3. Quantum statistical physics

In chapter 2 we laid some foundations for a statistical description of mechanical systems as governed by the Hamiltonian equations of motion for the particles which in turn rests on Newton's equations of motion. However those particles themselves are typically atoms or molecules the internal dynamics of which we know is governed by quantum mechanics. Depending on temperature and density the translational degrees of freedom may also have to be treated quantum mechanically. In this chapter we formulate methods to treat particle assemblies using quantum mechanics.

3.1. Physical limitations on the quantum description of macroscopic matter

We recall from the discussion in section 2.6 where we noted that in the quasi-classical limit the number of states within a volume of phase space $\Delta p \Delta q$ associated with motion involving a single degree of freedom (one spatial and one momentum dimension) is given by $\Delta p \Delta q / 2\pi\hbar$. If we have s degrees of freedom the number of states becomes

$$\# \text{states} = \frac{\Delta p_1 \Delta p_2 \cdots \Delta p_s \Delta q_1 \Delta q_2 \cdots \Delta q_s}{(2\pi\hbar)^s} \tag{3.1}$$

where in three dimensions s = 3N where N is the number of particles. As a result, for particle numbers of order Avogadro's number the *many body energy levels,* E_n, then become *exceeding dense*, essentially continuous. It then follows that the *spacing,* $\delta E_{n\pm1,n} = E_{n\pm1} - E_n$, between neighboring energy states, numbered in some way by the subscript n, becomes *exceedingly small.*

In order to prepare a system in a given many body quantum state E_n, the energy uncertainty $\Delta E_n \cong \hbar / \Delta t$, where Δt is the time that elapses in preparing it, must be less than the level spacing if we are to avoid exciting the system to neighboring levels; i.e., we must have $\Delta E_n << \delta E_{n,n\pm1}$. In practice the times Δt become forbiddingly long. In addition residual interactions with the outside world, which fluctuate in general, cannot be reduced to the point where they do not continuously drive transitions between energy levels within the system. It then follows that a macroscopic system can *never be in a pure quantum state*. The system is always coupled to the outside world; it is what is then called an *open quantum system*.

3.2. The statistical matrix

In an open quantum system, one that is connected to a still larger system, probabilities must be described by means of what is called the *density matrix*, an operator we will designate as

$\hat{\rho}$. The associated formalism is briefly reviewed in Appendix B, where it is shown that the time dependence of $\hat{\rho}$ is given by (see Eq. (B.11b))

$$\dot{\hat{\rho}} = \frac{i}{\hbar}\left[\hat{\rho}, \hat{H}\right].$$
(3.2)

For an equilibrium statistical distribution one takes $\dot{\hat{\rho}} = 0$, which can be interpreted as the quantum analog of the Liouville equation discussed in section 2.2. The structure of the matrix elements that make up $\hat{\rho}$ in the energy representation is given by Eq.'s (B.8) and (B.9). Note that the off diagonal elements in the energy representation *do not vanish* in general but instead have a time dependence $\rho_{mn} \propto e^{i\omega_{mn}t}$ where $\hbar\omega_{mn} = E_n - E_m$. If we are to take $\dot{\hat{\rho}} = 0$ it follows that $\hat{\rho}$ and $\hat{H}$ can be simultaneously diagonalized. Restricting $\hat{\rho}$ such that it has only diagonal elements implies that an *averaging procedure* has been carried out that eliminates the off diagonal elements; i.e., we are making the assumption that

$$\overline{\rho_{mn}} = w_n\delta_{mn}$$
(3.3)

where we designate the diagonal elements as w_n.[1] This procedure cannot yield an exact representation of the system; it only allows a statistical one.[2] The diagonal elements w_n form a representation of what is called the *statistical matrix*. According to the discussion following equation (B.13), to represent a system with a matrix of order N, the full density matrix would involve N^2 real quantities while a pure state would require 2N; however the statistical representation involves only N real quantities and hence must represent a *less than complete* picture. As with the classical system, however, an exact representation of the system, even if it were available, would be too detailed to be useful.

To be consistent with the discussion in section 3.1, it is important to recognize that the energies introduced to *statistically* represent w_n *cannot be the true energies* of the system, even for a so called isolated system. We again emphasize that because the density of energy levels in a macroscopic system scales rapidly (exponentially) with the number of particles, the resulting level spacings are such that uncertainties associated with i) residual interactions with the outside

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[1] Formally we now have probabilities, w_n, as opposed to the classical differential probability introduced in Eq. (2.7), since we are here considering discrete quantum states.

[2] Since the off diagonal elements oscillate in general, and they are taken to *vanish* for a system in statistical equilibrium, the distribution function is not, strictly speaking, a density matrix.

world, and/or ii) making a measurements on the system over some time interval Δt, (to determine some property of it) will exceed those level spacings. In this sense the energy levels will be quasi continuous. Hence the energies used to represent $w_n(E_n)$ are simply a set that formally approximates the spectrum of a system with the number of degrees of freedom and other properties of that being considered.

3.3. Taking quantum-statistical averages

Analogous to the classical prescription for taking an average of some quantity f, as given by Eq. (2.9), the expectation value of the corresponding quantum operator, $\hat{f}$, is $\bar{f} = \text{Tr}(\hat{w}\hat{f})$ in the density matrix formalism (see Eq. (B.10)). Hence for our chosen form (3.3)

$$\bar{f} = \sum_n w_n f_{nn} \quad \text{(in statistical equilibrium)} \tag{3.4}$$

where f_{nn} are the diagonal terms of the operator $\hat{f}$ in some basis (say plane waves for a gas). The probabilities, $w_n(E_n)$ associated with the energy levels E_n, which we have called the statistical matrix, must satisfy the normalization condition

$$\sum_n w_n(E_n) = 1, \tag{3.5}$$

which is analogous to the classical equation (2.8).

3.4. The Gibbs distribution; subsystems

We now break up the whole system into N subsystems numbered with a superscript index a, as we did in the classical case considered in Section 2.5; as discussed there, the subsystems are still taken to be macroscopically large. Each subsystem will be governed by a statistical matrix $w^{(a)}$. The statistical matrix for the whole system, w^{total}, is then the *product* of all the subsystem probabilities; i.e.,

$$w^{total} = \prod_{a=1}^{N} w^{(a)}. \tag{3.6}$$

The total energy and particle number are here taken to be strictly constant.

As in the classical case discussed in section 2.8, a formal way to introduce the constraint that the total energy is constant is to introduce a *differential total probability*, dw^{total}, with the form

$$dw^{total} \propto \delta(E - E_0), \tag{3.7}$$

where E_0 is the fixed value of the total energy of the isolated system as a whole. The subsystem energies must then satisfy the constraint

$$E_0 = \sum_a E^{(a)}.$$
(3.8)

We will postpone the further development of Eq. (3.7) to Section 3.7 and continue the discussion of the properties of the individual subsystem probabilities, $w^{(a)}$.

Let us now assume that the subsystems are closed (or become closed at some time); i.e., the interaction between them at their "boundaries" is shutoff in some way. This allows us to associate a set of many-body quantum mechanical eigenenergies, $E_n^{(a)}$, with the internal dynamics of these "isolated" subsystems. As discussed at the beginning of this chapter, these energies are vast in number and simultaneously very dense. The probability of finding the ath subsystem in the nth many-body eigen state will be denoted as $w_n^{(a)}$; this function is the analog of $\rho(p,q)$ introduced for the classical system. We now take the logarithm of the total probability w^{total}. From Eq. (3.6) we have

$$\ln w^{total} = \ln\left[\prod_{a=1}^{N} w_n^{(a)}\right] = \sum_{a=1}^{N} \ln w_n^{(a)};$$
(3.9)

we see that the log of the total probability is *additive in the logarithm* of the subsystem probabilities; this is the quantum analog of Eq. (2.21). Since the subsystem energies are also additive, we argue that $\ln w_n^{(a)}$ must involve a term that is *additive in the energies,* $E_n^{(a)}$, similar to what was the case for the classical system discussed in Section 2.6. We can then write[3,4]

$$\ln w_n^{(a)} = -\alpha^{(a)} - \beta E_n^{(a)}$$
(3.10)

or

$$w_n^{(a)} = e^{-\alpha^{(a)} - \beta E_n^{(a)}}.$$
(3.11)

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[3] The sign convention used here differs from that of Landau and Lifshitz but is in accord with that used in other treatments.

[4] An alternate route to obtaining the distribution function starts from the principle that the most likely state of a subsystem is that which has the highest probability. The total probability would then be $w = \prod_n w_n^{(a)}$. One then maximizes this probability under the constraint that the particle number and energy are fixed. The two Lagrange multipliers introduced to maintain these constraints are the parameters α and β in Eq. (3.10). We will take up this approach later.

where $\beta = 1/k_B T$ with k_B being Boltzmann's constant, as will be shown in Chapter 5 and $\alpha^{(a)}$ can be fixed by summing $w_n^{(a)}$ over all energies in which case it must give unity according to Eq. (3.5)[5].

With the availability of $w_n^{(a)}$ the expectation value, $\overline{f}^{(a)}$, of a quantum mechanical operator $\hat{f}^{(a)}$ acting within the ath sub system in the energy representation is given by

$$\overline{f}^{(a)} = \sum_n w_n^{(a)} f_{nn} . \tag{3.12}$$

3.5. Representing the density of energy levels; the effective occupied energy width

We now examine more carefully the calculation of the normalization of w_n using (3.5); here we temporarily suppress the sub system index a. We again emphasize that in a macroscopic system the distribution of energy levels is essentially continuous. Hence it is natural to replace the summation over quantum numbers, n, by an integration over energy, E. To do this we need to know the number of quantum states with energies E_n in an interval dE. To examine this let Γ be the number of quantum states in our sub system with representative energies E_n less than or equal to some chosen energy E in an "isolated" subsystem of the kind introduced above; this is depicted schematically in Fig. 3.1.
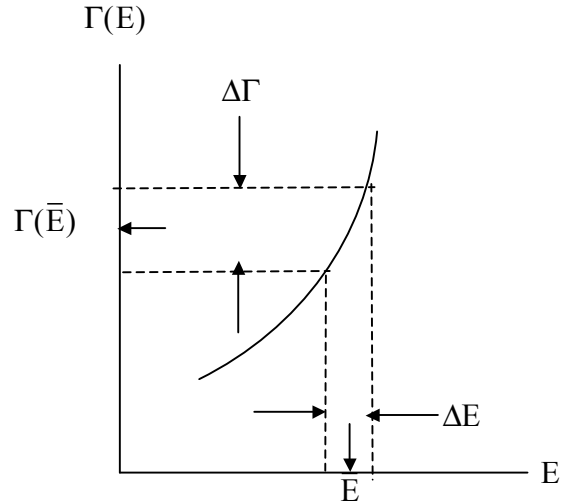

Fig. 3.1.

We can then differentiate Γ to obtain the[6] *many particle density of levels,* or equivalently the many particle *density of states,* $d\Gamma / dE$. With this quantity we can then write Eq. (3.5) as

$$1 = \sum_n w_n \rightarrow \int w(E) \frac{d\Gamma(E)}{dE} dE . \tag{3.13}$$

We now define a *probability distribution function* for the energy of our sub system as

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[5] The quantity $\alpha^{(a)}$ is also related to the free energy, F, as will be shown in a later chapter.

[6] We must not confuse this density of states $d\Gamma / dE$ for the many particle subsystem with the (vastly smaller) *single-particle* density of states.

$$W(E) = \frac{d\Gamma}{dE} w(E) \qquad (3.14)$$

where $w(E)$ denotes the occupation of *any* of the levels $E_n = E$. From (3.13) it follows that the function $W(E)$ must satisfy the normalization condition[7]

$$\int dE \ W(E) = 1. \qquad (3.15)$$

We now exploit the fact that if the subsystems are sufficiently large, their energies fluctuate *only slightly* about some mean value that we denote as $\overline{E}$. This being the case the functions $W(E)$ will be *highly peaked*[8] about $\overline{E}$, as illustrated schematically in Fig. 3.2. We can then replace $W(E)$ by a *rectangular form* with a height $W(\overline{E})$ and a width ΔE centered on $\overline{E}$ which satisfies the alternate normalization condition

Fig. 3.2. Approximating the function W(E) by a rectangular form

$$W(\overline{E})\Delta E = 1; \qquad (3.16)$$

as already remarked, the energy fluctuations in a large system are very small and hence $\Delta E \ll \overline{E}$.

From (3.14) we can now write

$$w(\overline{E})\Delta\Gamma = 1 \qquad (3.17)$$

where

$$\Delta\Gamma \cong \frac{d\Gamma(\overline{E})}{dE}\Delta E \ . \qquad (3.18)$$

Here $\Delta\Gamma$ is *an effective number of quantum states* that a subsystem fluctuating over a range of energies ΔE occupies. Since it is defined through (3.19) which involves $w(\overline{E};\alpha,\beta)$ (see Eq.
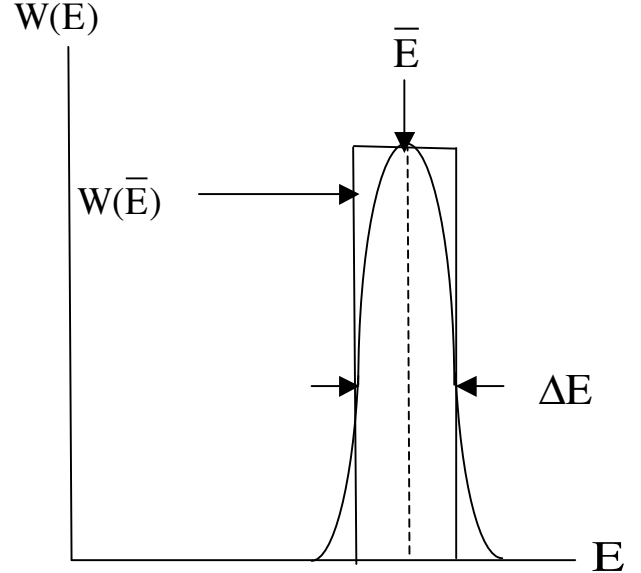
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[7] Here it may be useful to think of W(E) as the occupation of a kind of macroscopic average state that is formed by averaging over many microscopic states with energy E and occupation factors w_n. One might then say that W(E) measures the occupation of a kind of *macrostate* which is in turn composed of many possible *microstates* .

[8] This highly peaked behavior arises from the product of energy dependencies associated with the rapidly *increasing* many body density of states $d\Gamma(\overline{E}) / dE$ and the exponentially *decreasing* Boltzmann factor in w_n .

(3.11)) we have $\Delta\Gamma = \Delta\Gamma(E;\alpha,\beta)$; i.e., it is a function of the intrinsic thermodynamic variables, α and β. Note that although their product in (3.17) is constrained by its definition, $w(\overline{E})$ is (except at the very lowest temperatures) exceedingly small and hence $\Delta\Gamma$ is *exceedingly large*. In words, the probability that some particular level E_n is occupied among the possible levels in the immediate neighborhood of E is always very small at finite temperatures.

3.6. Entropy and its quantum mechanical definition

We now define a quantity we will call the *dimensionless entropy* for our subsystem a, $\sigma^{(a)}$, by

$$\sigma^{(a)} = l \, n \, \Delta\Gamma^{(a)}. \tag{3.19}$$

With this definition we see that entropy is related to the *effective number of quantum states a system occupies*. With this definition we are provided with a firm physical basis for understanding entropy[9].

Note that the smallest quantum number interval is *unity*; this situation corresponds to a sub system that is in its *ground state,* $E^{(a)} = E_{n=0}$. Assuming the ground state is non degenerate[10] we will have $\sigma^{(a)}(T=0) = 0$.[11] Hence we obtain the quantum statistical form of *the third law of thermodynamics*: the entropy of all systems approaches zero as the absolute temperature approaches zero.[12] In practice a macroscopic system can never be in its ground state hence $\Delta\Gamma^{(a)}$ is always a large number.

From Eq. (3.17) we may rewrite (3.19) as

$$\sigma^{(a)} = -l \, n(w^{(a)}(\overline{E})) \tag{3.20}$$

or equivalently

$$w^{(a)}(\overline{E}) = e^{-\sigma^{(a)}}. \tag{3.21}$$

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[9] Thereby removing much of the "mystery" that often surrounds the concept of entropy.

[10] It is generally assumed that systems in complete thermodynamic equilibrium are non-degenerate in their ground state. However frozen-in entropy at absolute zero is present in many systems, water ice being a well known example.

[11] Note that from our definitions, the entropy can never be less than zero.

[12] Unlike the thermodynamic formulation of the third law where only the change in entropy approaches zero, this quantum mechanical definition has the entropy itself approach zero.

For our Gibbs distribution, which follows from Eq. (3.10), $\ln(w_n^{(a)}(E))$ is linear in E, and we may therefore write $\ln(w^{(a)}(\overline{E}))$ as

$$\ln(w^{(a)}(\overline{E})) = \overline{\ln(w^{(a)}(E))}. \tag{3.22}$$

To formally calculate right hand side of (3.22) using our prescription for taking averages, we multiply $\ln(w^{(a)}(E))$ by the probability $w_n^{(a)}(E)$ of a given state n and sum over all n; Eq. (3.20) can then be written in the alternate form[13]

$$\sigma^{(a)} = -\sum_n w_n^{(a)} \ln w_n^{(a)} \tag{3.23}$$

which in operator form would be,

$$\sigma^{(a)} = -\text{Tr}(\hat{w}^{(a)} \ln \hat{w}^{(a)}). \tag{3.24}$$

However, as we have seen from Eq. (3.20) this is unnecessary.

Eq. (3.24) becomes identical to the Boltzmann definition of entropy if we multiply it by the Boltzmann constant k_B

$$S^{(a)} = k_B \sigma^{(a)}.$$

$$= -k_B \sum_n w_n^{(a)} \ln(w_n^{(a)}) \tag{3.27}$$

where $k_B = 1.3807 \times 10^{-23}$ Joule / K $= 1.3807 \times 10^{-16}$ erg/K. We then recover the units for the entropy used in thermodynamics. Consistent with the above discussion the entropy will be a function of our intrinsic thermodynamic variables: $S^{(a)} = S^{(a)}(\alpha^{(a)}, \beta^{(a)})$.

3.7. Expressing the micro canonical ensemble in terms of the entropy

We now return to a discussion of the distribution function w^{total} for the total (isolated) system and the method used to guarantee a fixed energy as represented by Eq. (3.7). To integrate over the delta function we need the differential level density for the *entire system* which is clearly the *product* of those for the subsystems; i.e.,

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[13] When written in this way any ambiguity in our introducing the rectangular form when writing Eq. (3.16) is removed. Our introduction of entropy through Eq. (3.19) follows Landau and Lifshitz, and has the virtue of clarifying its physical significance, as we have already remarked; most authors introduce entropy through Eq. (3.24). In doing so the connection between entropy and the effective occupation of states in quantum number space that is emphasized here is lost.

$$dΓ = \prod_a dΓ^{(a)} . \tag{3.28}$$

With this expression we can then explicitly write dw^{total} in Eq. (3.7) as

$$dw^{total} = const × δ(E - E_0)dΓ$$
$$= const × δ(E - E_0)\prod_a dΓ^{(a)}. \tag{3.29}$$

The constant can ultimately be fixed by requiring $\int dw^{total} = 1$.

Next we extend the definition of the effective number of contributing quantum states introduced in Eq. (3.17) to the system as a whole which is clearly the product of those for the individual subsystems; i.e.,

$$ΔΓ^{total} = \prod_a ΔΓ^{(a)} \tag{3.30}$$

or, in terms of the subsystem entropies given by Eq. (3.19),

$$\prod_a ΔΓ^{(a)} = \prod_a \exp\left(σ^{(a)}\right).$$

$$= \prod_a \exp\left(\frac{S^{(a)}}{k_B}\right) \tag{3.31}$$

It is then natural to define the *total* entropy as

$$S^{total} = k_B \ln ΔΓ^{total} = k_B \sum_a ln ΔΓ^{(a)} \tag{3.32}$$

$$= \sum_a S^{(a)} . \tag{3.33}$$

This definition is consistent with the experimentally observed property that the thermodynamic entropy is an *additive quantity*. With this definition Eq. (3.31) can also be written

$$\prod_a ΔΓ^{(a)} = \exp\left(\frac{S^{total}}{k_B}\right). \tag{3.34}$$

Our expression for the differential probability associated with the micro canonical ensemble, Eq (3.29), can now be written as

$$\mathrm{dw}^{\text{total}} = \text{const} \times \delta(E - E_0) \prod_a \frac{d\Gamma^{(a)}}{dE^{(a)}} dE^{(a)}$$

$$\cong \text{const} \times \delta(E - E_0) \prod_a \frac{\Delta\Gamma^{(a)}}{\Delta E^{(a)}} dE^{(a)} \tag{3.35}$$

where we used Eq. (3.18) in the second step. Note that in transitioning to finite differences in the second step, the numerator in the expression $\Delta\Gamma^{(a)} / \Delta E^{(a)}$ is far larger than the denominator due to the huge level density of a quantum many-body system. On substituting Eq. (3.34) for $\prod_a \Delta\Gamma^{(a)}$ and absorbing the product $\prod_a \frac{1}{\Delta E^{(a)}}$ into the multiplicative constant in (3.35), we obtain

$$\mathrm{dw}^{\text{total}} \cong \text{const} \times \delta(E - E_0) \exp\left(\frac{S^{\text{total}}}{k_B}\right) \prod_a dE^{(a)} . \tag{3.36}$$

Expressed in this way, the differential probability, $\mathrm{dw}^{\text{total}}$, is proportional to the product of the subsystem energy differentials, $dE^{(a)}$, falling in intervals between $E^{(a)}$ and $E^{(a)} + dE^{(a)}$ that also satisfy the total energy constraint, (3.8), but most importantly are weighted by the (huge) factors $\exp\left(S^{(a)}(\bar{E}) / k_B\right)$. Equation (3.34) will form the starting point for a discussion of fluctuations in thermodynamic systems, which we take up later in chapter 14.

3.8. Entropy in the classical limit

Let us now extend our definition of entropy into the classical limit. In Eq. (2.7) we wrote the differential probability for a classical system in the form $\mathrm{dw} = \rho(q; p) dq dp$. In place of Eq. (3.17), which involves an interval in quantum number space that the system occupies, it is then natural to introduce a corresponding interval in phase space, $\Delta p \Delta q$, in which the system moves as

$$\rho(\bar{E}; \alpha, \beta) \Delta p \Delta q = 1. \tag{3.35}$$

where $\rho(\bar{E}; \alpha, \beta)$ follows from Eq. (2.23); clearly this requires $\Delta p \Delta q = \Delta p \Delta q(\alpha, \beta)$.

As we have noted earlier, in the quasi-classical limit of quantum mechanics the number of translational states is related to a differential volume element of phase space according to

$$d\Gamma = dp dq / (2\pi\hbar)^s \tag{3.36}$$

with $dpdq \equiv \prod_s dp_s dq_s$ as usual. It is common to define the phase space associated with a single particle in three dimensions as

$$d\gamma = d\mathbf{p}d\mathbf{r} / (2\pi\hbar)^3 \qquad (3.37)$$

and we would then write

$$d\Gamma = \prod_N d\gamma$$

$$= \prod_N d\mathbf{p}d\mathbf{q} / (2\pi\hbar)^N . \qquad (3.38)$$

for N particles. With these identifications and extending them to macroscopic intervals of phase space we have

$$\Delta\Gamma = \frac{\Delta p \Delta q}{(2\pi\hbar)^s} \qquad (3.39)$$

With $\Delta\Gamma$ given by (3.39) and using Eq. (3.35) we can then write the entropy (3.19) as

$$\sigma^{(a)} = \ln \frac{\Delta p^{(a)} \Delta q^{(a)}}{(2\pi\hbar)^s}$$

or

$$S^{(a)} = k_B \ln \frac{\Delta p^{(a)} \Delta q^{(a)}}{(2\pi\hbar)^s} \qquad (3.39)$$

3.9. Non-equilibrium systems

In chapter 2 we introduced the concept of sub systems. There and in section 3.4 of the present chapter this idea proved useful in establishing the form of the Gibbs distribution by associating the additivity of both the energy and the log of the probability when the parts are in equilibrium. And as shown immediately above, the entropy is then also given by a sum over the parts.

The introduction of subsystems is particularly useful when considering large systems that are not in equilibrium. Establishing thermal equilibrium generally involves characteristic times. For a large system this time, call it τ_{total}, can be long (think of conducting energy between two widely separated regions of a large body). It is then useful to divide that body into parts or sub systems and, provided these subsystems are still macroscopic, local equilibrium may be achieved in much shorter times, $\tau^{(a)}$; i.e., $\tau^{(a)} \ll \tau_{total}$. If this is case one can introduce time and position dependent functions characterizing the system, e.g., $E(\mathbf{r},t)$, the behavior of which is determined

transport coefficients that measure the rate at which quantities like energy or particle number are transferred between individual volume elements, each representing a macroscopic sub system in local equilibrium. If, however, the system is driven too far from equilibrium, so as to involve time scales shorter than $\tau^{(a)}$, such a description breaks down.

Another kind of non-equilibrium situation occurs when multiple particle species are present that can undergo chemical reactions. Here the individual species can be in equilibrium with themselves and other species with regard to their *mechanical* degrees of freedom, but change their identities (through chemical reactions) on longer time scales. Time evolution equations, analogous to those involving energy or particle transport, can then be derived that govern particle numbers but where the environment stays in local mechanical equilibrium, although with the temperature rising or falling dependent on whether the reaction absorbs or generates energy.

Additional Reading

Our discussion in this chapter is adapted from L. D. Landau and E. M. Lifshitz, *Statistical Physics Part 1*, Pergamon Press, Oxford (1980). Their presentation is somewhat unique among statistical physics texts and deserves to be read repeatedly.

For a discussion of the density matrix in statistical physics see section 5 of *Statistical Physics Part 1*, L. D. Landau and E. M. Lifshitz, Pergamon Press, Oxford (1980).

For a concise description of the lives and contributions of the founders of thermodynamics and statistical physics see chapters 3 – 10 and 13 of *Great Physicists*, W. H. Cropper, Oxford University Press (2001).

Problems

3.1. In Section 2.7 Eq. (2.30) of Chapter 2 we introduced the so-called partition function. The quantum mechanical analog of that function would be

$$Z = \sum_n e^{-\beta E_n} \qquad (2.30)$$

where E_n are the eigenvalues of the Hamiltonian, $\hat{H}$, associated with some problem of interest. Suppose we have a single harmonic oscillator frequency with frequency ω. From quantum mechanics we know that the energy levels are $E_n = n\hbar\omega$ (here we will ignore the zero point energy).

a) Develop a formula analogous to Eq. (2.31) and obtain the average energy of this oscillator, $\bar{E} = \bar{E}(\beta, \omega)$, in a closed-form (i.e., not in the form of a series).

b) Now assume that you have N such three dimensional oscillators as in Problem 2a of Chapter 2, all with the same frequency ω. Calculate the heat capacity, C_V.

c) Obtain the high temperature limit of C_V and compare it with the result of Problem 2b.

3.2. According to Eq. 3.1 the energy levels of a single particle in a one-dimensional box of length L is given by

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2 .$$

a) Calculate the average energy $\bar{E} = \bar{E}(\beta)$ of this particle, again in closed form.

b) Calculate the heat capacity at constant L, $C_L = (\partial \bar{E} / \partial T)_L$ (the analog of the heat capacity at constant volume).