5. The Gibbs distribution and some applications

In Section 3.4 we obtained the Gibbs probability distribution function for a quantum sub system as (see Eq. (3.11))

$$w_n^{(a)} = e^{-\alpha^{(a)} - \beta E_n^{(a)}} \tag{5.1}$$

where $E_n^{(a)}$ are the representative many body energies[1] and $\alpha^{(a)}$ is fixed by the normalization condition (see Eq. (3.5))

$$\sum_n w_n^{(a)} = 1. \tag{5.2}$$

Eq. (5.1) is often called the Gibbs ensemble, or more completely, the Gibbs *petit ensemble*. In obtaining Eq. (3.11) we invoked the idea that the sub-system probabilities were multiplicative and, furthermore, that they must only depend on the additive mechanical constants of motion.

In Appendix 5A we derive Eq. (5.1) using a different strategy which employs the micro-canonical ensemble. In the process we will also establish that $\beta = 1/k_B T$ where T is the absolute temperature. We also establish this relation below in Section 5.2 using a thermodynamic argument.

5.1. Variable particle numbers

Up to this point we have been assuming that the number of particles in a sub-system remains fixed. But our sub systems generally have "boundaries" and it natural to consider the case where particles enter and leave a subsystem by crossing those boundaries[2]: i.e., whereas we might earlier have thought of the boundaries as distorting so as contain all particles in a sub system, we now regard their volume as fixed and the particles moving in or out across the "surface" that surrounds them. The representative many-body energy levels used to describe our sub system must then be generalized as $E_n^{(a)} \to E_{nN}^{(a)}$ and likewise the sub-system probabilities as $w_n^{(a)} \to w_{nN}^{(a)}$.

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[1] The energy levels here are the exact *many body energy* levels, E_n, of the system as a whole which implicitly include the effects of wavefunction symmetry: symmetric (Bose-Einstein) or antisymmetric (Fermi-Dirac). In an ideal gas one typically works with the non-interacting single particle energies, ε_n, and one must account for such effects which we take up in a later chapter.

[2] Boundaries can be interpreted in a more general sense than simply walls of a container. When multiple particle species are present they may change into other species via chemical reactions. When different "phases" of a material are present, such as liquid and solid, particles may pass between them.

Mechanics implicitly assumes *particle numbers* are conserved; i.e., they too are *additive*. Hence we are encouraged to write $w_{nN}^{(a)}$ as[3]

$$l n w_{nN}^{(a)} = -\alpha^{(a)} - \beta E_{nN}^{(a)} - \gamma N^{(a)}. \tag{5.3}$$

or

$$w_{nN}^{(a)} = e^{-\alpha^{(a)} - \beta E_{nN}^{(a)} - \gamma N^{(a)}}. \tag{5.4}$$

where γ is a parameter yet to be determined. This form is commonly called the Gibbs *grand ensemble*; it too is derived independently from the micro-canonical ensemble in Appendix 5A. Since $w_{nN}^{(a)}$ now has two indices, n and N, our normalization condition (5.2) must now be replaced by

$$\sum_N \sum_n w_{nN}^{(a)} = 1. \tag{5.5}$$

Taking the average of some quantity $f(E_{nN})$ with N-dependent energy levels, E_{nN}, likewise involves a sum over both n and N, as opposed the single sum over n for a quantity $f(E_n)$ in the petit ensemble. We will further develop this approach at various points later on in this chapter.

5.2. Connecting the probability function to the temperature.

Returning to our fixed N ensemble, our subsystem distribution function $w_n^{(a)}$ contains the parameter β which up to this point we have left undefined. In Chapter 4 we introduced the definition of the thermodynamic temperature as $1/T = dS/dE$ (see Eq. (4.5)). Given the distribution function we can calculate the entropy using Eq. (3.27); likewise we can calculate the average energy $\bar{E}$ using Eq. (3.12). Inserting Eq. (3.11) for w_n into both of these expressions gives

$$S(\beta) = -k_B \sum_n w_n l n w_n$$

$$= -k_B \sum_n e^{-\alpha - \beta E_n} \left(-\alpha - \beta E_n \right) \tag{5.6}$$

and

---

[3] Do not confuse the constant γ with the vector constant $\boldsymbol{\gamma}$ introduced earlier in connection with momentum additivity.

$$\bar{E}(\beta) = \sum_n E_n e^{-\alpha - \beta E_n} , \qquad (5.7)$$

where we have suppressed the subsystem index. Using the chain rule we can form the ratio $\frac{dS}{dE} = \frac{dS/d\beta}{d\bar{E}/d\beta} = \frac{1}{T}$. Carrying out the differentiations on (5.6) and (5.7) and rearranging the numerator we obtain

$$\frac{dS}{dE} = \frac{-k_B \sum_n e^{-\alpha - \beta E_n} \left(-\beta E_n (-d\alpha/d\beta - E_n) - (d\alpha/d\beta + E_n)(1 - \alpha) \right)}{\sum_n E_n e^{-\alpha - \beta E_n} (-d\alpha/d\beta - E_n)} . \qquad (5.8)$$

The second term in the numerator of (5.8) vanishes since it is proportional to the derivative of the normalization condition

$$\frac{d}{d\beta} \sum_n e^{-\alpha - \beta E_n} = -\sum_n e^{-\alpha - \beta E_n} \left(\frac{\partial \alpha}{\partial \beta} + E_n \right) = 0 . \qquad (5.9)$$

The remainder of the numerator and denominator then cancel apart from a factor $k_B \beta$ giving us

$$\beta = \frac{1}{k_B T} . \qquad (5.10)$$

5.3. Connecting the probability function to the thermodynamic potentials

5.3.1. The petit ensemble

We start with the petit ensemble and recall our thermodynamic definition of the free energy given in Eq. (4.24) which in terms of the statistical energy $\bar{E}$ we write as

$$F = \bar{E} - TS . \qquad (5.11)$$

Substituting Eq.'s (5.6) and (5.7) we can write F as

$$\begin{aligned}
F &= \bar{E} - TS \\
&= \sum_n E_n e^{-\alpha - \beta E_n} - k_B T \sum_n e^{-\alpha - \beta E_n} \left(\alpha + \beta E_n \right) \\
&= -k_B T \alpha \sum_n e^{-\alpha - \beta E_n} = -k_B T \alpha \sum_n w_n
\end{aligned}$$

which on using our normalization $\sum_n w_n = 1$ becomes

$$F = -k_B T \alpha . \qquad (5.12)$$

We can now rewrite our probability function as

$$w_n = e^{\beta F - \beta E_n}, \tag{5.13a}$$

or equivalently

$$w_n = e^{\frac{F - E_n}{k_B T}}. \tag{5.13b}$$

Applying our normalization condition to (5.14) and taking the log of the resulting expression we obtain a statistical physics expression for the free energy as

$$F = -\frac{1}{\beta} \ln \left(\sum_n e^{-\beta E_n} \right). \tag{5.14}$$

As in the classical case given by Eq. (2.30), one introduces the so called *partition function*, Z, as

$$Z \equiv \sum_n e^{-\beta E_n} \tag{5.15}$$

whereupon F can be written as

$$F = -\frac{1}{\beta} \ln Z \tag{5.16a}$$

$$= -k_B T \ln Z. \tag{5.16b}$$

Other thermodynamic properties are readily calculated from the free energy. As an example the entropy is given by (see Eq. (4.31a))

$$S = \left(\frac{\partial F}{\partial T} \right)_V = -\frac{\partial}{\partial T} \left(k_B T \ln Z \right). \tag{5.17}$$

Similarly the energy is calculated by combining the definition (5.11) and Eq. (5.17) as

$$\overline{E} = F + TS$$

$$= F - T \left(\frac{\partial F}{\partial T} \right)_V$$

$$= -k_B T \ln Z + T \frac{\partial}{\partial T} \left(k_B T \ln Z \right)$$

or

$$\overline{E} = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V. \tag{5.18}$$

Carrying out the differentiation in (5.18) gives

$$\overline{E} = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}. \tag{5.19}$$

5.3.2. The grand ensemble

To obtain corresponding equations for the grand ensemble we recall our definition of entropy which we continue to write as $S = -k_B \overline{\ln w_{nN}}$ but where N is now a variable with some average value $\overline{N}$. Inserting Eq. (5.4) gives

$$S = k_B \left(\alpha + \beta \overline{E}_{nN} + \gamma \overline{N} \right). \tag{5.20}$$

We recall the thermodynamic definition of the Gibbs free energy (see Eq.'s (4.25) and (4.44)),

$$\Phi = \mu \overline{N} = \overline{E} + PV - TS,$$

which we rewrite as

$$S = -\frac{\mu \overline{N}}{T} + \frac{\overline{E} + PV}{T}. \tag{5.21}$$

Comparing (5.20) and (5.21) and recalling our definition of Ω (see (4.46)) we see that

$$\alpha = -\frac{\Omega}{k_B T}, \qquad \beta = \frac{1}{k_B T}, \qquad \gamma = -\frac{\mu}{k_B T}; \tag{5.22a,b,c}$$

note the difference in α between the grand ensemble given here and that for petit ensemble in Eq. (5.12). Eq. (5.4) for the Gibbs grand ensemble can now be written

$$w_{nN} = e^{\beta(\Omega + \mu N - E_{nN})}; \tag{5.23}$$

given that $F = G + \Omega = \mu \overline{N} + \Omega$, Eq. (5.23) is identical to Eq. (5.13a), but writing it as we have here is preferred since it makes the particle number dependence explicit.

Applying our normalization condition (5.5) to Eq. (5.23) gives

$$\Omega = -\frac{1}{\beta} \ln \left[\sum_N \left(e^{\beta \mu N} \sum_n e^{-\beta E_{nN}} \right) \right]. \tag{5.24}$$

Hence the Ω potential in the grand ensemble plays a role similar to that of F in the petit ensemble (see Eq. (5.14)). Using the relation (see Eq. (4.47))

$$d\Omega = -SdT + PdV - \overline{N}d\mu \tag{5.25}$$

we have

$$S = \left(\frac{d\Omega}{dT} \right)_{\mu,V} \tag{5.26}$$

and

$$\bar{N} = \left(\frac{d\Omega}{d\mu} \right)_{T,V}.$$

(5.27)

5.3.3. Alternate normalizations

Rather than normalizing our probability functions through the exponent α it is also common to do it via a pre-factor to the exponent. For the petit ensemble we would write this as

$$w_n = A_P e^{-\beta E_n}$$

(5.28)

while for the grand ensemble it would be

$$w_{nN} = A_G e^{\beta(\mu N - E_{nN})}$$

(5.29)

where the constants that normalize these petit and grand cases differ and are given by

$$A_P = e^{\beta F}$$

(5.30)

or

$$A_G = e^{\beta \Omega}.$$

(5.31)

5.4. The classical and quasi-classical Gibbs distributions

5.4.1. The classical distribution function

The probability density in the classical limit was introduced through Eq. (2.24) where we have now identified $\beta = 1/k_B T$. Using the alternate normalization involving a prefactor A_c to the exponential, we can write the *classical* differential probability as (where we continue to suppress the subsystem index)

$$dw = A_C e^{-\beta E(p,q)} dp dq ;$$

(5.32)

with our normalization $\int dw = 1$ the constant A_C is given by

$$A_C = \frac{1}{\int dp dq e^{-\beta E(p,q)}}.$$

(5.33)

As in the quantum mechanical case, we can introduce a partition function through the definition

$$Z = \int dp dq e^{-\beta E(p,q)}$$

(5.34)

Sub system averages of a function $f(p,q)$ are then given

$$\bar{f} = \frac{\int dp dq f(p,q) e^{-\beta E(p,q)}}{\int dp dq e^{-\beta E(p,q)}}$$

(5.35a)

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or

$$\bar{f} = \frac{\int dpdq f(p,q) e^{-\beta E(p,q)}}{Z} \qquad (5.35b)$$

For many systems the energy can be written as $E(p,q) = K(p,q) + U(p,q)$, where $K(p,q)$ and $U(p,q)$ denote the subsystem kinetic and potential energies. We can then write the differential probability as a product $dw(p,q) = dw(p)dw(q)$ where

$$dw(p) = A_p e^{-\beta K(p)} dp \qquad (5.36a)$$

and

$$dw(q) = A_q e^{-\beta U(q)} dq, \qquad (5.36b)$$

with $A_C = A_p \cdot A_q$ and A_p and A_q determined separately by

$$\int dw_p = 1 \rightarrow \frac{1}{A_p} = \int dp e^{-\beta K(p)} \qquad (5.37a)$$

and

$$\int dw_q = 1 \rightarrow \frac{1}{A_q} = \int dq e^{-\beta U(q)}. \qquad (5.37b)$$

5.4.2 The quasi-classical distribution function

In taking the classical limit of the quantum mechanical probability (5.28) to obtain a differential probability, rather than writing it as in Eq. (5.32) it is more compatible with quantum mechanics to write it as

$$dw = A_Q e^{-\beta E(p,q)} \frac{dpdq}{(2\pi\hbar)^s}$$

$$= A_Q e^{-\beta E(p,q)} d\Gamma \qquad (5.38)$$

rather than (5.32) where $d\Gamma = dpdq / (2\pi\hbar)^s$. As far as calculating averages is concerned this change simply redefines the normalization constant, $A_C \rightarrow A_Q$, which in any case generally cancels out. In a similar way we would redefine the partition function and free energy as

$$Z = \int d\Gamma e^{-\beta E(p,q)} \qquad (5.39)$$

and

$$F = -\frac{1}{\beta} ln \int d\Gamma \, e^{-\beta E(p,q)}. \tag{5.40}$$

A more serious issue arises when we account for identical particles. Although classically particles are distinguishable, quantum mechanically identical particles, such as electrons, are not. Hence in integrating over phase space we must account for situations where identical particles have the "same coordinates" (more correctly are in the same quantum state). Here the issue of wave function symmetry arises which we will take up in chapter 9. In any case at high temperature this situation becomes progressively less likely.

But one *never* escapes the fact that interchanging two identical particles with different coordinates does not represent a different quantum state. Extending this to N such particles we see that to remove the effect of quantum-mechanically indistinguishable configurations of the particles one must *divide* $d\Gamma$ by N!, *the number of permutations* of the particles; i.e.,

$$Z = \frac{1}{N!} \int d\Gamma \, e^{-\beta E(p,q)} \tag{5.41}$$

or

$$F = -\frac{1}{\beta} ln \frac{1}{N!} \int d\Gamma \, e^{-\beta E(p,q)}. \tag{5.42}$$

5.5. The classical mechanics of an ideal gas: the Maxwell velocity distribution

As our first application we consider the properties of a collection of atoms in a gas. When the gas is dilute the potential energy can be largely ignored if the forces between the particles have a short range[4]. Here we will assume $U(q)$ vanishes[5] in which case the atoms *do not interact*, and each one can then be treated as a *separate subsystem*[6]. In the simplest case our gas consists of identical point particles of mass m. The kinetic energy of a single particle in three dimensions is

$$K(\mathbf{p}) = \sum_{i=1}^{N} \left(\frac{p_{x_i}^2}{2m} + \frac{p_{y_i}^2}{2m} + \frac{p_{z_i}^2}{2m} \right). \tag{5.43}$$

---

[4] Coulomb forces have a long range and special considerations are required in dealing with that case.

[5] Note this is an approximation since the velocities change continuously during a collision with the velocity of one particle affecting that of another in a position dependent manner. In other words the velocities of the different particles are not fully independent, and depend on the coordinates of the other particles.

[6] One must still assume that sufficient interactions are present so as to bring the system into thermal equilibrium.

We can split $dw_p = dw_{\mathbf{p}_1} dw_{\mathbf{p}_2} \cdots dw_{\mathbf{p}_N}$ where

$$dw_{\mathbf{p}_i} = A_{\mathbf{p}_i} e^{-\frac{\beta}{2m}\left(p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2\right)} dp_{x_i} dp_{y_i} dp_{z_i} \tag{5.44}$$

We fix the normalization constant $A_{\mathbf{p}_i}$ according to (5.36a) using the form

$$\int_{-\infty}^{+\infty} dx \exp(-\alpha x^2) = \sqrt{\pi / \alpha}$$

with the result

$$dw_{\mathbf{p}_i} = \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\frac{\beta}{2m}\left(p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2\right)} dp_{x_i} dp_{y_i} dp_{z_i} . \tag{5.45}$$

It is also common to express the differential probability with respect to the velocity normalized according to $\int dw_{\mathbf{v}_i} = 1$ with the result

$$dw_{\mathbf{v}_i} = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{\beta m}{2}\left(v_{x_i}^2 + v_{y_i}^2 + v_{z_i}^2\right)} dv_{x_i} dv_{y_i} dv_{z_i} . \tag{5.46}$$

This expression is called the *Maxwell velocity distribution*. Transforming to polar coordinates, where the velocity is isotropic, and dropping the index i, Eq. (5.46) takes the form

$$dw_{\mathbf{v}} = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m v^2} v^2 dv \sin\theta d\theta d\varphi . \tag{5.47}$$

The average value of any component of the velocity is zero by symmetry. The average of the square of the velocity of all components is the same; evaluating it for v_x^2 gives

$$\overline{v_x^2} = \int v_x^2 dw_{\mathbf{v}} = \left(\frac{\beta m}{2\pi}\right)^{3/2} \int v_x^2 e^{-\frac{\beta m}{2}\left(v_x^2 + v_y^2 + v_z^2\right)} dv_x dv_y dv_z$$

$$= \left(\frac{\beta m}{2\pi}\right)^{1/2} \int v_x^2 e^{-\frac{\beta m}{2} v_x^2} dv_x = \frac{1}{\beta m} .$$

Hence

$$\overline{v_x^2} = \frac{k_B T}{m} . \tag{5.48}$$

From the isotropy it follows that

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = \frac{3k_BT}{m}.$$ (5.49)

The average kinetic energy is then given by

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT.$$ (5.50)

With our normalization this result corresponds to the average energy *per particle*. A gas consisting of N atoms would then have an energy

$$E = \frac{3N}{2}k_BT$$ (5.51)

and hence a constant volume heat capacity of

$$C_V = \frac{3Nk_B}{2}$$ (5.52)

5.6. The Gibbs distribution for classical harmonic oscillators

Assume we have an array of N point particles bound to each other by a potential that can be represented as a quadratic form in the displacements, q_i, q_j, from their equilibrium positions. The Hamiltonian of such a system can be written as

$$H(p,q) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i,j}^{N} k_{ij}q_iq_j$$ (5.53)

where m are the particle masses and k_{ij} are the "spring constants" associated with sites i and j with $k_{ii} = 0$. As known from mechanics we can carry out a canonical (normal-mode) transformation on (5.53) to a new Hamiltonian involving a set of coordinates, p'_α, q'_α, which are linearly related to p_α, q_α but that oscillate *independently* of each other with angular frequencies[7], ω_α; in doing so we can write $p_i = \sqrt{m}\, p'_i$ so as to eliminate the masses[8]. The resulting energy can then be written

$$E(p',q') = \frac{1}{2}\sum_{\alpha=1}^{N}\left(p'^2_\alpha + \omega_\alpha^2 q'^2_\alpha\right).$$ (5.54)

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[7] For a single oscillator with mass m and spring constant k the frequency is $\omega = \sqrt{k/m}$.

[8] More generally, the particles can have different masses which can be incorporated into the transformation leading to the primed coordinates.

As in the case of the Maxwell gas, we treat each oscillator as an *independent subsystem*. The differential probabilities given by Eq.'s (5.36a,b) factor into products, one for the momentum and one for the position of each oscillator, α; after normalization according to (5.37a,b) we obtain

$$dw_{p'_\alpha} = \sqrt{\frac{\beta}{2\pi}} e^{-\frac{1}{2}\beta p'^2_\alpha} \tag{5.55}$$

and

$$dw_{q'_\alpha} = \sqrt{\frac{\beta\omega^2_\alpha}{2\pi}} e^{-\frac{1}{2}\beta\omega^2_\alpha q'^2_\alpha} \tag{5.56}$$

Given these forms we can then compute the averages

$$\overline{p'^2_\alpha} = \frac{1}{\beta} \tag{5.57}$$

and

$$\overline{q'^2_\alpha} = \frac{1}{\beta\omega^2_\alpha} . \tag{5.58}$$

With these expressions we can calculate the average energy, $\overline{\varepsilon_\alpha}$ of the mode α as

$$\overline{\varepsilon_\alpha} = \frac{1}{2}\left(\overline{p'^2_\alpha} + \omega^2_\alpha \overline{q'^2_\alpha}\right) = \frac{1}{\beta}$$

or

$$\overline{\varepsilon_\alpha} = k_B T . \tag{5.59}$$

Note this result is *independent of the oscillator frequency.* The total energy for N oscillators is then

$$\overline{E^{total}} = \sum_{\alpha=1}^{N} \overline{\varepsilon_\alpha} = Nk_B T . \tag{5.60}$$

The heat capacity (see Eq. (4.19)) is then $C = N k_B$.

In a three dimensional system each particle involves three different displacements so $N = 3N$ where N is the *number of atoms*; we then have

$$C = 3Nk_B ; \tag{5.61}$$

this is called the law of *Dulong and Petit*. Note it is *twice* the value we obtained for the case of free particles due to an equal contribution arising from the potential energy.

5.7. Quantum mechanical oscillators

After performing a normal mode transformation and replacing the momenta by operators the Hamiltonian operator analogous to Eq. (5.53) has the form

$$\hat{H} = \frac{1}{2} \sum_{\alpha=1}^{N} \left(\hat{p}_\alpha'^2 + \omega_\alpha^2 q_\alpha'^2 \right) \tag{5.62}$$

Since each oscillator is independent the total energy is

$$E^{total} = \sum_{\alpha}^{N} \varepsilon_{n_\alpha}, \tag{5.63}$$

and as shown in quantum mechanics text books, the energies of the individual oscillators are given by

$$\varepsilon_{n_\alpha} = \hbar\omega_\alpha \left(n_\alpha + \frac{1}{2} \right) \tag{5.64}$$

where n_α are integers associated with the individual oscillators.

5.7.1. The average energy

Again treating each oscillator as an independent sub system we calculate the average energy of the αth mode using Eq. (5.19)

$$\bar{\varepsilon}_\alpha = \frac{\sum_{n_\alpha} \varepsilon_{n_\alpha} e^{-\beta\varepsilon_{n_\alpha}}}{\sum_{n_\alpha} e^{-\beta\varepsilon_{n_\alpha}}} = \frac{\sum_{n_\alpha} \hbar\omega_\alpha \left(n_\alpha + 1/2 \right) e^{-\beta\hbar\omega_\alpha \left(n_\alpha + 1/2 \right)}}{\sum_{n_\alpha} e^{-\beta\hbar\omega_\alpha \left(n_\alpha + 1/2 \right)}}$$

and on dividing out the factor $e^{-\beta\hbar\omega_\alpha/2}$ obtain

$$\bar{\varepsilon}_\alpha = \frac{\sum_{n_\alpha} n_\alpha \hbar\omega_\alpha e^{-\beta n_\alpha \hbar\omega_\alpha}}{\sum_{n_\alpha} e^{-\beta n_\alpha \hbar\omega_\alpha}} + \frac{\hbar\omega_\alpha}{2}. \tag{5.65}$$

To evaluate this we first write the denominator as $S(x) = \sum_{n=0}^{\infty} x^n$ where $x = e^{-\beta\hbar\omega_\alpha}$. Using the expression for the sum of a geometric series,

$$S(x,N) = \sum_{n=0}^{N} x^n = \frac{1 + x^{N+1}}{1 - x},$$

and taking the limit $N \rightarrow \infty$ we obtain

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$$S(\beta\hbar\omega_\alpha) = \frac{1}{1 - e^{-\beta\hbar\omega_\alpha}}.$$

Next we note that the numerator of (5.65) can be written as

$$\frac{\partial}{\partial\beta} S(\beta\hbar\omega_\alpha) = -\frac{\hbar\omega_\alpha e^{-\beta\hbar\omega_\alpha}}{(1 - e^{-\beta\hbar\omega_\alpha})^2}.$$

Combining these two results and dividing out the factor $e^{-\beta\hbar\omega_\alpha}$ we can then write Eq. (5.65) as

$$\bar{\varepsilon}_\alpha = \frac{\hbar\omega_\alpha}{e^{\beta\hbar\omega_\alpha} - 1} + \frac{\hbar\omega_\alpha}{2}. \tag{5.66}$$

This is referred to as the *Planck distribution*.

At high temperatures $\beta \to 0$ and we can expand $e^{\beta\hbar\omega_\alpha} = 1 + \beta\hbar\omega_\alpha \cdots$ and Eq. (5.66) becomes $\bar{\varepsilon}_\alpha = k_B T$; i.e., we obtain the classical result obtained in the previous section, *independent* of the oscillator frequency[9]. At temperatures $k_B T \ll \hbar\omega$ we have

$$\bar{\varepsilon}_\alpha = \hbar\omega_\alpha \left(e^{-\beta\hbar\omega_\alpha} + \frac{1}{2} \right); \quad \beta \to \infty, \tag{5.67}$$

with a limiting value of $\bar{\varepsilon}_\alpha = \hbar\omega_\alpha / 2$, the zero-point energy.

5.7.2. Differential position probability for a quantum oscillator

We now construct the quantum mechanical differential probability, dw_q, in position space analogous to that for the classical case given by Eq. (5.56). To do this we recall the expression for the density matrix in terms of a basis set (see Eq. (B.7) in Appendix B)

$$\rho(q,q',t) = \sum_{m,n} \rho_{mn} \Psi_n^*(q',t) \Psi_m(q,t) \tag{5.68}$$

where $\Psi_n(q,t) = e^{-iE_n t/\hbar} \psi_n(q)$ and $\psi_n(q)$ are the normalized harmonic oscillator wave functions. The off-diagonal terms average to zero in a statistical description and we can then write

$$\rho(q,q,t) = \sum_n w_n \psi_n^2(q), \tag{5.69}$$

---

[9] Of course the temperatures required for a transition from quantum to classical behavior increase with the frequencies of the oscillators.

where $\rho_{nn} = w_n$ and we used the property that the wave functions are real. In quantum mechanics the probability of finding a particle at q is $\rho(q,q)$. Substituting w_n from Eq. (5.1) into (5.69) gives

$$\rho(q,q,t) = A\sum_n e^{-\beta\varepsilon_n} \psi_n^2(q) \tag{5.70}$$

and identifying $dw_q = \rho(q,q)dq$ we have

$$dw_q = \sum_n Ae^{-\beta\varepsilon_n} \psi_n^2 dq . \tag{5.71}$$

Our task now is to evaluate the sum in (5.71). We start by differentiating (5.60) as

$$\frac{d\rho(q)}{dq} = 2A\sum_n e^{-\beta\varepsilon_n} \psi_n(q)d\frac{d\psi_n}{dq} ; \tag{5.72}$$

exploiting well known properties of harmonic oscillator wave functions $d\psi_n / dq$ can be written

$$\frac{d\psi_n(q)}{dq} = \frac{i}{\hbar}\hat{p}\psi_n(q)$$

$$= \frac{i}{\hbar}\left[(\hat{p})_{n-1,n} \psi_{n-1} + (\hat{p})_{n+1,n} \psi_{n+1}\right]. \tag{5.73}$$

Using the relations $(\hat{p})_{n-1,n} = -i\omega(q)_{n-1,n}$ and $(\hat{p})_{n+1,n} = -i\omega(q)_{n+1,n}$, which follow from the Heisenberg equation for a harmonic oscillator, we can rewrite (5.73) as

$$\frac{d\psi_n(q)}{dq} = \frac{\omega}{\hbar}\left[(q)_{n-1,n} \psi_{n-1} - (q)_{n+1,n} \psi_{n+1}\right] \tag{5.74}$$

and Eq. (5.72) becomes

$$\frac{d\rho(q)}{dq} = \frac{2A\omega}{\hbar}\left[\sum_{n=0}^{\infty} q_{n-1,n}\psi_n\psi_{n-1}e^{-\beta\varepsilon_n} - \sum_{n=0}^{\infty} q_{n+1,n}\psi_n\psi_{n+1}e^{-\beta\varepsilon_n}\right]. \tag{5.75}$$

We change the index in the first summation from n to $n+1$, and note $q_{n+1,n} = q_{n,n+1}$, $\varepsilon_{n+1} = \varepsilon_n + \hbar\omega$ and $q_{-1,0} = 0$ which yields

$$\frac{d\rho(q)}{dq} = -\frac{2A\omega}{\hbar}\left(1 - e^{-\beta\hbar\omega}\right)\sum_{n=0}^{\infty} q_{n,n+1}\psi_n\psi_{n+1}e^{-\beta\varepsilon_n} . \tag{5.76}$$

Examining the effect of the position operator q in a similar way yields

$$q\rho(q) = A\left(1 + e^{-\beta\hbar\omega}\right)\sum_{n=0}^{\infty} q_{n,n+1}\psi_n\psi_{n+1}e^{-\beta\varepsilon_n} , \tag{5.77}$$

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and on comparing (5.76) with (5.77) we obtain

$$\frac{d\rho(q)}{dq} = -\frac{2\omega}{\hbar} \frac{\left(1 - e^{-\beta\hbar\omega}\right)}{\left(1 + e^{-\beta\hbar\omega}\right)} q\rho(q)$$

$$= -\frac{2\omega}{\hbar} \tanh\left(\frac{\beta\hbar\omega}{2}\right) q\rho(q).$$ (5.78)

Integrating this differential equation we obtain $\rho(q)$ as

$$\rho(q) = \text{const.} \times \exp\left[-\frac{q^2\omega}{\hbar} \tanh\left(\frac{\beta\hbar\omega}{2}\right) \rho(q)\right].$$ (5.79)

The integration constant is fixed by the normalization $\int dw(q) = \int dq\rho(q) = 1$ with the result

$$dw(q) = \left(\frac{\omega}{\pi\hbar} \tanh\frac{\beta\hbar\omega}{2}\right)^{1/2} \exp\left[-\frac{q^2\omega}{\hbar} \tanh\frac{\beta\hbar\omega}{2}\right] dq.$$ (5.80)

In the limit $\beta \to 0$ $(T \to \infty)$ we obtain the classical result given by (5.56); in the opposite limit $\beta \to \infty$ $(T \to 0)$ we obtain

$$dw(q) = \left(\frac{\omega}{\pi\hbar}\right)^{1/2} \exp\left(-\frac{q^2\omega}{\hbar}\right) dq,$$ (5.81)

which is the distribution characteristic of the ground state Gaussian wave function of a harmonic oscillator.

The analogous equation for the momentum distribution can be shown to be

$$dw(p) = \left(\frac{1}{\pi\hbar\omega} \tanh\frac{\beta\hbar\omega}{2}\right)^{1/2} \exp\left[-\frac{p^2}{\hbar\omega} \tanh\frac{\beta\hbar\omega}{2}\right] dp.$$ (5.82)

In the high temperature limit we recover Eq. (5.55).

Appendix 5A: The Gibbs distribution from the microcanonical ensemble

5A.1. Fixed particle numbers

In section 3.4 (see Eq. (3.11)) we argued the form of the Gibbs/Boltzmann distribution from the additivity of the log of the total probability of a set of weakly coupled sub systems. Here we will obtain it directly from the quantum microcanonical ensemble, Eq. (3.14). We start

by dividing a total (isolated) system having total energy E_0 into two parts: a large one with energy E' which acts as a medium (also called the bath), and a very small one representing our sub system, with an energy E_n equal to one of the levels used to represent a macrocanonical ensemble. The differential spectral energy width can now be written as $d\Gamma = d\Gamma' d\Gamma_n$ and Eq. (3.14) becomes

$$dw^{total} = const \times \delta(E - E_0) d\Gamma$$

$$= const \times \delta(E' + E_n - E_0) d\Gamma' d\Gamma_n. \tag{A5.1}$$

In the limit we are considering, where the sub system is in a single state for which $d\Gamma_n = 1$, the probability w_n follows from integrating out all the degrees of freedom of the bath so that

$$w_n = const \int \delta(E' + E_n - E_0) d\Gamma'. \tag{A5.2}$$

Proceeding as in Section 3.6 we write:

i) $d\Gamma' = \dfrac{d\Gamma'}{dE'} dE \cong \dfrac{\Delta\Gamma'}{\Delta E'} dE$ (see Eq. (3.20)),

and

ii) $\Delta\Gamma' = exp(S' / k_B)$ (see Eq. (3.32)).

Eq. (A5.2) then becomes

$$w_n = const. \times \left(\frac{exp(S'(E') / k_B)}{\Delta E'(E')} \right)_{E' = E_0 - E_n}. \tag{A5.3}$$

We now expand $w_n(E')$ around E_0. The dependence on E_n associated with the factor $\Delta E'(E')$ in the denominator of (A5.3) can be neglected relative to the numerator, which is huge, and we write it as $\Delta E'(E_0)$. In the numerator we have the factor $exp(S'(E') / k_B)$ containing the entropy. We now expanding as $S'(E')$ to first order in E_n

$$S'(E') = S'(E_0) - \left(\frac{\partial S'}{\partial E'} \right)_{S_0} E_n \cdots. \tag{A5.4}$$

Identifying $(\partial S' / \partial E')_{S_0} = T_0$, the temperature of the bath, and including the factor $exp(S_0(E_0) / k_B)$ together with $\Delta E'(E_0)$ into the constant in (A.5.3) we can now write our subsystem probability as (see Eq. (5.28))

$$w_n = A_P e^{\beta E_n} \tag{A5.5}$$

where A_P is a normalization constant and

$$\beta = 1/k_B T\,; \tag{A5.6}$$

(A5.5) is called the Gibbs distribution function or alternatively the Gibbs canonical ensemble.

5A.2. Variable particle numbers

When the particle number is taken as variable, the representative many-body energy levels used to describe our sub system must be generalized as $E_n \to E_{nN}$, and likewise the sub-system probabilities as $w_n \to w_{nN}$. We now make the particle number dependence in Eq. (A5.3) explicit and write the energy of the large system with energy E' introduced above as $E' = E_0 - E_{nN}$ and simultaneously introduce an additional variable $N' = N_0 - N$; in place of Eq. (A5.3) we then have

$$w_{nN} = \text{const.} \times \left(\frac{\exp\left(S'(E_0 - E_{nN}, N_0 - N)/k_B\right)}{\Delta E'(E_0 - E_{nN}, N_0 - N))} \right)_{E'=E_0-E_n, N_0-N}. \tag{A5.7}$$

We again argue the contribution of the subsystem to $\Delta E'$ can be ignored and combine it with the constant factor in (A5.7); using the thermodynamic relation (4.42a), $dE = TdS - PdV + \mu dN$, together with our constant volume constraint we expand the entropy to first order as

$$S'(E_0 - E_{nN}, N_0 - N) = S'(E_0, N_0) - \frac{E_{nN}}{T} + \frac{\mu N}{T} \tag{A5.8}$$

and (A5.7) becomes (see Eq. (5.29))

$$w_{nN} = A_G e^{\beta(\mu N - E_{nN})}. \tag{A5.9}$$

This is the generalized Gibbs distribution also called the *grand canonical ensemble*.

Problems

5.1. Obtain the analog of Eq. (5.81) but for the momentum distribution.

5.2. In section 5 we calculated the average $\overline{v^2}$ for a three dimensional classical Maxwell gas (see equation (5.49)). Using similar methods calculate the *mean square deviation* of this same quantity defined as $\overline{\left(\Delta v^2\right)^2} = \overline{\left(v^2 - \overline{v^2}\right)^2}$ together with $\sqrt{\overline{\left(\Delta v^2\right)^2}}\Big/\overline{v^2}$. How does the latter scale with the volume of the system.

5.3. Calculate $\overline{\left(\Delta v^2\right)^2}$ for a classical one-dimensional harmonic oscillator. Do the same for $\overline{\left(\Delta q^2\right)^2}$.

5.4. Consider a classical gas of N particles in a volume V that, in addition to their translational degree of freedom, have an electric dipole moment $\boldsymbol{\mu}_E$. Assume this gas is subjected to an electric field $\boldsymbol{\mathcal{E}}$ which shifts the energy of each particle by an amount $U = -\boldsymbol{\mu}_E \cdot \boldsymbol{\mathcal{E}}$.

a) With the understanding that the phase space to be integrated over now includes the orientation of the dipoles, calculate that part of the partition function which arises from the electric field.

b) Calculate the shift in the total energy of the system and show it can be written in the form

$$\Delta E_{\boldsymbol{\mathcal{E}}} = \frac{1}{2}\chi V \mathcal{E}^2$$

5.5. In addition to the elecrostatic energy associated with the gas in problem 5.4 we still have the translational kinetic energy, K(T), the total energy being then given by $E_{total} = K + \Delta E_{\boldsymbol{\mathcal{E}}}$. Assuming the pressure on our gas is held constant as the external electric field is applied, calculate the change in the resulting number density, N/V. This is an example of an effect called electrostriction. (You are free to use the expression derived in problem 5.4 even if you can't derive it.)