle$  and the heat capacity  $C_V$  are extensive quantities (i.e.,  $\langle E \rangle \propto N$ ,  $C_V \propto N$ ), (2.24) implies that the *relative* standard deviation  $\sqrt{\langle E^2 \rangle - \langle E \rangle^2} / \langle E \rangle$  scales with  $N^{-1/2}$ . Therefore, in the thermodynamic limit (2.1) the energy fluctuations become negligible and the canonical ensemble becomes equivalent to the microcanonical one.

Using (2.23), it is possible to generalize (2.24) as

$$\mathcal{K}_E^{(k)} = (-1)^k \frac{\partial^k \ln \mathcal{Z}_N}{\partial \beta^k} , \quad (2.25)$$

where  $\mathcal{K}_x^{(k)}$  denotes the  $k$ th *cumulant* of a random variable  $x$ . The first few cumulants ( $2 \leq k \leq 6$ ) are  $\mathcal{K}_x^{(2)} = \langle (\delta x)^2 \rangle$ ,  $\mathcal{K}_x^{(3)} = \langle (\delta x)^3 \rangle$ ,  $\mathcal{K}_x^{(4)} = \langle (\delta x)^4 \rangle - 3\langle (\delta x)^2 \rangle^2$ ,  $\mathcal{K}_x^{(5)} = \langle (\delta x)^5 \rangle - 10\langle (\delta x)^3 \rangle \langle (\delta x)^2 \rangle$ , and  $\mathcal{K}_x^{(6)} = \langle (\delta x)^6 \rangle - 15\langle (\delta x)^4 \rangle \langle (\delta x)^2 \rangle - 10\langle (\delta x)^3 \rangle^2 + 30\langle (\delta x)^2 \rangle^3$ , where  $\delta x \equiv x - \langle x \rangle$ .

The microcanonical $\leftrightarrow$ canonical ensemble equivalence can be further explored by considering the energy probability density function in the canonical ensemble,

$$\mathcal{P}_N(E; \beta, V) = \int d\mathbf{x}^N \delta(H_N(\mathbf{x}^N) - E) \rho_N(\mathbf{x}^N) = \frac{e^{-\beta E} \omega_{\Delta E}(E, V, N)}{\mathcal{Z}_N(\beta, V)} , \quad (2.26)$$

where (2.11) has been used again. While  $\omega_{\Delta E}(E, V, N)$  is a rapidly increasing function of  $E$  (in classical systems with no upper bound for energy),  $e^{-\beta E}$  is a rapidly decreasing function. Thus,  $\mathcal{P}_N(E)$  presents an extremely sharp peak at a certain value  $E = \tilde{E}$ . The extremal condition  $\partial \ln \mathcal{P}_N(E) / \partial E|_{E=\tilde{E}} = 0$  implies that  $\tilde{E}$  is implicitly given by

$$\beta = \left. \frac{\partial \ln \omega_{\Delta E}(E, V, N)}{\partial E} \right|_{E=\tilde{E}} . \quad (2.27)$$

Comparison with (2.14a) shows that, at given  $T$ ,  $N$ , and  $V$ , the most probable energy  $\tilde{E}$  in a closed system coincides with the unique (except for the energy tolerance  $\Delta E$ ) energy value in an isolated system.

From (1.12b) and (1.12c) (see also Table 1.1), we note that the pressure and the chemical potential are obtained from the partition function as

$$\beta p = \frac{\partial}{\partial V} \ln \mathcal{Z}_N(\beta, V) , \quad (2.28a)$$

$$\alpha \equiv -\beta\mu = \frac{\partial}{\partial N} \ln \mathcal{Z}_N(\beta, V) . \quad (2.28b)$$

## 2.5 Grand Canonical Ensemble: Open Systems

In an open system neither the energy nor the number of particles are determined but we can choose to fix their average values. As a consequence, the constraints are

$$\sum_{N=0}^{\infty} \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) = 1 , \quad (2.29a)$$

$$\sum_{N=0}^{\infty} \int d\mathbf{x}^N H_N(\mathbf{x}^N) \rho_N(\mathbf{x}^N) = \langle E \rangle , \quad (2.29b)$$

$$\sum_{N=0}^{\infty} N \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) = \langle N \rangle . \quad (2.29c)$$

In general, given a dynamical variable  $A_N(\mathbf{x}^N)$ , its grand canonical ensemble average is

$$\langle A \rangle = \sum_{N=0}^{\infty} \int d\mathbf{x}^N A_N(\mathbf{x}^N) \rho_N(\mathbf{x}^N) . \quad (2.30)$$

The solution to the maximization problem of the entropy functional (2.5) with the constraints (2.29) is

$$\rho_N(\mathbf{x}^N) = \frac{e^{-\alpha N} e^{-\beta H_N(\mathbf{x}^N)}}{C_N \Xi(\beta, V, \alpha)} , \quad (2.31)$$

where  $\alpha$  and  $\beta$  are Lagrange multipliers and the *grand partition function* is

$$\Xi(\beta, V, \alpha) = \sum_{N=0}^{\infty} \frac{e^{-\alpha N}}{C_N} \int d\mathbf{x}^N e^{-\beta H_N(\mathbf{x}^N)} . \quad (2.32)$$



From (2.18), the grand partition function can be rewritten as

$$\boxed{\Xi(\beta, V, \alpha) = \sum_{N=0}^{\infty} e^{-\alpha N} \mathcal{Z}_N(\beta, V) .} \quad (2.33)$$

Inserting (2.31) into (2.5), it is straightforward to check that the equilibrium entropy becomes

$$S = k_B (\ln \Xi + \beta \langle E \rangle + \alpha \langle N \rangle) . \quad (2.34)$$

From comparison with the first equality of (1.17) we can identify  $\beta = 1/k_B T$ ,  $\alpha = -\beta\mu$ , and

$$\boxed{\Omega(T, V, \mu) = -k_B T \ln \Xi(\beta, V, \alpha) .} \quad (2.35)$$

As happened in the canonical ensemble, the Lagrange multiplier  $\beta$  coincides with the inverse temperature parameter defined by (1.35) and (2.14a). Analogously, the multiplier  $\alpha$  is not but the scaled chemical potential defined by (2.14c).

The average energy and number of particles can be obtained from the grand partition function as

$$\langle E \rangle = -\frac{\partial \ln \Xi}{\partial \beta} , \quad (2.36a)$$

$$\langle N \rangle = -\frac{\partial \ln \Xi}{\partial \alpha} . \quad (2.36b)$$

As for the pressure, according to (1.17) or (1.19b), we simply have

$$\beta p V = \ln \Xi(\beta, V, \alpha) . \quad (2.37)$$

Similarly to (2.23), the moments associated with the energy and the number of particles are

$$\langle E^k \rangle = \frac{(-1)^k}{\Xi} \frac{\partial^k \Xi}{\partial \beta^k} , \quad (2.38a)$$

$$\langle N^k \rangle = \frac{(-1)^k}{\Xi} \frac{\partial^k \Xi}{\partial \alpha^k} . \quad (2.38b)$$

Consequently, the fluctuation relations become

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln \mathcal{E}}{\partial \beta^2} = k_B T^2 C_V, \quad (2.39a)$$

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{\partial^2 \ln \mathcal{E}}{\partial \alpha^2} = -\frac{\partial \langle N \rangle}{\partial \alpha}. \quad (2.39b)$$

Recalling that  $\alpha = -\beta\mu$  and taking into account the thermodynamic identity (1.30), we can write

$$\boxed{\langle N^2 \rangle - \langle N \rangle^2 = nk_B T \langle N \rangle \kappa_T}. \quad (2.40)$$

Since the isothermal compressibility is an intensive quantity, the *relative* standard deviation  $\sqrt{\langle N^2 \rangle - \langle N \rangle^2} / \langle N \rangle$  scales with  $\langle N \rangle^{-1/2}$  and thus decays in the thermodynamic limit. In that limit the microcanonical, canonical, and grand canonical ensembles become equivalent. On the other hand, as one approaches the vapor–liquid critical point the isothermal compressibility diverges (critical opalescence phenomenon) and so do the density fluctuations in a finite-volume cell.

As in (2.25), the cumulants of energy and number of particles in the grand canonical ensemble are

$$\mathcal{K}_E^{(k)} = (-1)^k \frac{\partial^k \ln \mathcal{E}}{\partial \beta^k}, \quad (2.41a)$$

$$\mathcal{K}_N^{(k)} = (-1)^k \frac{\partial^k \ln \mathcal{E}}{\partial \alpha^k}. \quad (2.41b)$$

This generalizes (2.39) to  $k \geq 3$ .

In analogy with (2.26), we can define the number probability distribution function

$$\mathcal{P}(N; \beta, V, \alpha) = \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) = \frac{e^{-\alpha N} \mathcal{Z}_N(\beta, V)}{\mathcal{E}(\beta, V, \alpha)}. \quad (2.42)$$

This function is the product of a rapidly increasing function ( $\mathcal{Z}_N$ ) and a rapidly decreasing function ( $e^{-\alpha N}$ ) of  $N$ , what gives rise to a sharp maximum at a value  $N = \tilde{N}$  given by the implicit condition

$$\alpha = \left. \frac{\partial \ln \mathcal{Z}_N(\beta, V)}{\partial N} \right|_{N=\tilde{N}}. \quad (2.43)$$

The agreement with (2.28b) reinforces the canonical  $\leftrightarrow$  grand canonical ensemble equivalence for large systems (thermodynamic limit).

## 2.6 Isothermal–Isobaric Ensemble: Isothermal–Isobaric Systems

In this ensemble, the volume is a fluctuating quantity and only its average value is fixed. Thus, similarly to the grand canonical ensemble, the constraints are

$$\int_0^\infty dV \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) = 1 , \quad (2.44a)$$

$$\int_0^\infty dV \int d\mathbf{x}^N H_N(\mathbf{x}^N) \rho_N(\mathbf{x}^N) = \langle E \rangle , \quad (2.44b)$$

$$\int_0^\infty dV V \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) = \langle V \rangle . \quad (2.44c)$$

Not surprisingly, the solution to the maximization problem of the Gibbs entropy functional (2.6) is

$$\rho_N(\mathbf{x}^N) = \frac{e^{-\gamma V} e^{-\beta H_N(\mathbf{x}^N)}}{V_0 C_N \Delta_N(\beta, \gamma)} , \quad (2.45)$$

where  $\gamma$  and  $\beta$  are again Lagrange multipliers, and the *isothermal–isobaric partition function* is

$$\Delta_N(\beta, \gamma) = \frac{1}{V_0 C_N} \int_0^\infty dV e^{-\gamma V} \int d\mathbf{x}^N e^{-\beta H_N(\mathbf{x}^N)} . \quad (2.46)$$

Again, use of (2.18) allows us to write

$$\Delta_N(\beta, \gamma) = \frac{1}{V_0} \int_0^\infty dV e^{-\gamma V} \mathcal{Z}_N(\beta, V) . \quad (2.47)$$

Taking into account (2.6), the entropy becomes

$$S = k_B (\ln \Delta_N + \beta \langle E \rangle + \gamma \langle V \rangle) . \quad (2.48)$$

From comparison with (1.13) we conclude that  $\beta = 1/k_B T$ ,

$$\gamma = \beta p , \quad (2.49)$$

and

$$G(T, p, N) = -k_B T \ln \Delta_N(\beta, \gamma) . \quad (2.50)$$

As before, the Lagrange multipliers are related to thermodynamic quantities:  $\beta$  is the inverse temperature parameter and  $\gamma$  is the pressure  $p$  divided by the thermal energy  $k_B T$ .

The average energy and volume are

$$\langle E \rangle = -\frac{\partial \ln \Delta_N}{\partial \beta}, \quad (2.51a)$$

$$\langle V \rangle = -\frac{\partial \ln \Delta_N}{\partial \gamma}. \quad (2.51b)$$

From here one can get the Maxwell relation

$$\frac{\partial \langle E \rangle}{\partial \gamma} = \frac{\partial \langle V \rangle}{\partial \beta}. \quad (2.52)$$

Equations (2.51) are complemented by

$$\alpha \equiv -\beta\mu = \frac{\ln \Delta_N}{N}, \quad (2.53)$$

which follows from the property  $\mu = G/N$  for one-component systems.

The energy and volume fluctuations are characterized by

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln \Delta_N}{\partial \beta^2} = k_B T^2 C_V, \quad (2.54a)$$

$$\langle V^2 \rangle - \langle V \rangle^2 = \frac{\partial^2 \ln \Delta_N}{\partial \gamma^2} = -\frac{1}{\beta} \left( \frac{\partial \langle V \rangle}{\partial p} \right)_{\beta, N} = k_B T \langle V \rangle \kappa_T. \quad (2.54b)$$

Equations (2.40) and (2.54b) are equivalent. Both show that the density fluctuations are proportional to the isothermal compressibility and decrease as the size of the system increases. In (2.40) the volume is constant, so that the density fluctuations are due to fluctuations in the number of particles, while the opposite happens in (2.54b).

Again, the cumulants can be obtained as

$$\mathcal{K}_E^{(k)} = (-1)^k \frac{\partial^k \ln \Delta_N}{\partial \beta^k}, \quad (2.55a)$$

$$\mathcal{K}_V^{(k)} = (-1)^k \frac{\partial^k \ln \Delta_N}{\partial \gamma^k}. \quad (2.55b)$$

The volume probability distribution function is

$$\mathcal{P}_N(V; \beta, \gamma) = \int d\mathbf{x}^N \rho_N(\mathbf{x}^N) = \frac{e^{-\gamma V} \mathcal{Z}_N(\beta, V)}{V_0 \Delta_N(\beta, \gamma)}. \quad (2.56)$$

**Table 2.1** Summary of statistical ensembles

Quantity	Statistical ensembles			
	Microcanonical	Canonical	Grand canonical	Isothermal–isobaric
$\rho_N(\mathbf{x}^N)$	$\frac{\Pi_{E,E+\Delta E}(H_N(\mathbf{x}^N))}{N!h^{dN}\omega_{\Delta E}(E, V, N)}$	$\frac{e^{-\beta H_N(\mathbf{x}^N)}}{N!h^{dN}\mathcal{Z}_N(\beta, V)}$	$\frac{e^{-\alpha N}e^{-\beta H_N(\mathbf{x}^N)}}{N!h^{dN}\Xi(\beta, V, \alpha)}$	$\frac{e^{-\gamma V}e^{-\beta H_N(\mathbf{x}^N)}}{V_0N!h^{dN}\Delta_N(\beta, \gamma)}$
Partition fcn.				
<i>Symbol</i>	$\omega_{\Delta E}(E, V, N)$	$\mathcal{Z}_N(\beta, V)$	$\Xi(\beta, V, \alpha)$	$\Delta_N(\beta, \gamma)$
<i>Expression</i>	$\int_{H_N=E}^{H_N=E+\Delta E} \frac{d\mathbf{x}^N}{N!h^{dN}}$	$\int \frac{d\mathbf{x}^N}{N!h^{dN}} e^{-\beta H_N(\mathbf{x}^N)}$	$\sum_{N=0}^{\infty} e^{-\alpha N} \mathcal{Z}_N(\beta, V)$	$\int_0^{\infty} \frac{dV}{V_0} e^{-\gamma V}$ $\times \mathcal{Z}_N(\beta, V)$
Potential	$S = k_B \ln \omega_{\Delta E}$	$F = -k_B T \ln \mathcal{Z}_N$	$\Omega = -k_B T \ln \Xi$	$G = -k_B T \ln \Delta_N$
$\beta \equiv \frac{1}{k_B T}$	$\frac{\partial \ln \omega_{\Delta E}}{\partial E}$	✓	✓	✓
$\gamma \equiv \beta p$	$\frac{\partial \ln \omega_{\Delta E}}{\partial V}$	$\frac{\partial \ln \mathcal{Z}_N}{\partial V}$	$\frac{\ln \Xi}{V}$	✓
$\alpha \equiv -\beta \mu$	$\frac{\partial \ln \omega_{\Delta E}}{\partial N}$	$\frac{\partial \ln \mathcal{Z}_N}{\partial N}$	✓	$\frac{\ln \Delta_N}{N}$
$E, \langle E \rangle$	✓	$-\frac{\partial \ln \mathcal{Z}_N}{\partial \beta}$	$-\frac{\partial \ln \Xi}{\partial \beta}$	$-\frac{\partial \ln \Delta_N}{\partial \beta}$
$N, \langle N \rangle$	✓	✓	$-\frac{\partial \ln \Xi}{\partial \alpha}$	✓
$V, \langle V \rangle$	✓	✓	✓	$-\frac{\partial}{\partial \gamma} \ln \Delta_N$

The check marks denote the control variables in each ensemble

As expected,  $\mathcal{P}_N(V)$  has a sharp peak at  $V = \tilde{V}$ , where

$$\gamma = \left. \frac{\partial \ln \mathcal{Z}_N(\beta, V)}{\partial V} \right|_{V=\tilde{V}}. \quad (2.57)$$

Now, comparison with (2.28a) shows the canonical  $\leftrightarrow$  isothermal–isobaric ensemble equivalence in the thermodynamic limit.

A summary of the main relations for the four ensembles considered in this chapter can be found in Table 2.1.

## 2.7 Ideal Gas

The exact evaluation of the partition functions (2.9), (2.18), (2.33), and (2.47) is in general a formidable task due to the involved dependence of the Hamiltonian on the coordinates of the particles. However, in the case of non-interacting particles (ideal

gas), the Hamiltonian depends only on the momenta:

$$H_N(\mathbf{x}^N) \rightarrow H_N^{\text{id}}(\mathbf{p}^N) = \sum_{i=1}^N \frac{p_i^2}{2m}, \quad (2.58)$$

where  $m$  is the mass of a particle. In this case the  $N$ -body Hamiltonian is just the sum over all the particles of the one-body Hamiltonian  $p_i^2/2m$  and the exact statistical-mechanical results can be easily obtained.

The expressions for the partition function, the thermodynamic potential, and the first derivatives of the latter for each one of the four ensembles considered above are listed in Table 2.2. In those expressions,  $\Gamma(x)$  is the well-known gamma function,

$$\zeta(\beta, V) \equiv \frac{V}{[\Lambda(\beta)]^d} \quad (2.59)$$

**Table 2.2** Physical quantities of an ideal gas

Quantity	Statistical ensembles			
	Microcanonical	Canonical	Grand canonical	Isothermal–isobaric
Partition fcn.				
<i>Symbol</i>	$\omega_{\Delta E}^{\text{id}}(E, V, N)$	$\mathcal{Z}_N^{\text{id}}(\beta, V)$	$\Xi^{\text{id}}(\beta, V, \alpha)$	$\Delta_N^{\text{id}}(\beta, \gamma)$
<i>Expression</i>	$\frac{[V(2\pi mE/h^2)^{d/2}]^N}{N!\Gamma(dN/2)} \frac{\Delta E}{E}$	$\frac{[\zeta(\beta, V)]^N}{N!}$	$\exp[e^{-\alpha}\zeta(\beta, V)]$	$\frac{\gamma^{-(N+1)}}{V_0[\Lambda(\beta)]^{dN}}$
Potential				
<i>Symbol</i>	$\frac{S^{\text{id}}(E, V, N)}{Nk_B}$	$\frac{F^{\text{id}}(T, V, N)}{Nk_B T}$	$\frac{\Omega^{\text{id}}(T, V, \mu)}{k_B T}$	$\frac{G^{\text{id}}(T, p, N)}{Nk_B T}$
<i>Expression</i>	$\ln \left[ \frac{V}{N} \left( \frac{4\pi mE}{dNh^2} \right)^{d/2} \right] + \frac{d+2}{2}$	$\ln \frac{N}{\zeta(\beta, V)} - 1$	$-e^{-\alpha}\zeta(\beta, V)$	$\ln \frac{p[\Lambda(\beta)]^d}{k_B T}$
$T$	$\frac{2}{d} \frac{E}{Nk_B}$	✓	✓	✓
$p^{\text{id}}$	$\frac{2}{d} \frac{E}{V}$	$\frac{N}{V} k_B T$	$k_B T e^{-\alpha} \frac{\zeta(\beta, V)}{V}$	✓
$\mu^{\text{id}}$	$-\frac{2}{d} \frac{E}{N} \ln \left[ \frac{V}{N} \left( \frac{4\pi mE}{dNh^2} \right)^{d/2} \right]$	$k_B T \ln \frac{N}{\zeta(\beta, V)}$	✓	$k_B T \ln \frac{p[\Lambda(\beta)]^d}{k_B T}$
$E, \langle E \rangle^{\text{id}}$	✓	$\frac{d}{2} Nk_B T$	$\frac{d}{2} k_B T e^{-\alpha} \zeta(\beta, V)$	$\frac{d}{2} Nk_B T$
$N, \langle N \rangle$	✓	✓	$e^{-\alpha} \zeta(\beta, V)$	✓
$V, \langle V \rangle$	✓	✓	✓	$\frac{Nk_B T}{p}$

The check marks denote the control variables in each ensemble

is the one-particle partition function and

$$\Lambda(\beta) \equiv \frac{h}{\sqrt{2\pi m/\beta}} \quad (2.60)$$

is the thermal de Broglie wavelength. When obtaining the thermodynamic potentials from the logarithm of the corresponding partition function, the thermodynamic limit ( $N \rightarrow \infty$ ) has been taken. This allows us to use the Stirling approximation  $\ln N! \approx N(\ln N - 1)$  and the limit  $N^{-1} \ln(\Delta E/E) \rightarrow 0$ .

Note that the expressions for the thermodynamic potentials and the thermodynamic variables (temperature, pressure, chemical potential, internal energy, number of particles, and volume) in a given ensemble are fully equivalent to those in any other ensemble. This is a manifestation of the ensemble equivalence in the thermodynamic limit, the only difference lying in the choice of independent and dependent variables.

## 2.8 Interacting Systems

Of course, particles do interact in real systems, so the Hamiltonian has the generic form

$$H_N(\mathbf{x}^N) = H_N^{\text{id}}(\mathbf{p}^N) + \Phi_N(\mathbf{r}^N), \quad (2.61)$$

where  $\Phi_N$  denotes the *total* potential energy. Since the interactions among the particles depend on the *relative* positions of the particles only, the potential energy function is invariant under translations, i.e.,

$$\Phi_N(\mathbf{r}_1 + \mathbf{a}, \mathbf{r}_2 + \mathbf{a}, \dots, \mathbf{r}_N + \mathbf{a}) = \Phi_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (2.62)$$

for any arbitrary displacement vector  $\mathbf{a}$ .

As a consequence of the decomposition (2.61), the canonical partition function factorizes into its ideal and non-ideal parts:

$$\mathcal{Z}_N(\beta, V) = \mathcal{Z}_N^{\text{id}}(\beta, V) \mathcal{Q}_N(\beta, V), \quad (2.63)$$

where  $\mathcal{Z}_N^{\text{id}}$  can be found in Table 2.2 and the non-ideal part

$$\mathcal{Q}_N(\beta, V) = V^{-N} \int d\mathbf{r}^N e^{-\beta \Phi_N(\mathbf{r}^N)} \quad (2.64)$$

is the *configuration integral*. We will refer to the exponential  $\exp[-\beta \Phi_N(\mathbf{r}^N)]$  in the integrand of  $\mathcal{Q}_N$  as the Boltzmann factor.

In the canonical ensemble,  $\mathcal{Q}_N$  is responsible for the *excess* contributions  $F^{\text{ex}} = F - F^{\text{id}}$ ,  $\langle E \rangle^{\text{ex}} = \langle E \rangle - \langle E \rangle^{\text{id}}$ ,  $p^{\text{ex}} = p - p^{\text{id}}$ ,  $\mu^{\text{ex}} = \mu - \mu^{\text{id}}$ :

$$F^{\text{ex}}(T, V, N) = -k_B T \ln \mathcal{Q}_N(\beta, V) , \quad (2.65a)$$

$$\langle E \rangle^{\text{ex}} = -\frac{\partial \ln \mathcal{Q}_N}{\partial \beta} , \quad (2.65b)$$

$$p^{\text{ex}} = k_B T \frac{\partial \ln \mathcal{Q}_N}{\partial V} , \quad (2.65c)$$

$$\mu^{\text{ex}} = -k_B T \frac{\partial \ln \mathcal{Q}_N}{\partial N} . \quad (2.65d)$$

In general, if  $A(\mathbf{r}^N)$  is a dynamical variable that depends on the particle positions only, its canonical-ensemble average is

$$\langle A \rangle = \frac{V^{-N}}{\mathcal{Q}_N(\beta, V)} \int d\mathbf{r}^N A(\mathbf{r}^N) e^{-\beta \Phi_N(\mathbf{r}^N)} . \quad (2.66)$$

The grand partition function does not factorize but can be written as

$$\Xi(\beta, V, \alpha) = 1 + \sum_{N=1}^{\infty} \frac{V^N \mathcal{Q}_N(\beta, V)}{N!} [\hat{z}(\beta, \alpha)]^N , \quad (2.67)$$

where we have taken into account that  $\mathcal{Q}_0 = 1$  and have introduced the quantity

$$\hat{z}(\beta, \alpha) \equiv \frac{z(\alpha)}{[\Lambda(\beta)]^d} , \quad (2.68)$$

$z$  being the fugacity defined by (2.15). Thus,  $\hat{z}$  is a *rescaled* fugacity with dimensions of a number density. According to (2.67), we observe that the configuration integrals  $\mathcal{Q}_N$  are directly related to the coefficients in the expansion of the grand partition function in powers of the quantity  $\hat{z}$ .

As for the isothermal–isobaric partition function, it is easy to obtain

$$\Delta_N(\beta, \gamma) = \frac{1}{V_0 N! [\Lambda(\beta)]^{dN}} \int_0^\infty dV e^{-\gamma V} V^N \mathcal{Q}_N(\beta, V) . \quad (2.69)$$

This shows that  $\Delta_N$  can be seen as proportional to the Laplace transform of  $V^N \mathcal{Q}_N$  with respect to volume.



## 2.9 Generalization to Mixtures

While so far we have restricted ourselves to one-component systems, most of the arguments and derivations can be easily generalized to mixtures. In particular, (2.8), (2.9), (2.17), (2.18), (2.31), (2.32), (2.45), and (2.46) generalize to

$$\rho_{\{N_v\}}(\mathbf{x}^N) = \frac{\Pi_{E,E+\Delta E}(H_{\{N_v\}}(\mathbf{x}^N))}{(\prod_v N_v!) h^{dN} \omega_{\Delta E}(E, V, \{N_v\})}, \quad (2.70a)$$

$$\omega_{\Delta E}(E, V, \{N_v\}) = \frac{1}{(\prod_v N_v!) h^{dN}} \int_{E \leq H_{\{N_v\}}(\mathbf{x}^N) \leq E + \Delta E} d\mathbf{x}^N, \quad (2.70b)$$

$$\rho_{\{N_v\}}(\mathbf{x}^N) = \frac{e^{-\beta H_{\{N_v\}}(\mathbf{x}^N)}}{(\prod_v N_v!) h^{dN} \mathcal{Z}_{\{N_v\}}(\beta, V)}, \quad (2.71a)$$

$$\mathcal{Z}_{\{N_v\}}(\beta, V) = \frac{1}{(\prod_v N_v!) h^{dN}} \int d\mathbf{x}^N e^{-\beta H_{\{N_v\}}(\mathbf{x}^N)}, \quad (2.71b)$$

$$\rho_{\{N_v\}}(\mathbf{x}^N) = \frac{\prod_v e^{-\alpha_v N_v} e^{-\beta H_{\{N_v\}}(\mathbf{x}^N)}}{(\prod_v N_v!) h^{dN} \mathcal{E}(\beta, V, \{\alpha_v\})}, \quad (2.72a)$$

$$\mathcal{E}(\beta, V, \{\alpha_v\}) = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \dots \frac{\prod_v e^{-\alpha_v N_v}}{(\prod_v N_v!) h^{dN}} \int d\mathbf{x}^N e^{-\beta H_{\{N_v\}}(\mathbf{x}^N)}, \quad (2.72b)$$

$$\rho_{\{N_v\}}(\mathbf{x}^N) = \frac{e^{-\gamma V} e^{-\beta H_{\{N_v\}}(\mathbf{x}^N)}}{V_0 (\prod_v N_v!) h^{dN} \Delta_{\{N_v\}}(\beta, \gamma)}, \quad (2.73a)$$

$$\Delta_{\{N_v\}}(\beta, \gamma) = \frac{1}{V_0 (\prod_v N_v!) h^{dN}} \int_0^{\infty} dV e^{-\gamma V} \int d\mathbf{x}^N e^{-\beta H_{\{N_v\}}(\mathbf{x}^N)}, \quad (2.73b)$$

respectively. For instance, from (2.72) it is easy to check that, in the grand canonical ensemble, one has

$$\langle N_v \rangle = -\frac{\partial \ln \mathcal{E}}{\partial \alpha_v}, \quad (2.74a)$$

$$\langle N_{v_1} N_{v_2} \rangle - \langle N_{v_1} \rangle \langle N_{v_2} \rangle = \frac{\partial^2 \ln \mathcal{E}}{\partial \alpha_{v_2} \partial \alpha_{v_1}} = -\frac{\partial \langle N_{v_1} \rangle}{\partial \alpha_{v_2}}. \quad (2.74b)$$

Equation (2.74b) is a generalization of (2.39b).

Table 2.2 can be generalized to ideal-gas mixtures. In particular,

$$\Delta_{\{N_v\}}^{\text{id}}(\beta, \gamma) = \frac{\gamma^{-(N+1)} N!}{V_0 \prod_v N_v! [\Lambda_v(\beta)]^{dN_v}}, \quad (2.75a)$$

$$G^{\text{id}}(T, p, \{N_v\}) = k_B T \sum_v N_v \ln \frac{x_v p [\Lambda_v(\beta)]^d}{k_B T}, \quad (2.75b)$$

$$\mu_v^{\text{id}}(T, p, x_v) = k_B T \ln \frac{x_v p [\Lambda_v(\beta)]^d}{k_B T}, \quad (2.75c)$$

where  $\Lambda_v(\beta)$  is the thermal de Broglie wavelength of species  $v$ , which is given by (2.60) with the replacement  $m \rightarrow m_v$ , where  $m_v$  is the mass of a particle of species  $v$ .

## Exercises

**2.1** Use the Lagrange multiplier method to maximize the entropy functional (2.3) with the constraint (2.7) and prove the microcanonical distribution (2.8). Derive (2.12).

**2.2** Use the Lagrange multiplier method to maximize the entropy functional (2.3) with the constraints (2.16) and prove the canonical distribution (2.17). Derive (2.20).

**2.3** Derive (2.23).

**2.4** Check (2.25) for  $3 \leq k \leq 6$ .

**2.5** Use the Lagrange multiplier method to maximize the entropy functional (2.5) with the constraints (2.29) and prove the grand canonical distribution (2.31). Derive (2.34).

**2.6** How should the derivative in (2.36a) be interpreted, at constant  $\alpha = -\beta\mu$  or at constant  $\mu$ ? Are both interpretations equivalent?

**2.7** Derive (2.38b).

**2.8** Use the Lagrange multiplier method to maximize the entropy functional (2.6) with the constraints (2.44) and prove the isothermal–isobaric distribution (2.45). Derive (2.48).

**2.9** Derive (2.51b).

**2.10** How should the derivative in (2.51a) be interpreted, at constant  $\gamma = \beta p$  or at constant  $p$ ? Are both interpretations equivalent?

**2.11** Prove that the area and the volume of a hypersphere of radius  $R$  in  $k$  dimensions are

$$\frac{2\pi^{k/2}}{\Gamma(k/2)} R^{k-1}, \quad \frac{\pi^{k/2}}{\Gamma(k/2 + 1)} R^k, \quad (2.76)$$

respectively. Hint: Evaluate the multiple Gaussian integral  $\int d\mathbf{r}^k e^{-r^2}$  in both Cartesian and spherical coordinates.

**2.12** Making use of (2.76), prove that the microcanonical partition function for an ideal gas,  $\omega_{\Delta E}^{\text{id}}$ , is indeed given by the expression shown in Table 2.2.

**2.13** Prove (2.59).

**2.14** Check the expressions of Table 2.2.

**2.15** Using Table 2.2, prove that for an ideal gas the energy, number, and volume probability distribution functions (2.26), (2.42), and (2.56) reduce to

$$\mathcal{P}_N^{\text{id}}(E) = \beta \frac{e^{-\beta E} (\beta E)^{dN/2-1}}{\Gamma(dN/2)}, \quad (2.77a)$$

$$\mathcal{P}^{\text{id}}(N) = e^{-\langle N \rangle} \frac{\langle N \rangle^N}{N!}, \quad (2.77b)$$

$$\mathcal{P}_N^{\text{id}}(V) = \beta p \frac{e^{-\beta p V} (\beta p V)^N}{N!}, \quad (2.77c)$$

respectively.

**2.16** Define the scaled quantities  $E^* = E / \langle E \rangle = 2\beta E / dN$ ,  $N^* = N / \langle N \rangle$ ,  $V^* = V / \langle V \rangle = \beta p V / N$  and obtain the corresponding distributions  $\mathcal{P}_N^{\text{id}}(E^*) = \langle E \rangle \mathcal{P}_N^{\text{id}}(E)$ ,  $\mathcal{P}^{\text{id}}(N^*) = \langle N \rangle \mathcal{P}^{\text{id}}(N)$ , and  $\mathcal{P}_N^{\text{id}}(V^*) = \langle V \rangle \mathcal{P}_N^{\text{id}}(V)$  from (2.77). Explore the shape of those functions as  $N$  (or  $\langle N \rangle$ ) increases.

**2.17** Justify (2.70)–(2.73).

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