Statistical Mechanics

Contents

1 Thermodynamics

Course information: the lecturer; outline; books; problems, classes and credit; exam details; are all on Blackboard and/or the unit description.

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Small text is supplementary non-examinable material. It will improve your understanding of the rest of the course material.

Production of useful work is limited by the laws of thermodynamics, but the production of useless work seems to be unlimited. Donald Simanek.

1.1 Thermodynamic systems

In this first section, we will put aside the notion that matter is composed of atoms (or more exotic particles) and consider a macroscopic description of thermodynamics, the study of transformations of energy and other conserved quantities. For many situations, at a sufficiently large length scale we can forget about microscopic interactions and fluctuations; the microscopic world shows up only as relations between temperature, density, pressure, viscosity, thermal conductivity, chemical reaction rates etc. One very important aspect of statistical mechanics is predicting these properties from microscopic laws. Also at small scales ("nanotechnology") and for special systems such as Bose-Einstein condensates, the macroscopic description can break down. First, however, we turn to the description of this macroscopic world.

We know from mechanics that there are fundamental conservation laws applying to isolated systems. These include energy, momentum and the total number of any type of particle that cannot be created or destroyed (for example the number of hydrogen atoms in a chemical reaction). Most systems we consider will be (macroscopically) at rest or mechanically connected to the Earth, so let's ignore momentum for now. This suggests the following classification of thermodynamic systems:

Isolated Cannot exchange energy, or particles with the environment. Both of these remain conserved quantities.

Closed Can exchange energy with the environment, for example by heat conduction, or by doing work as in a piston. Particles still conserved, but energy on average determined by the temperature (defined below) of the environment if at equilibrium (defined below).

Open Can exchange both energy and particles with the environment, as in a container without a lid. No conserved quantities, energy determined on average by the temperature and particles determined on average by the chemical potential(s) (defined below) at equilibrium.

Some further definitions we will need to describe thermodynamic systems:

Phase Homogeneous part of the system, for example a bottle of water may contain two phases, liquid water (with a little dissolved air) and a gas phase which is a mixture of water vapour and air.

Phase boundary Surface separating phases; is the liquid in one place or distributed as a fog?

State variable Macroscopic quantity, for example energy E, volume V, particle number N, entropy S, temperature T, pressure p, chemical potential μ, and also such quantities as viscosity, chemical composition and the size of phase boundaries. Purely microscopic quantities such as the position and velocity of individual particles are excluded.

Equation of state An equation relating state variables to each other, for example low density gases approximate the "ideal gas equation of state" $pV = Nk_BT$, where $k_B = 1.380658 \times 10^{-23} JK^{-1}$ is Boltzmann's constant, and all of these quantities have yet to be precisely defined.

1.2 Additive thermodynamics

In most cases we consider, the conserved variables are all proportional to each other as the system is made larger. In this case the system is called **extensive**. Furthermore if a system is split into two, the total system has properties given by the sums of the individual systems, ie $N = N_1 + N_2$ and similarly for E and V. In this case the system is called **additive**. Combining two systems of identical substances shows that all additive systems are extensive, but the converse may not be true.

Let us explore when the additive assumption fails:

- Small systems, for which the surface (and hence its energy) is relatively large, and generally different to the bulk. These are non-extensive.
- Quantum systems, such as Bose-Einstein condensation (at the end of the unit) in which the wave function of a single particle can fill the whole volume.
- Systems with long range forces. Assume there is a potential energy between pairs of particles of the form $V \sim r^{-\alpha}$ at large distances. Then the contribution of this to the total energy is roughly $\sum V \sim r^{2d-\alpha}$ where d is the number of dimensions (normally 3, but we sometimes consider 1 or 2). Comparing this with the number of particles $N \sim r^d$ we see that the system is non-extensive if $\alpha < d$, the system is borderline and probably non-additive if $\alpha = d$, and the system is additive (ie short ranged force assumption works) if $\alpha > d$.

In practice uncharged atoms have forces that behave like r^{-6}, so we are usually safe in considering systems to be additive, which is also consistent with normal experience. However for new areas of study like nanotechnology and Bose-Einstein condensation, it will be important to relax this assumption. The additive assumption is made throughout most of the unit, but its use will be highlighted to facilitate the more difficult treatment of non-additive systems if required.

For additive (including extensive) systems we define

Additive/Extensive State variables Those state variables (including N, V, E with the additive or extensive property defined above.

Intensive State variables Those which remain constant as the system changes size, ie ratios of extensive state variables, also pressure, temperature and others.

1.3 Equilibrium and the zeroth law

It is observed that an isolated system after sufficient time settles into a stationary state, in which all state variables become constant. Such a stationary state is called thermodynamic equilibrium. Non-isolated systems can also settle into a stationary state, but this may be a non-equilibrium stationary state, for example if there is a constant flow of energy through the system. Equilibrium is always an approximate concept, applicable to a particular timescale; on longer timescales the isolated approximation will break down due to slow chemical or nuclear reactions or imperfect thermal insulation.

Two systems are in mutual equilibrium (often just called equilibrium) if they are each in thermodynamic equilibrium, and the combined system remains in equilibrium (ie there are no changes) when the systems are put in contact. The contact can allow transfer of heat (thermal equilibrium), volume (mechanical equilibrium), and/or particles (chemical equilibrium). If all three, the systems are said to be in mutual thermodynamic equilibrium.

Recall that for a relation denoted by $\sim$ the requirements for an equivalence relation are

$$\begin{aligned} X &\sim X && \text{(reflexivity)} \\ X \sim Y &\Rightarrow Y \sim X && \text{(symmetry)} \\ X \sim Y \text{and} Y \sim Z &\Rightarrow X \sim Z && \text{(transitivity)} \end{aligned}$$

The property of being in (any type of) equilibrium is found to be an equivalence relation. The first two properties are somewhat obvious, but the last is an important physical law.

> **The zeroth law of thermodynamics:** Thermal equilibrium is transitive, and hence an equivalence relation.

Note that the laws of thermodynamics are often expressed in different ways. This law was not recognised to be an important physical law in its own right until the twentieth century, hence the "Zeroth" designation.

An equivalence relation allows us to partition thermodynamic systems into sets, in which all systems are in mutual equilibrium, and between which no systems are in mutual equilibrium. For thermal equilibrium, we say that all systems in the same set have the same temperature. Similar laws (not commonly stated) for mechanical and chemical equilibrium similarly then allow us to define the concepts of pressure and chemical potential, respectively. The equivalence relation argument does not tell us what type of mathematical object temperature etc. should be, but we will assume that all state variables are real.

Notice that many state variables are only defined at equilibrium. There exists in general no definition of temperature etc. far from equilibrium, however we often consider the case of local thermodynamic equilibrium, in which equilibrium (and hence the definition of temperature etc.) is obtained approximately over small space and time domains.

1.4 State transformations I

Given that many state variables are only defined at equilibrium, it makes sense to consider the class of transformations that take place very close to equilibrium; these are called quasistatic. For example, consider expansion of a gas in a piston. If the piston is released very slowly, the process is quasistatic, and if there is no other source of energy, the work done by the gas means that the final energy is lower. If however there is a small hole leading into an empty container, the process is still slow, but the combined system (including both sides of the piston) has greatly different pressures and hence is not in equilibrium; no work is done and the final energy is equal to the initial energy. Thus free expansion is not a quasistatic process, even though it may be slow.

Quasistatic processes move continuously around the state space, which due to equations of state, is relatively low dimensional. For example a gas of a single substance at equilibrium can be completely characterised by two intensive variables, say p and T, in terms of which all other intensive quantities E/V, μ, S/V, N/V can be expressed; extensive quantities also depend trivially on V. If the system moves along a curve in state space parametrised by some real variable λ, the variation of state variables is given by the chain rule, for example

$$\frac{dE}{d\lambda} = \left(\frac{\partial E}{\partial p}\right)_{TV} \frac{dp}{d\lambda} + \left(\frac{\partial E}{\partial T}\right)_{pV} \frac{dT}{d\lambda} + \frac{E}{V}\frac{dV}{d\lambda}$$

where the subscripts outside the brackets indicate what is to be kept constant in the partial derivative. This is important if we want to switch to a description in terms of different variables. Such an equation is valid for all choices of parameter, so we usually abstract this to

$$dE = \left(\frac{\partial E}{\partial p}\right)_{TV} dp + \left(\frac{\partial E}{\partial T}\right)_{pV} dT + \frac{E}{V}dV$$

1.5 The first law

The origin of thermodynamics was the discovery (eg Joule 1843) that heat is a form of energy, for example noting an increase in temperature when a liquid is stirred vigorously. The first law of thermodynamics is a statement of conservation of energy, thus

$$dE = \delta W + \delta Q$$

where W is work done on the system and Q is heat transferred to the system. In thermodynamics, "work" includes any macroscopic form of energy, for example mechanical or electrical, while "heat" is energy in the form of random microscopic motions.

Note that W and Q are not state variables, hence the use of δ rather than d. While the total work done on the system is

$$W = \int \frac{\delta W}{d\lambda} d\lambda$$

this integral depends on the path taken in state space between the fixed initial and final states, and similarly for Q. Thus it is impossible to define these as state variables. The situation is analogous to conservative and nonconservative forces in mechanics. For a nonconservative force the work done is path-dependent, hence there is no possibility of defining a potential energy function.

Mathematically, we say that a differential form is exact if its integral is path-independent, or equivalently it is the derivative of a state function. In simply connected spaces (as here) it is also equivalent to the statement that the form is closed, that is, an exterior (antisymmetric) derivative of it is zero.

Example: Consider the differential form $xydx + y^2dy$. This is exact if we can write it as the derivative of some state variable f. Thus we have

$$xydx + y^2dy = f_xdx + f_ydy$$

which is equivalent to two equations, $f_x = xy$ and $f_y = y^2$. The second gives us $f = y^3/3 + C(x)$ including an arbitrary function $C(x)$, but this is inconsistent with the first equation. Alternatively, we can compute an antisymmetric derivative $f_{xy} - f_{yx} = (xy)_y + (y^2)_x = x \neq 0$ so the form is not closed, and no f exists.

The physical content of the first law as a restriction on physical processes is clear. It is impossible to create a machine which creates energy out of nowhere; such a machine is called a perpetual motion machine (perpetuum mobile) of the first kind. No assumptions are made anywhere about equilibrium; it is completely general. Despite this well founded law, such machines are still being proposed by inventors.

1.6 The second law

The second law concerns the observed irreversibility of the universe, and has many formulations. We will use the Kelvin (1851) definition:

> The second law: A process whose only effect is the conversion of heat into work cannot occur

Thus converting work into heat is irreversible.

Example: If you boil water in an electric kettle, you have converted electrical energy (work) into heat. You may be able to convert some of this back to electricity (by a steam turbine) but never all of it. The steam turbine is not forbidden as it has other effects, such as warming the environment - note the word 'only' in the definition - but there is no process by which you can return to the original state, of a cold environment, cold water, and electrical energy.

The existence of steam turbines shows that it is possible to generate work from a temperature difference, at the expense of narrowing that difference. This leads to another common formulation of the second law, that transferring energy from a colder to a hotter body without other effects is impossible. Otherwise we could use it to convert unlimited amounts of heat into work. The same applies to other conserved quantities, ie we cannot increase a pressure or chemical potential difference without other effects. All non-equilibrium processes involve spontaneous decreases in differences of temperature, pressure and/or chemical potential, so any process that is not quasistatic is irreversible.

The concept of irreversibility can be represented mathematically by introducing a state variable, the entropy S which for an isolated system is constant in reversible processes and increases in irreversible processes. Thus the second law reads $\Delta S \geq 0$, and equilibrium of an isolated system corresponds to a maximum of S (subject to the constraints) once we have found an operational definition for S. Like the first law, the second law is general, applying both to equilibrium and nonequilibrium states. However like the other state variables, it will turn out to be much easier to define the entropy for states at equilibrium, or at least local equilibrium. There are also frequent proposals for perpetual motion machines of the second kind, that is, violating the second law.

1.7 State transformations II

State transformations can move through state space in arbitrary ways, but are typically under one of the following conditions, which simplify the chain rule:

Adiabatic No heat transfer (eg. thermal insulation).

Isentropic Constant entropy: adiabatic and reversible.

Isobaric Constant pressure (eg. frictionless piston).

Isochoric/isovolumetric Constant volume (eg. rigid walls).

Isothermal Constant temperature (eg. in contact with a large thermal reservoir)

Polytropic Constant pV^x for some real number x. Reduces to $x = 0$ for isobaric, $x = \infty$ for isochoric, and for ideal gases $x = 1$ for isothermal, $x = \gamma$ for adiabatic (see later).

In addition, it is very common to specify that the number of particles is constant (as in a closed system).

1.8 Definition of state quantities

To proceed further, we need not just existence theorems, but operational definitions of the various state quantities, which we will derive using the laws of thermodynamics.

The easiest type of equilibrium to understand from the mechanics we already know is mechanical equilibrium, that is, the forces perpendicular to the surface separating the systems must balance. As we change the area of contact, this force is proportional to the area, with the proportionality constant

$$p = \frac{F_\perp}{A}$$

called the pressure. The SI unit of pressure is the Pascal (one Newton per square metre), and is also the unit of energy density. The “standard atmosphere” has pressure 101325 Pa. A gas in a piston will do work as it expands,

$$\delta W = -Fdx = -pAdx = -pdV$$

where the minus sign indicates a decrease in energy in the gas, ignoring all other work and heat processes.

Unit	Symbol	AZ	FP	BP
Farenheit	^{o}F	-459.67	32	212
Celsius	^{o}C	-273.15	0	100
Kelvin	K	0	273.15	373.15

Table 1: Common temperature units. Absolute zero (AZ) is the temperature at which the (extrapolated) pressure drops to zero in the ideal gas law. Freezing and boiling points (FP, BP) are for water at standard pressure. Note that kelvins are just like other SI units, and have no degree symbol.

The particle number density N/V can be determined once the mass of a particle is known, and the total mass of particles. The mass of atoms or molecules is expressed in atomic mass units (symbol u), so that a Carbon-12 atom has mass 12u. The number of atomic mass units in a gram is known as Avogadro's number N_A, ie

$$\frac{1g}{1u} = N_A = 6.0221367 \times 10^{23}$$

An amount N_A of particles is called one mole of particles. We commonly encounter the combination Nk_B, thus it is useful to use

$$R = N_A k_B = 8.3145112 J K^{-1} mol^{-1}$$

which is also called the “gas constant”.

At this point we will take the ideal gas law (for low density gases) $pV = Nk_BT$ as an experimental observation; later we will derive it. Its physical content is that at constant temperature (as defined using the zeroth law) pressure is proportional to N/V. We will (for now) define temperature to be this proportionality constant, with an extra constant k_B to allow for our choice of units. The SI unit of temperature is the kelvin (symbol K) which has the same spacing as Celsius, but shifted to the correct zero of the ideal gas law, see Table 1. Standard temperature is 273.15K. STP is standard temperature and pressure as defined above.

Adding particles to a thermodynamic system at equilibrium also increases the total energy by an amount comparable to the average energy per particle,

$$\delta W = \mu dN$$

which defines the chemical potential μ. If there is more than one type of particle, there will be a chemical potential corresponding to each conserved particle number, so in general we have

$$\delta W = \sum_i \mu_i dN_i$$

where N_i are the changes in the conserved particle numbers.

Adding energy to a system increases the temperature at a rate determined by a heat capacity C, which depends on the process. Assuming constant N we define

$$C_p = \left(\frac{\delta Q}{dT}\right)_p$$

$$C_V = \left(\frac{\delta Q}{dT}\right)_V$$

"Specific" heat capacity is an intensive version, per mole or per unit mass; for water at standard pressure and $3.98^o C$, $C_p/M = 1kcalK^{-1}kg^{-1} = 4.184kJK^{-1}kg^{-1}$. Example: drop mass $M \quad kg$ of water from a height of $1 \quad m$. It will have kinetic energy $K = Mgh = 9.8M \quad J$; if all the energy goes into heating the water, the temperature will rise by $K/C_p = 9.8/4184 = 0.0023$ degrees.

Various other derivatives of state quantities are also named, for example changes in volume (at constant N) are defined by

$$VdV = \alpha dT - \kappa_T dp$$

where α is the expansion coefficient and κ_T is the isothermal compressibility.

1.9 The ideal gas

For following calculations we need to establish the relation between energy and temperature in an ideal gas; because this is the low density limit, we can ignore any forces between the particles. We also assume the gas is monatomic, that is, the energy is simply translational kinetic energy. Less us assume a cuboid container, side lengths L_x etc. A particle with mass m, velocity v_x etc. will collide with the right x-wall with a frequency $v_x/2L_x$ and impart a momentum $2mv_x$ each time. Thus the total amount of momentum per unit time transferred to the wall is mv_x^2/L_x for each particle. Summing over all particles, dividing by the area of the wall and assuming that the velocity distribution is the same in all directions the pressure is thus $2E/3V$. Thus we have $E = 3NkT/2$. For a general ideal gas this is $E = fNkT/2$ where f is the total number of active degrees of freedom (translation, rotation, vibration etc.). Active means that the temperature is sufficiently high for thermal excitation to the second quantum state; $f = 5$ is a good approximation for (mostly diatomic) air at normal temperatures.

We will also need to consider the adiabatic law, ie calculate the polytropic constant for an ideal gas. Substituting $dE = -pdV$ for the work done, the above expression for E and the ideal gas law for p, we find

$$-\frac{NkT}{V}dV = \frac{f}{2}NkdT$$

Integrating,

$$VT^{f/2} = \text{const}$$

$$pV^\gamma = \text{const}; \qquad \gamma = 1 + 2/f$$

We also have enough information to compute the heat capacities,

$$\delta Q = dE - \delta W = fNkdT/2 + pdV$$

which gives $C_V = fNk/2$ and $C_p = (f+2)Nk/2$ so that $\gamma = C_p/C_V$.

1.10 The Carnot engine

We now consider how to reversibly (ie with greatest efficiency) convert a temperature difference into useful work, the Carnot engine. We have two temperature reservoirs $T_c < T_h$and a piston of ideal gas, initially at temperature T_h. We need to take heat from the top reservoir reversibly, and do this by letting the gas expand from V_a to V_b, doing work and absorbing heat from the reservoir. The amount of work done is given by

$$\Delta W_{ab} = -\int_{V_a}^{V_b} pdV = -\int_{V_a}^{V_b} \frac{NkT}{V}dV = -NkT_h \ln(V_b/V_a)$$

Now for the ideal gas we have shown that the energy is constant at constant temperature. Thus we find that

$$\Delta Q_{ab} = -\Delta W = NkT_h \ln(V_b/V_a)$$

Next, we need to lower the temperature to T_c by an adiabatic expansion so we can impart heat to the other reservoir reversibly. This gives a volume of

$$V_c = V_b(T_h/T_c)^{d/2}$$

$$\Delta W_{bc} = \Delta E = dNk(T_c - T_h)/2$$

The third stage mirrors the first; we do isothermal compression to give heat to the cooler reservoir. We have

$$\Delta W_{cd} = -NkT_c \ln(V_d/V_c)$$

$$\Delta Q_{cd} = NkT_c \ln(V_d/V_c)$$

Finally we do an adiabatic compression to return to the initial point. This gives the equations

$$V_a = V_d(T_c/T_h)^{d/2}$$

$$\Delta W_{da} = dNk(T_h - T_c)/2$$

Combining the volume equations leads to

$$V_d/V_c = V_a/V_b$$

Thus the energy balance is as follows: Heat taken at T_h is T_hC where $C = Nk\ln(V_b/V_a)$ is a constant, heat added at T_c is T_cC, remainder $(T_h - T_c)C$ is converted into work (the area on a pV diagram). The efficiency is

$$\eta = \frac{|\Delta W|}{\Delta Q_1} = 1 - \frac{T_c}{T_h}$$

is the maximum possible for those temperatures, since it is reversible (leading to a refrigeration device). A greater efficiency would allow violations of the second law by applying the super-efficient engine followed by the Carnot refrigerator.

1.11 Entropy

It should be noted that in the reversible Carnot engine the quantity δQ does not integrate to zero around the closed loop, but the quantity $\delta Q/T$ does. In fact, by approximating a general loop by lots of Carnot engines we can see that in general $\delta Q/T$ is an exact differential for reversible processes in the ideal gas. Thus we have

$$dS = \frac{\delta Q_{rev}}{T}$$

The state variable S defined in this way is called the entropy, and is extensive. We also observe that in an irreversible heat engine, more heat would be transferred for the same amount of work, leading to a positive value of ΔS, ie

$$dS > \frac{\delta Q_{irrev}}{T}$$

We can see this explicitly in the case of thermal equalization. An amount Q of heat is transferred from a warmer to a cooler body. The warm body loses entropy Q/T_h while the cool body gains a greater entropy Q/T_c, thus the total entropy change in this irreversible process is positive.

Let us assume that a general isolated system has such an entropy function $S(N_i, V, E)$ which is extensive, smooth, and maximised at equilibrium. We consider the isolated system to be composed of two subsystems, with a boundary that is permeable to a specified combination of the conserved quantities. At equilibrium we have both subsystems in equilibrium and in mutual equilibrium. Allowing transport of energy, we have

$$E = E_1 + E_2$$

$$0 = dS = \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_2}{\partial E_2} dE_2$$

thus

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

at equilibrium, hence $\partial S/\partial E$ must be a function of temperature. Our ideal gas definition of entropy and temperature is consistent with the more general definition

$$\left(\frac{\partial S}{\partial E}\right)_{V,N_i} = \frac{1}{T}$$

If the energy is unbounded (as in systems of gas molecules) the temperature is always positive, but there are some systems such as collections of quantum spins that can have negative temperatures, if the non-spin degrees of freedom are ignored. We can do this trick with the other conserved quantities, and find that the partial derivatives with respect to V and N_i must be related to pressure and chemical potentials respectively. The first law can be rearranged,

$$dE = \delta Q + \delta W = TdS - pdV + \sum_i \mu_i dN_i$$

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \sum_i \frac{\mu_i}{T} dN_i$$

and thus

$$\left(\frac{\partial S}{\partial V}\right)_{E,N_i} = \frac{p}{T}$$

$$\left(\frac{\partial S}{\partial N_i}\right)_{V,E,N_{j\neq i}} = -\frac{\mu_i}{T}$$

This form of the first law no longer singles out energy as the most important conserved quantity; however the historical definitions of T, p, μ are constructed with the energy representation in mind.

It might be noted that the zeroth law has now become effectively redundant. If we postulate a function $S(N_i, V, E)$ which is differentiable, extensive and concave (see problem 2.3) we can now derive the zeroth law and the concept of temperature, as well as pressure and chemical potential. However there are limitations to this approach. It is useful only for equilibrium, extensive systems. The second law implies the existence of entropy more generally, but does not give an easy method of calculating the entropy of nonequilibrium and/or nonextensive systems (more on this later). In addition, the differentiability is a minor additional (but reasonable) postulate.

The extensivity property of (S, E, N_i, V) leads to an important equation relating state quantities, as follows. We can write an equation of state for the energy of a system expanded by an arbitrary amount λ,

$$E(\lambda N_i, \lambda V, \lambda S) = \lambda E(N_i, V, S)$$

Then differentiate with respect to λ

$$\lambda \left(\sum_i N_i \frac{\partial E}{\partial N_i} + V \frac{\partial E}{\partial V} + S \frac{\partial E}{\partial S} \right) \Bigg|_{\lambda N_i, \lambda V, \lambda S} = E(N_i, V, S)$$

and set $\lambda = 1$, substituting known values for the partial derivatives,

$$\sum_i \mu_i N_i - pV + TS = E$$

Differentiating and subtracting the expression for dE from the first law, we obtain the Gibbs-Duhem relation

$$\sum_i N_i d\mu_i + SdT - Vdp = 0$$

1.12 Thermodynamic potentials

We have discovered that the function $S(N_i, V, E)$ has a maximum at equilibrium, and that all thermodynamic state variables can be obtained by differentiation. For heat capacity we have for example

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = T\left(\frac{dS}{dT}\right)_V$$

Thus it has similar properties to potential energy in mechanics, and is called a thermodynamic potential for isolated systems, ie at constant (N_i, V, E). We now wish to find thermodynamic potentials for closed or open systems.

Consider the case of a closed system of constant volume, which will come to an equilibrium depending on the constants N_i, V and the temperature T imposed by the environment. We need to maximise the total entropy of the system and the environment, and have as a free parameter the energy E of the system. Adding dE to the system will raise the entropy of the system by $\partial S/\partial E dE$ and lower the entropy of the environment by dE/T. Thus thermal equilibrium corresponds to

$$0 = \frac{\partial S}{\partial E} - \frac{1}{T} = \frac{\partial}{\partial E}(S - E/T)$$

Conventionally this is written as minimising the Helmholtz free energy

$$F(N_i, V, T) = E - TS(N_i, V, E)$$

The fact that F does not depend on E can be verified by differentiating the RHS of this equation. It is an example of a Legendre transformation: In general the Legendre transformation of a function $f(x)$ is $g(p)$ where

$$g(p) = px(p) - f(x(p))$$

where $x(p)$ is the solution of the equation $p = f'(x)$. Note: some people use a different sign convention. For example the Legendre transformation of $f(x) = x^2$ is $g(p) = px - x^2 = p^2/4$. Another example is the relationship between the Lagrangian and Hamiltonian functions in mechanics. We have (from the first law)

$$dF = -SdT - pdV + \sum_i \mu_i dN_i$$

so F is a thermodynamic potential, which generates all the state variables by differentiation.

The energy $E(N_i, V, S)$ is a minimum at equilibrium given its arguments. This follows from the maximum entropy statement together with the positivity of temperature, as follows: Let us fix N_i, V and consider states with different E, S. Let us consider an equilibrium state (E_0, S_0). If it does not minimise energy there is another (equilibrium or nonequilibrium) state (E_1, S_0) with $E_1 < E_0$. Now since temperature is positive, $S(E)$ is strictly increasing, so $S(E_1) < S(E_0)$. But since $S(E_1)$ is the maximum entropy possible for energy E_1, the state (E_1, S_0) cannot exist. Hence the energy must be minimised at constant entropy. We have already seen how to calculate various quantities as derivatives using the first law, so energy is also a thermodynamic potential.

By similar processes (ie Legendre transforms of entropy or energy) we obtain two more thermodynamic potentials. The enthalpy is

$$H(N_i, p, S) = E + pV$$

for fixed pressure and entropy (ie adiabatic). These conditions are very common for chemical reactions and phase changes, hence the change in enthalpy (rather than say energy) of the reaction is typically stated. For a phase change, the enthalpy is called the ‘latent heat of fusion/vaporisation’, and the addition of heat causes the phase change, not an increase in temperature (as in heat capacity). eg for water at standard pressure, $334kJkg^{-1}$ for fusion, $2258kJkg^{-1}$ for vaporisation. We have

$$dH = TdS + Vdp + \sum_i \mu_i dN_i$$

The Gibbs free energy is

$$G(N_i, p, T) = E + pV - TS = \sum_i \mu_i N_i$$

for fixed pressure and temperature, and is suitable for investigating the chemical potential(s). We have

$$dG = -SdT + Vdp + \sum_i \mu_i dN_i$$

Under their various conditions, equilibrium is obtained at the minimum of all four functions (E, F, G, H).

We could do different Legendre transformations to obtain functions of chemical potentials rather than particles, but in the case of a single species of particle, the four functions (E, F, G, H) are more than sufficient to obtain any combination of $(TS, pV, \mu N)$. For each the thermodynamic potential there is an equation stating that the mixed derivatives are equal. For example

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S}$$

$$-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

These are called Maxwell relations and there are four, corresponding to (E, F, G, H).

1.13 The third law

For completeness, we state the third law of thermodynamics, which has had less impact than the others:

> The third law: The function $S(N_i, V, E)$ approaches a constant (often taken to be zero) in the limit of zero temperature.

It should be noted that near absolute zero the rate of most processes (such as resolution of lattice defects) is very slow, so it is difficult to measure equilibrium properties. Alternatively

> The third law: It is impossible to reach absolute zero by a finite number of steps.

Finally, it is easy to remember the following reformulation of the laws of thermodynamics:

1. You can't win
2. You can't break even except on a very cold day
3. It never gets that cold

1.14 Applications

Example 1: Solar furnaces

Question What are these?

Answer The sunlight is focussed onto a small area, leading to very high temperatures. Useful work is obtained by some kind of heat engine.

Question What are the thermodynamic limitations of such a system?

Answer The second law implies that the temperature cannot be hotter than the sun, since then heat would be spontaneously flowing from a "cold" to a hot object. The surface of the sun is at about $6000K$, and in practice the temperature of solar furnaces is up to $2000K$. Above this there are also technical problems - the heat engine would melt or vaporise!

Question What is the maximum theoretical efficiency of such a system?

Answer Using a Carnot cycle, and assuming an ambient temperature of $300K$ we obtain

$$\frac{W}{Q} = 1 - \frac{T_c}{T_h} = \begin{cases} 0.95 & T_h = 6000K \\ 0.85 & T_h = 2000K \\ 0.625 & T_h = 800K \end{cases}$$

Clearly it is advantageous using the highest feasible temperature, but there are other considerations.

Question What is an example of how this works in practice?

Answer The Solar Two experimental power plant in California (see http://www.energylan.sandia.gov/sunlab/Snapshot/STFUTURE.HTM) operated using a molten salt at about $800K$ to run a conventional steam turbine. The advantage with this approach is that the hot salt can be stored until needed (eg in the evening). $43MW$ of solar energy was converted to $10MW$ of electrical power, thus an efficiency of about 0.24. Of course the real question is the cost per kWh which depends on the amount of sunlight, cost of land, maintenance etc.

Question Can a solar furnace work on a smaller scale?

Answer Yes. One application is as a cheap cooker in developing countries.

Question How does the efficiency compare with solar cells?

Answer The best experimental solar cells have an efficiency over 0.3 (also using some light concentration features). In practice, about 0.15.

Example 2: Refrigeration

Question What is the theoretical minimum power required to maintain the contents of a fridge at say 4^oC if the ambient temperature is 19^oC?

Answer Zero. You only need perfect thermal insulation, which does not in itself violate the laws of thermodynamics.

Question Apart from limitations from thermal insulation, why do real fridges require power?

Answer You also need to remove heat from food at room temperature that is placed in the fridge.

Question How could a perfectly efficient fridge do this?

Answer The optimal fridge would do a cycle of isothermal compression at room temperature, followed by adiabatic expansion to fridge temperature. This is not practical, as for example the fridge would need to extract $4.186 \times 15 = 63kJ$ of energy to lower the temperature of $1kg$ water from 19^oC to 4^oC. Water and food are not very compressible, so very high pressures would be required to achieve this: $dW = -pdV$. Somewhat more practically, it could use some kind of heat exchanger in which food moves along a conveyor belt, cooled by pipes just below the current temperature of the food; the quasistatic requirement is still in contrast to the need to cool the food as quickly as possible so that it doesn't spoil.

Question How could a perfectly efficient fridge maintain a fixed temperature in the presence of processes heating the inside (such as warm food or thermal conduction), and what would its efficiency be?

Answer A reverse Carnot cycle: Isothermal compression at the higher temperature, adiabatic expansion, isothermal expansion at the lower temperature, and then adiabatic compression to the original state point. We have

$$\eta = \frac{|W|}{|Q_h|} = 1 - \frac{T_c}{T_h} = 1 - \frac{277}{292} \approx 0.05$$

for the ratio of the work (electricity input) to the heat released to the environment. Here we are at fairly similar temperatures, so relatively little work is required. The heat absorbed from the inside of the fridge is of course $|Q_c| = |W| - |Q_h|$, so in terms of this we have

$$|W| = \left(\frac{T_h}{T_c} - 1\right) |Q_c|$$

In general the word "efficiency" needs to be carefully defined, as it means different things in different situations.

Question How do real fridges work?

Answer Typically, they have a coolant which has a boiling temperature similar or just below the fridge operating temperature (used to be CFCs, now ammonia or others). Compression and condensation at the higher temperature, expansion and evaporation at the lower temperature. The latent heat from the phase change allows more energy to be transferred for the same temperature and pressure changes. The work is done by a pump which drives the fluid around the cycle. Roughly six times as much power is used in real refrigerators than the optimal efficiency given by the second law; the fact that the cycle must take finite time means that the processes are not quasistatic.

Example 3: The atmosphere.

Question Is the atmosphere in thermodynamic equilibrium?

Answer No, it is well known that the temperature decreases with height, thus it is not in thermal equilibrium. Also, wind is an indication of mechanical dis-equilibrium and rain is an indication of chemical dis-equilibrium.

Question What are some thermal processes involved?

Answer Surface heated by solar light and geothermal heat. Infrared radiation blocked by 'greenhouse' gases in atmosphere. Heat conduction in gases is slow, main process is adiabatic convection. Far infrared radiation mostly from cool upper atmosphere. Complications from water evaporation and condensation and surface temperature differences, etc.

Question What about the decrease in pressure with height?

Answer This is consistent with equilibrium; note that energy is now not $-pdV$ due to gravitational potential energy thus mechanical ("kinetic") pressure p is not constant at equilibrium. Balancing forces on a fluid element we find that $dp/dz = -\rho g$ for mechanical equilibrium where z is height, g is gravity and $\rho = mN/V$ is mass density.

Question What temperature profile is predicted for an adiabatic atmosphere? Assume mechanical equilibrium and local thermodynamic equilibrium (ie the molecular scales such as the mean free path are much smaller than the scales of variation).

Answer Assume $f = 5$ ideal gas as above, $pV^{7/5} = const$, or $\rho/\rho_0 = (p/p_0)^{5/7}$, where ρ_0 and p_0 are at $z = 0$, say sea level. Substituting into p equation we find

$$\frac{dp}{dz} = -g(p/p_0)^{5/7}\rho_0$$

$$(p/p_0)^{2/7} = 1 - \frac{2\rho_0 g z}{7p_0}$$

From the adiabatic equation we then find

$$(\rho/\rho_0)^{2/5} = 1 - \frac{2\rho_0 g z}{7p_0}$$

and from the ideal gas equation $pV = NkT$ we find

$$T = \frac{mp}{k\rho} = T_0\left(1 - \frac{2mgz}{7kT_0}\right)$$

which is a linear decrease with height of $2mg/7k$. A typical molecule has mass $28u$, so we have $2 \times 28 \times 9.81/7 \times 8314$. The result is $9.44 \times 10^{-3} Km^{-1}$. If the temperature gradient is higher than this, adiabatic convection will equalise it. The gradient can however be lower and still stable, (eg thermal equilibrium at zero gradient). The adiabatic atmosphere predicts a sharp cut off at a height of about $30km$, but other processes and lack of convection lead to discrepancies from about $20km$. High humidity can lower the temperature gradient since condensing water deposits latent heat into the upper atmosphere.

2 Dynamics

2.1 Hamiltonian dynamics

In this section we consider the microscopic dynamical laws, in preparation for the next section, in which dynamics and thermodynamics are related, which is statistical mechanics proper. We begin with the Hamiltonian, which is a dynamical potential, in the sense that the equations of motion of the particles are given by derivatives of a single function. The Hamiltonian is a function H (not to be confused with enthalpy!) of q_i and p_i, $i = 1 \ldots 3N$, a total of $6N$ variables corresponding to the positions and momenta of N particles in three dimensions. The q_i constitute "configuration space", the p_i "momentum space" and the full set of variables "phase space". It is also possible for the Hamiltonian to depend explicitly on time t, but we will ignore this possibility. The equations of motion are

$$\frac{d}{dt}q_i = \frac{\partial H}{\partial p_i} \qquad \frac{d}{dt}p_i = -\frac{\partial H}{\partial q_i}$$

The derivation is not required. You will find a discussion, including the Lagrangian (the Legendre transform of the Hamiltonian) in a problem set. For this unit, the Hamiltonian will be of the form

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} + V(\mathbf{q})$$

where now i indicates particles, vectors with subscripts are 3-vectors and m_i is the mass of the ith particle. The first term is the kinetic energy and the second term is the potential energy, for example

$$V(\mathbf{q}) = \sum_{i<j} U_{int}(|\mathbf{q}_i - \mathbf{q}_j|) + \sum_i U_{ext}(\mathbf{q}_i)$$

where the first term is a two-body central force potential, and the second term might include gravity, or repelling walls of the container. We will often not be concerned with the details, and ignore the external potential energy. Substituting this Hamiltonian into the Hamiltonian equations of motion gives

$$\dot{\mathbf{q}}_i = \mathbf{p}_i/m_i$$

$$\dot{\mathbf{p}}_i = -\nabla_i V$$

which is just Newton's equations of motion for positions $\mathbf{q}_i$ and momenta $\mathbf{p}_i = m_i\dot{\mathbf{q}}_i$.

The time evolution of any phase variable $A(\mathbf{q},\mathbf{p})$ is given by the chain rule

$$\frac{dA}{dt} = \frac{d\mathbf{q}}{dt}\cdot\frac{\partial A}{\partial \mathbf{q}} + \frac{d\mathbf{p}}{dt}\cdot\frac{\partial A}{\partial \mathbf{p}} = \frac{\partial H}{\partial \mathbf{p}}\cdot\frac{\partial A}{\partial \mathbf{q}} - \frac{\partial H}{\partial \mathbf{q}}\cdot\frac{\partial A}{\partial p} \equiv \{A,H\}$$

where the Poisson bracket is defined by

$$\{A,B\} = \sum_{i=1}^{3N} \frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i}$$

Clearly $\{H,H\} = 0$ so

$$\frac{dH}{dt} = 0$$

the Hamiltonian is conserved. This is no surprise here, as it is just the total energy.

2.2 Time reversibility

Consider a set of autonomous first order ODEs

$$\dot{\mathbf{x}} = \mathbf{v}(\mathbf{x})$$

where $x \in \Gamma$ represents phase space (ie $(\mathbf{q},\mathbf{p})$) and $\mathbf{v} : \Gamma \to \Gamma$ is a vector field giving the equations of motion. We define a flow $\Phi^t : \Gamma \to \Gamma$ which give the solution after time $t \in \mathbb{R}$ of initial condition $\mathbf{x} \in \Gamma$, ie

$$\mathbf{x}(t) = \Phi^t(\mathbf{x}(0))$$

with the obvious properties

$$\Phi^0 = Id$$

$$\Phi^s \circ \Phi^t = \Phi^{s+t}$$

The theory of ODEs shows that a solution exists for some positive and negative time under very mild conditions; the solution may diverge at finite time if Γ is not a compact space.

The flow Φ^t is called (time) reversible if there exists a map $M : \Gamma \to \Gamma$ with the property

$$M \circ \Phi^t \circ M = \Phi^{-t}$$

Note that putting $t = 0$ here shows that M is an involution (ie its square is the identity). Thus for each trajectory $\mathbf{x}(t)$ satisfying the equations of motion, there is a reversed trajectory $\mathbf{y}(t) = M(\mathbf{x}(-t))$ which also satisfies the equations.

In the case of a Hamiltonian given by kinetic and potential energy as above, the map

$$M(\mathbf{q},\mathbf{p}) = (\mathbf{q}, -\mathbf{p})$$

has the required property, and hence the system is reversible. This can be shown by putting $\mathbf{p} \to -\mathbf{p}$ and $t \to -t$ in the equations of motion and showing that they are still valid. The significance is that we need to explain the second law of thermodynamics which is irreversible, since dynamical reversibility shows that entropy decreasing trajectories exist. The answer lies not in the equations of motion but in the initial (rather than final) conditions which are low entropy. For the Universe as a whole this means the big bang.

2.3 Liouville's theorem

We do not know the motions of 10^{23} particles exactly, the best we can hope for is some understanding of the probability density $\rho(\mathbf{x})$. A collection of copies of the system with realisations $\mathbf{x} \in \Gamma$ given according to a specified probability density is called an "ensemble". This approach is useful also in low-dimensional chaotic systems, in which instabilities imply that infinite precision would be required for long term precision, and in stochastically perturbed systems, in which the equations of motion themselves are not deterministic. We could be more general and talk about a (possibly singular) probability measure, but for equilibrium systems it turns out that for the most useful ensembles have a smooth density function with respect to Lebesgue measure.

We assume that the probability density is normalised,

$$\int \rho(\mathbf{x}) d^{6N}x = 1$$

We can also calculate expectation values of phase variables

$$\langle A \rangle = \int \rho(\mathbf{x}) A(\mathbf{x}) d^{6N}x$$

so that $\langle 1 \rangle = 1$ by the normalisation.

Let us consider the time evolution of a probability density under the dynamics, so now we consider $\rho(\mathbf{x},t)$. The flux (ie amount per unit surface per unit time) of probability is $\rho\mathbf{v}$. Thus the rate of change of the probability of being in some domain $D \subset \Gamma$ is

$$\frac{d}{dt}\int_D \rho(\mathbf{x},t)d\mathbf{x} = -\int_{\partial D} \rho(\mathbf{x},t)\mathbf{v}(\mathbf{x})\cdot d\mathbf{S}$$

where the RHS is a surface integral over the boundary of D. Applying the divergence theorem and putting the time derivative in the integral we have

$$\int_D \left[\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v})\right] d\mathbf{x} = 0$$

But this is true for all domains, so we have the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

which is also used, eg for conservation of mass in fluid dynamics.

Rather than $\partial\rho/\partial t$ which gives the change in density at a fixed point in phase space, it is useful to know how ρ varies along the flow. Using the chain rule and the continuity equation

$$\frac{d}{dt}\rho(\mathbf{x}(t), t) = \frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho = -\rho \nabla \cdot \mathbf{v}$$

where we can identify $\mathbf{v} \cdot \nabla \rho = \{\rho, H\}$ the Poisson bracket. In the case of a Hamiltonian system, we have

$$\nabla_x \cdot \mathbf{v} = \nabla_q \cdot \nabla_p H - \nabla_p \cdot \nabla_q H = 0$$

thus

$$\frac{d}{dt}\rho(\mathbf{x}(t), t) = 0$$

which is called Liouville's theorem. Physically, the Hamiltonian equations preserve volume in phase space, so that the convected density remains constant under the flow. An important consequence of the Liouville theorem is that any function $\rho(E)$ where E is the conserved energy, is an invariant density under the flow, ie is a time-independent solution to the equation.

Example: Write down Liouville's theorem for a system with a frictional force described by

$$\dot{\mathbf{q}} = \mathbf{p}/m$$

$$\dot{\mathbf{p}} = -\nabla_q V(\mathbf{q}) - \alpha \mathbf{p}$$

where $m, \alpha > 0$ are constants and $\mathbf{q}, \mathbf{p} \in \mathbb{R}^{3N}$. We compute

$$\nabla_x \cdot \mathbf{v} = \nabla_q \cdot \mathbf{p}/m - \nabla_p \cdot (\nabla_q V + \alpha \mathbf{p}) = -3N\alpha$$

Thus

$$\frac{d\rho}{dt} = 3N\alpha\rho$$

The fact that the right hand side is not zero means that the system is not Hamiltonian, at least in these coordinates; the volume in phase space contracts under the dynamics. Physically, ρ increases with time since the probability is getting concentrated on the final state, in which the system finds minima of the potential energy V and remains there.

2.4 Poincare recurrence

Liouville's theorem has a strange consequence called the Poincare recurrence theorem, which we now discuss. Assume that Γ has finite volume. This is certainly true if the energy is bounded and the physical volume is finite. Then Poincare recurrence states that the set of points which do not return arbitrarily close to their starting point has zero volume. For example, almost all (in the sense of probability) states in which all the gas molecules are in one corner of the container return to that state after sufficiently long time. Like time reversibility, this seems to violate thermodynamics.

The proof is quite short. Consider a set $A \subset \Gamma$ with finite but arbitrarily small volume. Assume, in contradiction with Poincare recurrence, that there is a set $B_0 \subset A$ of finite volume which leaves A after some time τ and never returns. Define $B_n = \Phi^{n\tau} B_0$ for all positive integers n. From the Liouville theorem the volumes of all these sets are equal. Suppose they are not disjoint, and there is overlap between B_i and B_j, with $i < j$ say. Then there is overlap between $\Phi^{-i\tau} B_i = B_0$ and $\Phi^{-i\tau} B_j = B_{j-i}$. But this is impossible since $B_0 \subset A$ and we said that the future evolution of this set never returns to A. Thus all B_n are disjoint. However they all have the same nonzero volume, so their union must have infinite volume. But this is impossible since it is a subset of Γ which by assumption has finite volume. Thus the theorem is proved.

Poincare recurrence is not observed for any systems with a significant number of particles in practice, since the recurrence time is very long. For example, let us consider a container and ask for the time until all N particles are in the right half. Assuming the configurations change randomly every time τ, we have to wait roughly $2^N \tau$ before we see all particles in the right half (a probability of 2^{-N}). If $N \approx 10^{23}$ it is not surprising that we have not seen this phenomenon.

Poincare recurrence illustrates the importance of time scales in statistical mechanics. There is no point proving a theorem which involves a time beyond experimental scales or beyond which the assumptions of the model cease to be valid.

There remains the question of the second law of thermodynamics. Is it violated in small systems (in which the Poincare recurrence time might be reasonable?). Well to take advantage of the unusual low entropy configuration of the particles we need to measure the system 2^N times; this will require more energy than we can extract from the low entropy system (this can be formulated precisely). Thus fluctuations on small scales are not expected to violate thermodynamics. However the statement that the entropy of an isolated system never decreases must be modified; it does so, but macroscopic decreases only happen with vanishingly small probability. Alternatively, a microscopic formulation of entropy that is non-decreasing must include not only the state of the system, but also the observer's knowledge about the system, for example represented in $\rho(\mathbf{x},t)$. In the case of large systems this effect is negligible - no human or computer can know the locations or velocities of 10^{23} molecules!

2.5 Ergodic theory

Before considering how to define entropy microscopically, we will consider another dynamical issue raised by the Poincare recurrence theorem - in what sense can we expect the time evolution of a dynamical system to behave randomly? The branch of mathematics that seeks to answer this question is called ergodic theory.

We can define two types of averages over a phase quantity A. We have an ensemble average

$$\langle A\rangle = \int A(\mathbf{x})\rho(\mathbf{x})d\mathbf{x}$$

over an invariant probability measure (eg $\rho(E)d\mathbf{x}$ as discussed in connection with Liouville's theorem). A is assumed to be absolutely integrable with respect to this measure, that is $\langle|A|\rangle < \infty$. We can also define the time average

$$\bar{A} = \lim_{T\to\infty}\frac{1}{T}\int_0^T A(\Phi^t(\mathbf{x}))dt$$

which might depend on $\mathbf{x}$.

The Birkhoff Ergodic theorem (1931) states that the limit in $\bar{A}$ exists for almost all $\mathbf{x}$ with respect to the invariant measure. We have,

$$\begin{aligned}\bar{A}(\Phi^\tau\mathbf{x}) &= \lim_{T\to\infty}\frac{1}{T}\int_0^T A(\Phi^{t+\tau}(\mathbf{x}))dt\\ &= \lim_{T\to\infty}\frac{1}{T}\int_{-\tau}^{T-\tau} A(\Phi^t(\mathbf{x}))dt\\ &= \lim_{T\to\infty}\frac{1}{T}\left[\int_{-\tau}^0+\int_0^T+\int_T^{T-\tau}\right]A(\Phi^t(\mathbf{x}))dt\\ &= \bar{A}(\mathbf{x})\end{aligned}$$

since the other two integrals are finite and vanish in the limit. Thus the time average is the same for any point on the same trajectory. This means that if the measure is invariant we have

$$\langle\bar{A}\rangle = \langle A\rangle$$

For an ensemble to describe the dynamics of an individual system we want to have

$$\langle A\rangle = \bar{A}$$

in other words, time averages are in some sense independent of the initial condition. It can be shown that it is always possible to decompose phase space into "ergodic components", each with its own "ergodic" invariant measure, so that for almost all initial conditions (with respect to the ergodic measure) the above statement is true. Phase points with different energies (or other known conserved quantities) are in different ergodic components, but it is possible for the energy surface to be a single ergodic component. This is Boltzmann's ergodic hypothesis. In practice ergodicity has been shown only for a very small class of systems such as those with infinitely hard collisions, and is believed to be false in typical systems of interacting particles. Physically, it is important to understand the timescales (as for Poincare recurrence) and also whether for example one ergodic component is so big that the others can be ignored in practice. This nonergodicity and whether it has any physical implications is an active area of research.

Let us consider approach to equilibrium. We assume that the state is $\rho(\mathbf{x},t)$ satisfying the Liouville equation, for example $\rho(\mathbf{x},0)$ could be the characteristic function of some small volume in phase space in which the system is initialised. The time-dependent average of a phase function A is given by

$$\int A(\mathbf{x})\rho(\mathbf{x},t)d\mathbf{x} = \int A(\mathbf{x})\rho_0(\Phi^{-t}(\mathbf{x}))d\mathbf{x}$$

This will tend to a constant given by the equilibrium average of A if we have

$$\langle AB\circ\Phi^t\rangle \to \langle A\rangle\langle B\rangle$$

for all A, B. noting that This latter property is called mixing. Note that $\langle\rho_0\rangle = 1$ by normalisation. If A and B are the characteristic function of an ergodic component, the equation shows that $\langle A\rangle = 1$, in other words, mixing implies ergodicity. Again there is a timescale issue - what is the rate of approach to equilibrium? There are many other ergodic properties, but these are all we will need to understand statistical mechanics.

Example: the 1D harmonic oscillator,

$$H = \frac{1}{2}(x^2+p^2)$$

has trajectories given by

$$x = \sqrt{2E}\cos\theta \qquad p = \sqrt{2E}\sin\theta \qquad \theta = \theta_0 - t$$

where E is the conserved energy and θ_0 is the initial angle in the phase plane. The average of a phase function $A(E,\theta)$ is

$$\bar{A} = \frac{1}{2\pi}\int_0^{2\pi} A(E,\theta)d\theta \equiv \langle A\rangle$$

which is a function of E only. Thus the ergodic components are the constant energy curves and the system is ergodic. The correlation function of two functions A and B on the same energy curve is

$$\langle A\Phi^t(B)\rangle = \frac{1}{2\pi}\int_0^{2\pi} A(E,\theta)B(E,\theta-t)d\theta$$

which is periodic in t and does not generally have a limit, thus this system is not mixing.

Showing that a given system is mixing is beyond the scope of this unit, however an example is given at http://www.maths.bris.ac.uk/~macpd/gallery/diamond.gif

2.6 The virial and equipartition theorems I

By definition, the time average of the time derivative of some phase variable is just the total difference divided by the time. If the phase variable is bounded, this then tends to zero. For the virial theorem we consider the quantities

$$G_i = q_i p_i$$

for $i \in \{1, \ldots, 3N\}$ which is bounded in systems we normally consider. Thus we have

$$0 = \frac{d\bar{G}_i}{dt} = \overline{\dot{q}_i p_i} + \overline{q_i \dot{p}_i}$$

If the Hamiltonian takes the usual kinetic plus potential form, this becomes

$$\overline{p_i^2/m_i} = -\overline{q_i F_i}$$

where $F_i = \dot{p}_i$ is the ith component of the force. Summing over i we find

$$\bar{T} = -\frac{1}{2}\overline{\sum_i q_i F_i}$$

where T is the kinetic energy and the averaged quantity on the RHS is called the virial; this statement is called the virial theorem. We can also take an ensemble average of both sides using an invariant density, and so following the discussion around the Birkhoff theorem, we have

$$\langle T \rangle = -\frac{1}{2}\langle \sum_i q_i F_i \rangle$$

An important case is that of an external central potential of the form $U(r) = Cr^\alpha$ (for constants C, α) in which we find

$$\mathbf{q} \cdot \mathbf{F} = \mathbf{q} \cdot (\mathbf{q}(-U'(r))/r) = -rU'(r) = -\alpha U(r)$$

and hence

$$\langle T \rangle = \frac{\alpha}{2}\langle V \rangle$$

where V is the total potential energy. Thus for $\alpha = 2$, ie a harmonic oscillator, which is by Taylor's theorem an approximation for generic small oscillations, we have

$$\langle T \rangle = \langle V \rangle$$

which is called "equipartition of energy". The term "external potential" can be interpreted somewhat freely; for sufficiently dilute systems the molecules can be approximated by 2-body systems with centre of mass coordinates moving freely and relative coordinates obeying the virial theorem; the Hamiltonian expressed in these coordinates takes the usual form.

Example: Show that the velocity of an orbiting satellite is given by the escape velocity divided by $\sqrt{2}$. We have $\alpha = -1$ so $\langle T \rangle = -\langle V \rangle/2$. Now the kinetic energy of an escaping particle is just $-\langle V \rangle$, so the ratio of the velocities in the two cases is $\sqrt{2}$.

3 Classical statistical mechanics

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the same work, died similarly in 1933. Now it is our turn to study statistical mechanics. Perhaps it will be wise to approach the subject cautiously. David Goodstein.

3.1 Boltzmann entropy

Summarizing the results of the classical dynamics section, if we postulate that the microscopic equations are Hamiltonian we have conservation of phase space volume (Liouville's theorem). If we assume further that this volume is finite we find that almost all trajectories are recurrent (Poincare recurrence theorem). We can further assume that almost all trajectories fill the constant energy surface uniformly on average (ergodicity), or further that initial probability densities approach (in a weak sense) the uniform density (mixing). This justifies to a certain degree the postulate made by Boltzmann:

Equal a priori probability In equilibrium the probability density on the constant energy surface is uniform.

The reason that low entropy configurations (eg involving all the particles in one corner of the container) have low probability is that they correspond to a small volume of phase space (for classical systems) or number of states (for quantum systems). In other words, each macroscopic state corresponds to a different volume or number of microscopic states. If the system starts in a macroscopic state of small phase space volume, it can easily move to one with more volume, but has very low probability of moving to one with less volume. Thus entropy of a macrostate can be associated with an increasing function of the volume or number of microstates associated with it. The fact that for two separate systems entropy is additive (ie extensive) and phase space volume is multiplicative, leads to another formula of Boltzmann

$$S = k \ln \Omega$$

where Ω is the phase space volume and k is a constant which we will identify with the ideal gas constant.

In calculating Ω we need a dimensionless volume, unlike $d^{3N}q d^{3N}p$ which has units of action to the power $3N$. Classically we don't know what to put here, but a quantum mechanical result called Weyl's theorem makes an equivalence between the number of quantum states and phase space volume measured in units of h^{3N} where $h = 6.626 \times 10^{-34} Js$ is Planck's constant. Also, in both classical and quantum mechanics, there is often a symmetry due to interchange of identical particles. If this is the case, the true phase space or number of states is less by a factor $N!$. Thus we have

$$\Omega = \begin{cases} \int \frac{d^{3N}q d^{3N}p}{N! h^{3N}} & \text{classical} \\ \sum \text{states} & \text{quantum} \end{cases}$$

We will consider quantum systems in more detail later.

Now S is a thermodynamic potential; other quantities can be calculated from it my differentiation. Thus we can now (in principle) calculate all quantities from microscopic considerations. This formula also clarifies the third law of thermodynamics, which now becomes the statement that the degeneracy of the ground state $T = 0$ of a quantum system is unity (or at least smaller than exponential in the system size).

Remark: The Boltzmann entropy suffers from a couple of philosophical problems. One is that it depends on the definition of the macro and micro states of the system, and is thus mathematically ambiguous. For example what is the resolution or sensitivity of the measuring apparatus? The other is that it does not take into account the information known by the observer, so occasionally the entropy will decrease due to rare fluctuations. Thus the second law is only statistically valid under this definition.

We now look at some examples of entropy calculations.

3.2 Volumes of hyperspheres

It is clear that the surface of constant energy corresponds to a $3N$-dimensional sphere in momentum space, so we first need to calculate the surface and volume of high dimensional spheres. Let the volume of a sphere of radius r in d dimensions, ie the set defined by

$$\sum_{i=1}^{d} x_i^2 < r^2$$

be

$$V(r) = V_d r^d$$

The volume between spheres of radius r and $r + \delta r$ is

$$V(r+\delta r) - V(r) = V_d[(r+\delta r)^d - r^d]$$

For small δr this approaches $\delta r S(r)$ where $S(r)$ computes the surface area of the same sphere,

$$S(r) = \lim_{\delta r \to 0} \frac{V(r+\delta r) - V(r)}{\delta r} = V'(r) = dV_d r^{d-1}$$

We can write this as

$$S(r) = S_d r^{d-1} \qquad S_d = dV_d$$

Now let us compute the following integral over $\mathbf{x} \in \mathbb{R}^d$ in two ways:

1. Expand as a product of exponentials:

$$\int \exp(-\mathbf{x}^2) d\mathbf{x} = \left[\int_{-\infty}^{\infty} \exp(-x^2) dx\right]^d = (2I_1)^d$$

2. Move to hyperspherical coordinates:

$$\int \exp(-\mathbf{x}^2) d\mathbf{x} = \int_0^{\infty} \exp(-r^2) S_d r^{d-1} dr = S_d I_d$$

Now change variable to $u = r^2$

$$\begin{aligned} I_d &= \int_0^{\infty} \exp(-r^2) r^{d-1} dr \\ &= \int_0^{\infty} \exp(-u) u^{(d-2)/2} du/2 \\ &= \Gamma(d/2)/2 \end{aligned}$$

since this is the definition of the Gamma function. We have $\Gamma(1) = 1$ trivially and $\Gamma(n+1) = n\Gamma(n)$ using integration by parts, thus $\Gamma(n+1) = n!$. From above we have

$$2^d I_1^d = S_d I_d$$

$$S_d = \frac{2^d I_1^d}{I_d} = \frac{2\Gamma(1/2)^d}{\Gamma(d/2)}$$

Now we know the circumference of a circle,

$$2\pi = S_2 = \frac{2\Gamma(1/2)^2}{\Gamma(1)}$$

thus

$$\Gamma(1/2) = \sqrt{\pi}$$

and hence

$$S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$$

$$V_d = \frac{2\pi^{d/2}}{d\Gamma(d/2)}$$

We will be concerned with large dimensions, so we will use Stirling's formula for factorials of large argument, eg

$$x! \sim x^x e^{-x} \sqrt{(2x + 1/3)\pi}$$

Note that even though this formula is asymptotic, its maximum relative error in $x > 0$ is about 2%.

3.3 Entropy of an ideal gas

We want to calculate the equilibrium entropy as a function of state variables N, V, E for an ideal gas with no spin or other degrees of freedom. We should allow a small uncertainty in the energy, ie consider energies from E to $E + \delta$. Classically this allows us to use the volume element $d\mathbf{x}$ in Liouville's theorem. Quantum mechanically this will be necessary since the energy levels are discrete. We have

$$\Omega(E) = \Sigma(E+\delta) - \Sigma(E) \approx \delta\Sigma'(E)$$

where

$$\begin{aligned} \Sigma(E) &= \frac{1}{N!h^{3N}} \int_{\mathbf{p}^2/2m<E} d^{3N}q d^{3N}p \\ &= \frac{V^N}{N!h^{3N}} \frac{2\pi^{3N/2}}{3N\Gamma(3N/2)} (2mE)^{3N/2} \end{aligned}$$

from previous calculations. Thus

$$\begin{aligned} S &= k \ln \Omega \\ &= k \left[N \ln V (2\pi mE/h^2)^{3/2} - \ln(N!(3N/2-1)!) \right. \\ &\quad \left. + \ln(\delta/E)\right] \end{aligned}$$

Ignoring the constant $\ln\delta$, assuming $N\gg 1$ and putting in the leading part of Stirling's formula

$$\ln N! = N\ln N - N + O(\ln N)$$

we find

$$S = Nk\left[\frac{5}{2}+\ln\left\{\frac{V}{N}\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right\}\right]$$

which is called the Sackur-Tetrode equation. Note that if we forgot the $N!$ we would have an extra $N\ln N$ term which is non-extensive, but the correct equation has only intensive quantities V/N and E/N inside the logarithm.

Differentiating we obtain other state variables. It is easiest to solve for

$$E(N,V,S)=\frac{3h^2N^{5/3}}{4\pi mV^{2/3}}\exp\{\frac{2S}{3Nk}-\frac{5}{3}\}$$

then differentiate to obtain

$$T=\frac{\partial E}{\partial S}=\frac{2E}{3Nk}\qquad E=\frac{3}{2}NkT$$

$$-p=\frac{\partial E}{\partial V}=-\frac{2E}{3V}\qquad pV=NkT$$

$$\mu=\frac{\partial E}{\partial N}=\frac{5E}{3N}-\frac{2ES}{3N^2k}=kT\ln\{\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\}$$

Thus k is indeed the same constant as in the thermodynamics section. We can also of course calculate $F=E-TS$ and the other potentials and derivatives such as specific heats.

If the ideal gas has spin degrees of freedom, we get an extra term $(2s+1)Nk$ in the entropy. However when we differentiate the temperature and pressure are unchanged, so it is not classically measurable. Rotations or vibrations will be discussed later in connection with the equipartition theorem.

3.4 Entropy of mixing

Initially we have two different gases, at states N_1,V_1,E_1 and N_2,V_2,E_2. We want them to be in thermal equilibrium, so $T_1=T_2$ thus $E_1/N_1=E_2/N_2$. Then we allow them to mix, filling the whole container, so the final state has

$$V=V_1+V_2$$
$$E=E_1+E_2$$
$$N=N_1+N_2$$

The final entropy can be calculated as above, with $\Sigma(E)$ determined by the volume of the ellipsoid

$$\frac{\mathbf{p}_1^2}{2m_1}+\frac{\mathbf{p}_2^2}{2m_2}<E$$

Scaling the p_1 coordinates by a factor $\sqrt{m_1}$ etc this becomes a sphere and, we find that

$$\Sigma(E)=\frac{V^N}{N_1!N_2!h^{3N}}\frac{2\pi^{3N/2}}{3N\Gamma(3N/2)}(2E)^{3N/2}m_1^{3N_1/2}m_2^{3N_2/2}$$

leading to

$$S(N,E,V)=S(N_1,E_1,V)+S(N_2,E_2,V)$$

as expected (the gases don't interact). There has been an increase in entropy given by

$$\begin{aligned}\Delta S &= S(N_1,V,E_1)+S(N_2,V,E_2)\\ &\quad -S(N_1,V_1,E_1)-S(N_2,V_2,E_2)\\ &= N_1k\ln(V/V_1)+N_2k\ln(V/V_2)\end{aligned}$$

This is expected: mixing of gases is an irreversible process. However what if the two gases are the same? Then mixing them should not increase the entropy. This is called Gibbs' paradox. The solution is that if the gases are the same the factor $N!$ (rather than $N_1!N_2!$) is included in the entropy, so there is no increase (recall that the entropy we calculated was extensive). This is often given as the physical reason the $N!$ is required in the classical case.

3.5 The microcanonical (N,V,E) ensemble

We can calculate the entropy in terms of the volume of phase space, but other phase variables must be calculated as ensemble averages $\langle f\rangle$ previously defined, where for an isolated system at equilibrium, the probability density is given by the postulate of equal a priori probability that we have already used

$$\rho_{\mu c}(\mathbf{x})=\begin{cases}1/\Omega(N,V,E) & E<H(\mathbf{x})<E+\delta\\ 0 & \text{otherwise}\end{cases}$$

Here μc is short for microcanonical. Liouville's theorem shows us that it is preserved under Hamiltonian dynamics. We need to be consistent with the $N!$ terms: since we have included it in Ω, the space $\mathbf{x}$ must comprise only a single copy of the identical microstates obtained by interchanging identical particles, and phase averages are calculated over the full space using

$$\langle f\rangle_{\mu c}=\int f(\mathbf{x})\rho_{\mu c}(\mathbf{x})\frac{d^{3N}pd^{3N}q}{N!h^{3N}}$$

We can calculate phase quantities like the average energy per particle this way; it also turns out that we can calculate thermodynamic quantities such as the entropy and hence its derivatives. We have

$$S(N,V,E)=k\ln\Omega(N,V,E)$$

which is a constant (does not depend on phase point on the energy shell ignoring the small quantity δ). Thus

$$\begin{aligned}S(N,V,E) &= k\langle\ln\Omega\rangle\\ &= k\int_{E<H(\mathbf{q},\mathbf{p})<E+\delta}\frac{\ln\Omega}{\Omega}\frac{d^{3N}pd^{3N}q}{N!h^{3N}}\\ &= -k\int\rho_{\mu c}\ln\rho_{\mu c}\frac{d^{3N}pd^{3N}q}{N!h^{3N}}\end{aligned}$$

noting that the domain can be extended by defining

$$y\ln y|_{y=0}=\lim_{y\to 0}y\ln y=0$$

Thus we can write

$$S(N,V,E)=\langle -k\ln\rho_{\mu c}\rangle$$

This is the Gibbs expression for the entropy, and is the point of connection between thermodynamic entropy and similar expressions used in information theory.

It is very tempting to treat this dynamically, ie start with a general $\rho_0(\mathbf{x})$, evolve it using the Liouville equation, and see whether the Gibbs entropy increases. We have

$$\frac{dS}{dt}=-k\int\frac{\partial}{\partial t}(\rho\ln\rho)\frac{d^{3N}pd^{3N}q}{N!h^{3N}}$$

The integrand is

$$\begin{aligned}(\ln\rho+1)\frac{\partial\rho}{\partial t} &= -(\ln\rho+1)\nabla\cdot(\rho\mathbf{v})\\ &= -(\ln\rho+1)(\mathbf{v}\cdot\nabla\rho+\rho\nabla\cdot\mathbf{v})\\ &= -\nabla\cdot(\rho\ln\rho\mathbf{v})-\rho\nabla\cdot\mathbf{v}\end{aligned}$$

using the continuity equation. The divergence theorem together with the vanishing of ρ at the boundary kills the first term and we are left with

$$\frac{dS}{dt}=\langle k\nabla\cdot\mathbf{v}\rangle=0$$

for Hamiltonian systems. Thus the Gibbs entropy is constant. This can be interpreted as the statement that our knowledge of the system remains the same during deterministic time evolution and volume preserving dynamics, but it does not explain the second law. In practice the density ρ is getting mixed throughout phase space so that on a macroscopic level there is no way of using the information about the past low entropy state of the system. Thus we return to the issues of a nonequilibrium entropy that is dependent on the measurement resolution. Alternatively we note that no system is completely isolated, and that small random perturbations could smear out the "mixed" density to a true uniform one. In the meantime we can use the Gibbs entropy to compute equilibrium properties of systems.

3.6 The canonical (N,V,T) ensemble

The microcanonical ensemble is limited mathematically in that it is often difficult to calculate the relevant phase space volumes and ensemble averages, and physically in that most systems are not isolated, ie they share energy with the environment and the equilibrium state is better written in terms of the temperature of the environment than the energy of the system.

We consider the system S_1 in contact with a much larger heat bath S_2 at equilibrium and temperature T. The combined system is isolated, so it is described by the microcanonical ensemble. We have $E=E_1+E_2$, $E_1\ll E$. The probability of the system being in a state with energy E_1 is the probability of the bath having energy $E-E_1$, which is proportional to $\Omega_2(E-E_1)$. We expand the entropy of the heat bath in the small parameter

$$k\ln\Omega_2(E-E_1)\approx k\ln\Omega_2(E)-\frac{\partial}{\partial E}(k\ln\Omega_2(E))E_1+\ldots$$

but the derivative is just $\partial S/\partial E=1/T$ for the bath. Thus the probability is proportional to

$$\Omega_2(E-E_1)\approx\Omega_2(E)\exp(-E_1/kT)$$

Normalising removes the constant and we obtain the canonical ensemble density function

$$\rho_c(\mathbf{x})=\frac{e^{-\beta H(\mathbf{x})}}{Z(N,V,T)}$$

where the normalisation factor

$$Z(N,V,T)=\frac{1}{N!h^{3N}}\int e^{-\beta H(\mathbf{x})}d^{3N}qd^{3N}p$$

is called the canonical partition function and $\beta=1/kT$ is a common notation for the inverse temperature.

Let us now check the Gibbs expression for the entropy.

$$\begin{aligned}S &= \langle -k\ln\rho_c\rangle\\ &= -\frac{k}{N!h^{3N}}\int\rho_c(\mathbf{x})\ln\rho_c(\mathbf{x})d\mathbf{x}\\ &= \frac{k}{N!h^{3N}}\int(\beta H+\ln Z)\frac{e^{-\beta H}}{Z}d\mathbf{x}\\ &= k\beta\langle H\rangle+k\ln Z\\ &= k\beta E+k\ln Z\end{aligned}$$

since the ensemble average of the energy function is just what we mean macroscopically by the energy. Differentiating, we find

$$\begin{aligned}\frac{1}{T} &= \frac{\partial S}{\partial E}\\ &= kE\frac{\partial\beta}{\partial E}+k\beta+k\frac{\partial\ln Z}{\partial E}\end{aligned}$$

Now we have

$$\frac{\partial\ln Z}{\partial E}=\frac{\partial\ln Z}{\partial\beta}\frac{\partial\beta}{\partial E}=-E\frac{\partial\beta}{\partial E}$$

thus

$$\frac{1}{T}=k\beta$$

as expected. Also

$$k\ln Z=S-\beta kE$$

is just $-F/T$ where $F(N,V,T)$ is the free energy found to be the thermodynamic potential for this system. Thus we have

$$F(N,V,T)=-kT\ln Z(N,V,T)$$

which is the canonical equivalent to

$$S(N,V,E) = k\ln\Omega(N,V,E)$$

Thus a typical approach is to compute $Z(N,V,T)$, take the logarithm to get F and then derivatives to get other thermodynamic quantities.

Another approach to the canonical (and later) ensembles is a variational principle. If we define S using the Gibbs formula and maximise the quantity $S-\beta E$ over all ensembles (ie functions ρ) we can show that the maximum value is reached for $\rho=\rho_c$ and takes the value $\ln Z$.

3.7 Computations in the canonical ensemble

We usually have

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{q})$$

Then we can separate the configuration and momentum parts of the integral to get

$$Z = \frac{1}{N!h^{3N}}\left[\int e^{-\beta\sum_i \mathbf{p}_i^2/2m_i} d^{3N}p\right]\left[\int e^{-\beta V(\mathbf{q})}d^{3N}q\right]$$

Remark: In quantum mechanics q and p are non-commuting operators, so the exponential cannot generally be separated in this way. Also the $N!$ needs to be replaced by the relevant combinatoric factor depending on which particles are indistinguishable. If there is an external potential (such as gravity) but no interparticle interactions we have

$$V(\mathbf{q}) = \sum_i U(\mathbf{q}_i)$$

we have

$$\int \exp[-\beta\sum_i U(\mathbf{q}_i)]d^{3N}q = \left[\int e^{-\beta U(\mathbf{q})}d^3q\right]^N$$

The momentum integral separates into a product over integrals of the form

$$\int e^{-\beta p^2/2m}dp = \sqrt{2mkT}\int e^{-u^2}du = \sqrt{2\pi mkT}$$

see I_1 in the earlier section. The result is

$$\int \exp[-\beta\sum_i \mathbf{p}_i^2/2m_i]d^{3N}p = (2\pi kT)^{3N/2}\prod_i m_i^{3/2}$$

Thus for N identical non-interacting particles we have

$$\begin{aligned} Z(N,V,T) &= \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\left[\int e^{-\beta U(\mathbf{q})}d^3q\right]^N \\ &= \frac{Z(1,V,T)^N}{N!} \end{aligned}$$

Examples of the configuration integral:

1. Ideal gas in a container, volume V:

$$U=0 \qquad \text{incontainer}$$

$$\int e^{-\beta U}d^3q = V$$

2. Constant gravitational field, surface area A, $z>0$:

$$U = mgz$$

$$\int e^{-\beta U}d^3q = \frac{kTA}{mg}$$

3. 3D Harmonic oscillator potential:

$$U = \frac{m\omega^2}{2}(x^2+y^2+z^2)$$

$$\int e^{-\beta U}d^3q = \left(\frac{2\pi kT}{m\omega^2}\right)^{3/2}$$

Of course, if the particles interact with each other, we need to do a $3N$ dimensional integral, which is much more involved.

Back in the thermodynamic potential section we learnt how to calculate using the free energy $F(N,V,T)$:

$$S = -\frac{\partial F}{\partial T} = k\ln Z + \frac{kT}{Z}\frac{\partial Z}{\partial T}$$

$$p = -\frac{\partial F}{\partial V} = \frac{kT}{Z}\frac{\partial Z}{\partial V}$$

$$\mu = \frac{\partial F}{\partial N} = -\frac{KT}{Z}\frac{\partial Z}{\partial N}$$

The energy itself is an ensemble average

$$\begin{aligned} E &= \langle H\rangle \\ &= \frac{1}{Z}\int He^{-\beta H}\frac{d^{3N}qd^{3N}p}{N!h^{3N}} \\ &= -\frac{\partial}{\partial\beta}\ln Z \end{aligned}$$

Thus for an ideal gas we find, as before

$$p = kT\partial_V\ln Z = kT\partial_V(N\ln V+\ldots) = \frac{NkT}{V}$$

$$E = -\partial_\beta\ln Z = -\partial_\beta(-(3N/2)\ln\beta+\ldots) = 3NkT/2$$

3.8 1-particle distributions

In this section we want to discuss the distribution of positions and momenta of individual microscopic particles, which can be obtained by taking the phase density $\rho_c(\mathbf{x})$ and integrating out the other degrees of freedom, or equivalently as ensemble averages of phase variables depending on one particle. If the particles do not interact, the distributions of different particles are statistically independent, and the calculation is straightforward.

If we choose a domain in 1-particle phase space $D \subset \mathbb{R}^6$, the probability that particle 1 will be there is

$$\int_D \rho_1(\mathbf{q},\mathbf{p}) d^3q d^3p = \langle \chi_D(\mathbf{q}_1,\mathbf{p}_1)\rangle$$

where χ_D is a characteristic function equal to 1 if particle 1 is in D and zero otherwise. This equation defines the 1-particle density $\rho_1(\mathbf{q},\mathbf{p})$. Take a very small domain and divide by the domain volume, ie do not integrate over $(\mathbf{q}_1,\mathbf{p}_1)$. This can also be written in terms of the Dirac distribution:

$$\rho_1(\mathbf{q},\mathbf{p}) = \langle \delta(\mathbf{q}-\mathbf{q}_1)\delta(\mathbf{p}-\mathbf{p}_1)\rangle$$

We can likewise define $\rho_1(\mathbf{q})$ and $\rho_1(\mathbf{p})$. From the normalisation we have

$$\int \rho_1(\mathbf{q},\mathbf{p}) d^3q d^3p = 1$$

We can ask for the probability density that any particle is at a point in 1-particle phase space; this is

$$\rho(\mathbf{q},\mathbf{p}) = \sum_{i=1}^{N} \rho_i(\mathbf{q},\mathbf{p}) = N\rho_1(\mathbf{q},\mathbf{p})$$

where the last equality holds if the particles are identical.

We can also ask for the distribution only in momentum space:

$$\rho_1(\mathbf{p}) = \langle \delta(\mathbf{p}-\mathbf{p}_1)\rangle = \frac{e^{-\mathbf{p}^2/2mkT}}{(2\pi mkT)^{3/2}}$$

This follows because $e^{\beta H}$ is a product of kinetic and potential terms, and the kinetic term is a product over individual particles. The Gaussian distribution of momenta is general (ie independent of whether the particles are interacting) and is called the Maxwell-Boltzmann distribution. To find a typical velocity for a particle we need to compute properties of this distribution. For example, the mean square momentum is (using spherical coordinates):

$$\begin{aligned}\int \mathbf{p}^2 \rho_1(\mathbf{p}) d^3p &= 4\pi \int_0^\infty p^4 \frac{e^{-p^2/2mkT}}{(2\pi mkT)^{3/2}} dp \\ &= \frac{4mkT}{\sqrt{\pi}} \int_0^\infty u^{3/2} e^{-u} du \\ &= 3mkT\end{aligned}$$

which checks with the known energy $3NkT/2$ in the ideal gas case. Notice that we have a general result for the average kinetic energy, even in systems with interactions. Alternatively we can ask for the most likely momentum $p = |\mathbf{p}|$ by integrating the distribution over the angles,

$$\rho_1(p) = 4\pi p^2 \frac{e^{-p^2/2mkT}}{(2\pi mkT)^{3/2}}$$

and differentiating to find the maximum,

$$0 = \rho_1'(p) = 4\pi \frac{e^{-p^2/2mkT}}{(2\pi mkT)^{3/2}} (2p - p^3/mkT)$$

$$p^2 = 2mkT$$

If there are no interactions we can factorise the configuration part also, giving

$$\rho_1(\mathbf{q},\mathbf{p}) = \frac{e^{-\beta[\mathbf{p}^2/2m+U(\mathbf{q})]}}{\int e^{-\beta(\mathbf{p}^2/2m+U(\mathbf{q})} d^3q d^3p}$$

$$\rho_1(\mathbf{q}) = \frac{e^{-\beta U}}{\int e^{-\beta U} d^3q}$$

$$\rho_1(\mathbf{p}) = \frac{e^{-\mathbf{p}^2/2mkT}}{(2\pi mkT)^{3/2}}$$

The distribution in configuration space is given using the integrals we did above:

1. Ideal gas
$$\rho_1(\mathbf{q}) = 1/V$$
2. Gravity
$$\rho_1(\mathbf{q}) = \frac{mg}{kTA} e^{-mgz/kT}$$
The exponential decay of density with height is as calculated in a problem sheet; this is the isothermal atmosphere since we are at equilibrium.
3. Harmonic oscillator
$$\rho_1(\mathbf{q}) = \left(\frac{m\omega^2}{2\pi kT}\right)^{3/2} e^{-m\omega^2\mathbf{q}^2/2kT}$$

The $e^{-E/kT}$ dependence in the canonical ensemble, even for kinetic energy of single particles, implies this form for the low temperature limit of the rate of any process that requires a minimum energy input ("activation energy"). Examples are

- Chemical reaction rates
- Evaporation rates

Example: The sublimation rate of ice is about $10^{-12} ms^{-1}$ at -130^oC. The enthalpy of sublimation is about $3 \times 10^6 Jkg^{-1}$. The molecular mass is $18u$. Estimate the temperature at which sublimation of one metre of ice would take 3×10^9 years (ie 10^{17} seconds).

Solution: We have a sublimation rate $R \approx Ce^{-E/kT}$ where C is a constant, E is the activation energy, which we will approximate by the sublimation enthalpy per particle. This is probably a lower bound on E as it may in fact require more concentrated energy to release a particle, with the remaining energy returning to the solid. We then estimate

$$\frac{E}{k} = \frac{3 \times 10^6 \times 18}{8314} = 6495K$$

Thus from the given data we calculate

$$C = Re^{E/kT} = 10^{-12} \times e^{6495/143} = 5.3 \times 10^7$$

Then the required temperature for the new rate is

$$T = -\frac{E/k}{\ln(R/C)} = -\frac{6495}{\ln(10^{-17}/5.3 \times 10^7)} = 114K$$

or -159^oC. A better estimate would be obtained by fitting E from further experimental data.

Molecule	Translation	Rotation	Total	C_V
monatomic	3	0	3	3Nk/2
linear	3	2	5	5Nk/2
nonlinear	3	3	6	3Nk

Table 2: Specific heats of polyatomic ideal gases at low temperature (ie ignoring vibrations).

3.9 The virial and equipartition theorems II

In the previous section we found that an amount $kT/2$ is present for each component of the kinetic energy of every particle. Combining this with the equipartition theorem for small vibrations of a diatomic molecule we conclude that the potential energy contains also $kT/2$. Thus a diatomic molecule can be expected to have total average energy $7kT/2$, of which $3kT/2$ is translational kinetic energy of the centre of mass, $2kT/2$ is rotational kinetic energy and $2kT/2$ is vibrational kinetic and potential energy. The vibrational modes are however only effective at temperatures at which the typical energy scale kT is comparable to the quantum energy level spacing $h\nu$ where $\nu = \omega/2\pi$ is the frequency of oscillations. At low temperatures (ie ignoring vibrations) we have results for ideal gases given in Tab. 2.

A related observation is that an improved version of the virial theorem can be proved using the canonical ensemble. We have for $i, j \in \{1 \dots 6N\}$

$$\begin{aligned}\langle x_i \frac{\partial H}{\partial x_j}\rangle &= \frac{1}{Z}\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H}\frac{d^{6N}x}{h^{3N}N!}\\ &= \frac{1}{Z}\frac{\delta_{ij}}{\beta}\int e^{-\beta H}\frac{d^{6N}x}{h^{3N}N!}\\ &= \delta_{ij}kT\end{aligned}$$

integrating by parts with respect to x_j and noting that the boundary term vanishes. This reduces to the kinetic energy and earlier virial theorem statements by substituting p_i or q_i (respectively) for x_i. It also shows that the average is zero for different components, ie kinetic or virial components are mutually uncorrelated for different particles or different spatial components.

3.10 Fluctuations and ensemble equivalence

We can also use the canonical ensemble to calculate the fluctuations in energy of the system. If these are small we might conclude that the microcanonical and canonical ensembles are equivalent in some sense (as we have found for the ideal gas): it doesn't matter much whether we fix the energy (within a range δ) or let it fluctuate around its mean value. However if fluctuations are large, they might have observable consequences for the system, and isolated/closed systems might behave very differently.

We start by noting that the partition function integrand depends only on the energy. Thus we can write it as

$$Z = \int e^{-\beta H(\mathbf{q},\mathbf{p})}\frac{d^{3N}qd^{3N}p}{N!h^{3N}} = \int e^{-\beta E} g(E)dE$$

where

$$g(E) = \frac{\partial}{\partial E}\int_{H(\mathbf{q},\mathbf{p})<E}\frac{d^{3N}qd^{3N}p}{N!h^{3N}} = \Sigma'(E)$$

is called the density of states, ie volume of phase space corresponding to each energy. The quantum interpretation is clear - it becomes the number of states per unit energy interval. Thus the probability density of finding an energy E in the canonical ensemble, $g(E)e^{-\beta E}$, has a maximum given by the competition of the fast growing $g(E)$ and the fast decaying $e^{-\beta E}$. The average energy, as we have seen, is

$$\langle E\rangle = \frac{1}{Z}\int Ee^{-\beta E}g(E)dE = -\frac{\partial}{\partial\beta}\ln Z$$

We can repeat this trick to get

$$\frac{\partial^2}{\partial\beta^2}\ln Z = \frac{Z''}{Z} - \left(\frac{Z'}{Z}\right)^2 = \langle E^2\rangle - \langle E\rangle^2$$

which is just the variance σ^2 of the distribution. The primes are β derivatives. Thus

$$\sigma^2 = -\frac{\partial E}{\partial\beta} = kT^2\frac{\partial E}{\partial T} = kT^2 C_V$$

The width relative to the average energy is

$$\frac{\sigma}{E} = \frac{\sqrt{kT^2C_V}}{E} = O(N^{-1/2})$$

using the fact that E and C_V are extensive. Thus equivalence of the microcanonical and canonical ensembles is valid as long as the system is large (and extensive and has finite C_V). In practice the canonical ensemble is easier to work with.

3.11 The grand canonical (μ, V, T) ensemble

Now we consider open systems, in which particles can be shared with the environment. For example, the fluid in a fluid/vapour system is an open system, and has a fluctuating number of particles. For fixed number of particles we know that the probability density at equilibrium is given by the canonical ensemble, now we need the probability that the given system will have a given number of particles. At first we will stick to the case of a single type of particle.

The derivation closely follows that of the canonical ensemble. We have a system S_1 in contact with a much larger heat and particle bath S_2 at equilibrium and conditions (μ, T). We have

$$N = N_1 + N_2 \qquad N_1 \ll N$$

$$E = E_1 + E_2 \qquad E_1 \ll E$$

The probability of being in a particular state with N_1, E_1 is proportional to $\Omega_2(N - N_1, E - E_1)$. We expand as before

$$\begin{aligned} k \ln \Omega_2(N - N_1, E - E_1) &\approx k \ln \Omega_2 - N_1 \frac{\partial}{\partial N}(k \ln \Omega_2) \\ &\quad - E_1 \frac{\partial}{\partial E}(k \ln \Omega_2) \end{aligned}$$

where on the RHS the system is evaluated at (N, E). Remark: We are treating N as a continuous variable here. This should be a good approximation as long as the number of particles is sufficiently high. Notice that we assume that the heat bath S_2 is large, but the system S_1 may be arbitrarily small. The derivatives are just

$$\frac{\partial}{\partial N} \ln \Omega_2 = -\frac{\mu}{T}$$

$$\frac{\partial}{\partial E} \ln \Omega_2 = \frac{1}{T}$$

Thus

$$\Omega_2(N - N_1, E - E_1) \propto \Omega_2(N, E) \exp[-\beta(E - \mu N)]$$

where $\beta = 1/kT$ as before. The coefficient is just a constant, so we can normalise to get the grand canonical (also called macrocanonical) density function

$$\rho_{gc}(N, \mathbf{x}) = \frac{e^{-\beta(H(\mathbf{x}) - \mu N)}}{\mathcal{Z}(\mu, V, T)}$$

with normalisation

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int e^{-\beta(H(\mathbf{x}) - \mu N)} d^{3N}q d^{3N}p$$

Notice that the grand canonical density is now spread over the phase spaces corresponding to all numbers of particles. An ensemble average is now

$$\langle f \rangle_{gc} = \sum_{N=0}^{\infty} \int f(N, \mathbf{x}) \rho_{gc}(N, \mathbf{x}) \frac{d^{3N}p d^{3N}q}{N! h^{3N}}$$

where as usual the $N!$ applies only for indistinguishable particles. The relation between the canonical and grand canonical partition functions is

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} z^N Z(N, V, T)$$

where $z = e^{\beta\mu}$ is called the fugacity.

As before, we check the Gibbs expression for the entropy:

$$\begin{aligned} S &= \langle -k \ln \rho_{gc} \rangle \\ &= k \langle \ln \mathcal{Z} + \beta H - \beta \mu N \rangle \\ &= k \ln \mathcal{Z} + k\beta E - k\beta\mu N \end{aligned}$$

where E and N now refer to ensemble averaged values. We can now check that the derivatives of this quantity give the correct expressions:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k\beta$$

noting that both β and μ (and hence $\mathcal{Z}$) depend on E. Similarly for $\partial S/\partial N$.

We also find that

$$-kT \ln \mathcal{Z} = E - ST - \mu N = -pV$$

a thermodynamic potential for the (μ, V, T) system. This is also by complete analogy with the canonical ensemble. Thus the grand canonical ensemble is useful for calculating equations of state:

$$pV/kT = \ln \mathcal{Z}$$

. We can also calculate quantities in terms of derivatives:

$$d(pV) = -dE + d(ST) + d(\mu N) = pdV + SdT + Nd\mu$$

using the first law and the Gibbs-Duhem relation. Thus for example

$$N = \frac{\partial}{\partial \mu} kT \ln \mathcal{Z}(\mu, V, T)$$

This is also clear by writing N is an ensemble average:

$$\begin{aligned} \langle N \rangle &= \frac{\sum_N N e^{\mu N/kT} Z(N, V, T)}{\sum_N e^{\mu N/kT} Z(N, V, T)} \\ &= kT \frac{\partial}{\partial \mu} \ln \sum_N e^{\mu N/kT} Z(N, V, T) \end{aligned}$$

3.12 The ideal gas in the GCE

For systems of noninteracting particles the Hamiltonian separates, so that the canonical partition function is

$$Z(N, V, T) = \frac{1}{N!} Z(1, V, T)^N$$

Then the grand canonical partition function is

$$\mathcal{Z}(\mu, V, T) = \sum_N \frac{z^N}{N!} Z(1, V, T)^N = \exp(zZ(1, V, T))$$

where $z = \exp(\mu/kT)$. We can see already that the grand canonical ensemble naturally includes the $N!$ symmetry terms, and is in fact often easier to use than the canonical ensemble.

For a monatomic ideal gas with no external potential, we had

$$Z(1, V, T) = \frac{V}{\lambda_T^3}$$

where

$$\lambda_T = \left(\frac{h^2}{2\pi m k T} \right)^{1/2}$$

is the "thermal wavelength", a function of temperature and some constants. Thus

$$\mathcal{Z}(\mu, V, T) = \exp(\exp(\mu/kT)V/\lambda_T^3))$$

and the equation of state is

$$\frac{pV}{kT} = \ln \mathcal{Z} = \exp(\mu/kT)V/\lambda_T^3$$

We compute $N(\mu, V, T)$ by differentiation:

$$N = \frac{\partial}{\partial \mu} kT \ln \mathcal{Z}(\mu, V, T) = \exp(\mu/kT)V/\lambda_T^3$$

Thus

$$\frac{pV}{kT} = N$$

as expected.

Also, this gives the previous expression for μ,

$$\mu = kT \ln(N\lambda_T^3/V)$$

and hence the fugacity

$$z = e^{\beta\mu} = \frac{N\lambda_T^3}{V}$$

which is the number density multiplied by a function of temperature. For solids and liquids in equilibrium with a vapour at a (temperature-dependent) low pressure, we know that the fugacity is just the fugacity of the vapour.

3.13 Fluctuations in the GCE

We have

$$\mathcal{Z}(z, V, \beta) = \sum_N z^N \int e^{-\beta E} g(N, E) dE$$

where

$$g(N, E) = \frac{\partial}{\partial E} \int_{H(\mathbf{q},\mathbf{p})<E} \frac{d^{3N}q d^{3N}p}{N! h^{3N}}$$

as before (it depended on N but we didn't write this explicitly). Notice the arguments - when we do partial derivatives, keeping z constant is different from keeping μ constant. We can see that as before we have

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}$$

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln \mathcal{Z}$$

and also

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \mathcal{Z}$$

$$\langle N^2 \rangle - \langle N \rangle^2 = z \frac{\partial}{\partial z} z \frac{\partial}{\partial z} \ln \mathcal{Z}$$

Thus we can write

$$\sigma_E^2 = -\frac{\partial E}{\partial \beta}$$

$$\sigma_N^2 = z \frac{\partial N}{\partial z}$$

however it is useful to write these in more standard forms than (z, V, β) derivatives. We have

$$\left(\frac{\partial z}{\partial N}\right)_{VT} = \beta z \left(\frac{\partial \mu}{\partial N}\right)_{VT} = \beta z \frac{V}{N} \left(\frac{\partial p}{\partial N}\right)_{VT}$$

using the Gibbs-Duhem relation in the form

$$N d\mu = V dp - S dT$$

Now p is an intensive quantity, so it can only depend on the ratio N/V and not on each variable independently (T is constant here). Thus

$$dp = \frac{\partial p}{\partial N} dN + \frac{\partial p}{\partial V} dV = 0$$

if

$$d(N/V) = dN/V - N dV/V^2 = 0$$

In other words

$$\left(\frac{\partial p}{\partial N}\right)_{TV} = -\frac{V}{N} \left(\frac{\partial p}{\partial V}\right)_{TN}$$

Putting this together we find

$$\frac{\sigma_N}{N} = \sqrt{kT\kappa/V}$$

where

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_{TN}$$

is the isothermal compressibility, and is intensive. Thus the relative fluctuations of the number of particles are order $1/\sqrt{N}$, ie small unless the compressibility diverges (eg at phase transitions).

For the energy we have

$$\left(\frac{\partial E}{\partial \beta}\right)_{zV} = \left(\frac{\partial E}{\partial \beta}\right)_{NV} + \left(\frac{\partial E}{\partial N}\right)_{\beta V} \left(\frac{\partial N}{\partial \beta}\right)_{zV}$$

The first term is what we had in the canonical ensemble. After some calculation (see Greiner) the result simplifies to

$$\frac{\sigma_E^2}{E^2} = \frac{kT^2}{E^2} C_V + \frac{\sigma_N^2}{E^2} \left[\left(\frac{\partial E}{\partial N}\right)_{TV}\right]^2$$

which we interpret as two positive contributions, from the intrinsic fluctuations in energy, and from the fluctuations in particles. As before, the relative fluctuations are of order $1/\sqrt{N}$ and so are small unless the system is small or has diverging properties.

3.14 Other ensembles

We can start to see a pattern. For systems at certain conditions there are thermodynamic potentials and ensembles. We now bring all these ensembles together in a more unified way. The thermodynamic potentials discussed previously were of two types: those obtained by

Legendre transformations of $S(N,V,E)$ and those obtained by Legendre transformations of $E(N,V,S)$. We begin with the former:

We have α_i, $i = 1 \ldots n$, which are a complete set of independent extensive conserved quantities (such as (N,V,E)). Equilibrium corresponds to the maximum of $S(\alpha_i)$. We define intensive thermodynamic conjugate variables by

$$\beta_i = \frac{1}{k}\frac{\partial S}{\partial \alpha_i}$$

here, $(-\beta\mu, \beta p, \beta)$. Now the thermodynamic state is given by some combination of the conserved and the conjugate variables, except that it cannot be all intensive variables, say $(\alpha_1, \ldots, \alpha_j, \beta_{j+1}, \ldots, \beta_n)$. The equilibrium state now corresponds to the maximum of a thermodynamic potential given by Legendre transformations of S:

$$\Phi = S - k \sum_{i=j+1}^{n} \alpha_i \beta_i$$

The full differential of this is

$$d\Phi = k \sum_{i=1}^{j} \beta_i d\alpha_i - k \sum_{i=j+1}^{n} \alpha_i d\beta_i$$

from which all quantities can be found by differentiation. The thermodynamic potential is given in terms of the partition function of an ensemble obtained by appropriate Laplace transforms of the microcanonical ensemble:

$$\Phi = k \ln \zeta(\alpha_1, \ldots, \alpha_j, \beta_{j+1}, \ldots, \beta_n)$$

$$\zeta = \int \exp(-\sum_{i=j+1}^{n} \alpha_i \beta_i) g(\alpha) \prod_{i=j+1}^{n} d\alpha_i$$

$g(\alpha)$ is the density of states (effectively $\Omega(\alpha)$). In the case of discrete variables such as the number of particles, the integral is replaced by a sum.

Example: the (N,p,T) ensemble, which allows volume fluctuations determined by a fixed pressure, but without transfer of particles. We have a potential

$$\Phi = S - E/T - pV/T = -G/T$$

with differential

$$d\Phi = -kEd\beta + k\beta V dp - k\beta\mu dN$$

Ensemble averages are computed over systems with a range of volumes:

$$\langle f \rangle = \frac{1}{\zeta} \int dV e^{-\beta p V} \int f(V,\mathbf{x}) e^{-\beta H(\mathbf{x})} \frac{d^{3N}q d^{3N}p}{N! h^{3N}}$$

where $\zeta(N,p,T)$ is determined by the requirement that $\langle 1 \rangle = 1$. Then we have

$$\Phi = k \ln \zeta$$

leading to the Gibbs potential:

$$G = -kT \ln \zeta$$

The other class of ensemble have been discussed more recently and consist of those at constant entropy, ie adiabatic. For example, let us consider the case of the enthalpy $H(N,p,S) = E + pV$. There can be no heat bath as this would allow transfer of heat, ie fluctuations in entropy. Thus the system is isolated. However the enthalpy must be fixed while energy and volume fluctuate. The solution is to allow volume as a phase variable and apply a constant external pressure. This fixes the enthalpy, allowing the microcanonical ensemble (with energy replaced by enthalpy) to be used. We will not discuss this in detail here.

Finally, because ensembles are equivalent (at least if the fluctuations are not too large), it is usually sufficient to choose the most convenient ensemble to work with. For small systems and phase transitions the choice of ensemble can be important.

4 Quantum statistical mechanics

4.1 Quantum mechanics, Weyl's law

An exact treatment of molecular interactions requires quantum mechanics, although to a lesser degree than one might think - the "effective" classical theory is accurate for many purposes. Here we only sketch the few formulas that we will need. Note that, in particular, you are not required to solve the Schrodinger equation below.

The abstract formulation of quantum mechanics is that of a "complex inner product space" which has the following ingredients

- Scalars α, β are complex numbers
- Vectors ϕ, ψ represent the state of the system at a given time, in a possibly infinite dimensional space V (sometimes denoted H for Hilbert space). The operations are
  - Addition $\phi + \psi \in V$
  - Multiplication by a scalar $\alpha V \in V$
  - Inner ("dot") product $\langle \phi | \psi \rangle \in \mathbb{C}$ is conjugate symmetric, linear in the second argument, positive and non-degenerate:

$$\begin{aligned} \langle \phi | \psi \rangle &= \langle \psi | \phi \rangle^* \\ \langle \phi | \alpha_1 \psi_1 + \alpha_2 \psi_2 \rangle &= \alpha_1 \langle \phi | \psi_1 \rangle + \alpha_2 \langle \phi | \psi_2 \rangle \\ \langle \psi | \psi \rangle &> 0 \qquad (\text{except } \psi = 0) \\ \langle \phi | \psi \rangle &= 0 \quad \forall \psi \Rightarrow \phi = 0 \end{aligned}$$

where the star indicates complex conjugation. The wave function is usually normalised:

$$\langle \psi | \psi \rangle = 1$$

Remark: $\sqrt{\langle \psi | \psi \rangle}$ is a norm, which then permits notions of limits and derivatives, etc.

- Operators $\hat{A}$ represent observables, satisfying
$$\begin{aligned} \hat{A}(\alpha_1\psi_1+\alpha_2\psi_2) &= \alpha_1\hat{A}\psi_1+\alpha_2\hat{A}\psi_2 \qquad \text{linear} \\ \langle\hat{A}\phi|\psi\rangle &= \langle\phi|\hat{A}\psi\rangle \qquad \text{Hermitian} \end{aligned}$$
  We can define addition and multiplication of operators by
$$\begin{aligned} (\hat{A}+\hat{B})\psi &= \hat{A}\psi+\hat{B}\psi \\ (\hat{A}\hat{B})\psi &= \hat{A}(\hat{B}\psi) \end{aligned}$$
  Note that the sum and product of Hermitian operators is Hermitian, and that the product is associative but not necessarily commutative. The Hermitian property also implies that an orthonormal set of eigenvectors can be found, and that the eigenvalues are real. A measurement of a state gives a random result, with expectation value $\langle\psi|\hat{A}\psi\rangle$, which is easily shown to be a real number, equal to the eigenvalue if ψ is an eigenvector of $\hat{A}$.

Hamilton's equations of motion are replaced by the Schrodinger equation for the wave function $\Psi(t)\in V$
$$\hat{H}\Psi=-\frac{h}{2\pi i}\frac{\partial\Psi}{\partial t}$$
$i=\sqrt{-1}$ and $h=2\pi\hbar$ is Planck's constant. We assume the Hamiltonian operator $\hat{H}$ is not a function of time, and we can separate variables to get the general solution
$$\Psi(t)=\sum_n a_n e^{-2\pi i E_n t/h}\psi_n$$
where a_n are arbitrary complex coefficients and
$$\hat{H}\psi_n=E_n\psi_n$$
is called the time-independent Schrodinger equation; it is an eigenvalue equation for the linear operator $\hat{H}$, and the E_n are the energies of the quantum states ψ_n. We also assume that the energy eigenvectors ψ_n form a complete set, ie any wave function can be written as a linear combination of them.

Given a classical Hamiltonian function $H(\mathbf{q},\mathbf{p})$ we can "quantize" it, ie specify a corresponding quantum system, in which the vector space is the set of complex valued functions on the configuration space, ie $\Psi(\mathbf{q},t)\in\mathbb{C}$ with the usual inner product
$$\langle\phi|\psi\rangle=\int\phi^*(\mathbf{q})\psi(\mathbf{q})d^{3N}q$$
The Hamiltonian operator is
$$\hat{H}\psi=H(\hat{\mathbf{q}},\hat{\mathbf{p}})\psi$$
where $\hat{\mathbf{q}}$ and $\hat{\mathbf{p}}$ are Hermitian linear operators defined by
$$\hat{\mathbf{q}}\psi(\mathbf{q})=\mathbf{q}\psi(\mathbf{q})$$
$$\hat{\mathbf{p}}\psi(\mathbf{q})=\frac{h}{2\pi i}\nabla_q\psi(\mathbf{q})$$
The operators $\hat{\mathbf{q}}$ and $\hat{\mathbf{p}}$ do not commute, but for Hamiltonians of the form kinetic plus potential energy there is no ordering ambiguity. The quantum expectation of the operator $\hat{\mathbf{q}}$ shows that the probability density for finding the system at configuration point $\mathbf{q}$ is $|\psi(\mathbf{q})|^2$.

Where the potential energy grows at infinity (ie the surfaces of constant energy have finite volume) there are a discrete set of allowed energy eigenvalues $-\infty<E_0\leq E_1\leq\ldots$. Equality indicates that the eigenvalue is degenerate; we will count this as a separate energy level, and not explicitly indicate the degeneracy in sums over levels. The classical and quantum dynamics are connected by a result called Weyl's law, which says that the number of states up to energy E is related to the classical phase space volume by
$$\sum_{n:E_n<E}1\sim\frac{1}{h^{3N}}\int_{H(\mathbf{x})<E)}d\mathbf{x}$$
where $\sim$ means the ratio approaches 1 in the limit $E\to\infty$. Effectively, each quantum state corresponds to a phase space volume of h^{3N}. The vector space is thus effectively finite dimensional.

Example: A free particle in one dimension. The Hamiltonian is
$$\hat{H}=\frac{\hat{p}^2}{2m}=\frac{1}{2m}\left(\frac{h}{2\pi i}\right)^2\frac{\partial}{\partial q}$$
The eigenvectors of this are exponentials
$$\psi_\lambda(q)=e^{2\pi i q/\lambda}$$
which have wavelength (spatial period) λ momentum $p=h/\lambda$, and energy $E=p^2/2m=h^2/(2m\lambda^2)$. The solution of the original time-dependent Schrodinger equation is then a wave
$$\Psi_k(q,t)=e^{2\pi i(q/\lambda-ft)}=e^{2\pi i(q-wt)/\lambda}$$
with frequency $f=E/h$ and wave velocity $w=f\lambda=E/p$.

Remark: The relation $w=f\lambda$ is completely general for waves. The relations $E=hf$ and $p=h/\lambda$ follow from Schrodinger's equation and the momentum operator respectively, and so are completely general in quantum mechanics. The classical velocity of the above particle $v=p/m$ is not equal to the wave velocity $w=E/p=p/2m$. Actually we can add a constant to the energy, which will change the wave frequency and velocity but not affect the physics.

Remark: In relativity there are different relations between E,p,v,m, and there is no freedom to add a constant to the energy. In particular for light we have $v=c$ ($c=299792458ms^{-1}$ constant speed of light), $E=pc$ and $m=0$. Thus $w=E/p=c=v$.

Remark: We do not have a Weyl theorem since the phase space volume is infinite. In particular the energy states are continuous, and the wave function is not normalisable.

Example: A free particle in a cubic box of side length L. The classical Hamiltonian is just

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{q})$$

where the potential energy $V(\mathbf{q})$ is zero inside the box and infinite outside. The quantum version is thus

$$\hat{H}\psi(q_1,q_2,q_3) = \left[\frac{1}{2m}\frac{h^2}{(2\pi i)^2}\nabla^2 + V(\mathbf{q})\right]\psi(q_1,q_2,q_3)$$

The effect of the infinite potential energy is to enforce the condition $\psi = 0$ at the boundary. The solution of the eigenvalue equation is

$$\begin{aligned}\psi(q_1,q_2,q_3) &= \left(\frac{2}{L}\right)^{3/2}\sin(n_1\pi q_1/L) \\ &\quad\times\sin(n_2\pi q_2/L)\sin(n_3\pi q_3/L) \\ E &= (l_1^2+l_2^2+l_3^2)\frac{h^2}{8mL^2}\end{aligned}$$

with $l_i = 1,2,3,\ldots$ the discrete "quantum numbers" defining the state.

Example: N non-interacting particles, given the solution to the 1-particle eigenvalue problem, $\phi_j(\mathbf{q})$ with energies ϵ_j.

We have

$$\hat{H} = \sum_{j=1}^{N}\hat{H}_j$$

with each $\hat{H}_j$ identical except that it acts on a different particle. Thus any product of 1-particle solutions is a solution:

$$\psi(\mathbf{q}) = \prod_{k=1}^{N}\phi_{j_k}(\mathbf{q}_k), \qquad E = \sum_{k=1}^{N}\epsilon_{j_k}$$

where j_k is the 1-particle state j corresponding to the particle k. It is often useful to ask how many particles are in each 1-particle state, ie

$$n_l = \sum_{k=1}^{N}\delta_{l,j_k}$$

$$N = \sum_{j=1}^{\infty}n_j$$

$$E = \sum_{j=1}^{\infty}n_j\epsilon_j$$

This is not the full story, see spin below.

We can use these examples to check Weyl's law. Consider an ideal gas of N particles of mass m confined to a cubical box of side length L. In the classical case the energy is a function only of momentum, so we do the configuration integral directly (here q_i, $i = 1\ldots 3N$ are components of position, since all components are equivalent):

$$\int d^{3N}q = L^{3N}$$

and the momentum integral is the volume of a $3N$-dimensional sphere of radius $\sqrt{2mE}$:

$$\int_{\mathbf{p}^2/2m<E} d^{3N}p = V_{3N}(\sqrt{2mE})^{3N}$$

with the constant V_{3N} as before. The quantum system has wavefunctions of the form

$$\psi(\mathbf{x}) = \phi_{l_1}(q_1)\phi_{l_2}(q_2)\ldots\phi_{l_{3N}}(q_{3N})$$

where the $\phi_n(q)$ satisfy the 1D free Schrodinger equation The total energy of the state ψ is

$$E = \frac{h^2}{8mL^2}\sum_{j=1}^{3N}l_j^2$$

which are just the squares of distances to the origin of a $3N$-dimensional lattice. Those with energy less than E form the part of a sphere of radius $\sqrt{8mEL^2/h^2}$ with all coordinates positive, thus approximating the volume

$$\frac{V_{3N}}{2^{3N}}\left(\frac{8mEL^2}{h^2}\right)^{3N/2} = V_{3N}(2mE)^{3N/2}\frac{L^{3N}}{h^{3N}}$$

which gives Weyl's law.

4.2 Spin and statistics

Quantum systems can also have effects that do not show up in the classical dynamics, ie are not the quantizations of a classical system. The most important of these is "spin" which mathematically comes from possible transformation laws ("irreducible representations") under the rotation group. The spin J of a particle can take half-integer non-negative values $0, 1/2, 1, \ldots$. It has two effects - expanding the single particle configuration space to $(\mathbf{q}, s)$ where $s = \{-J, -J+1, \ldots, J\}$ and (in the absence of other quantum effects) much extra degeneracy in the energy spectrum; and defining the symmetry of a many-particle wavefunction.

Classically, a system containing identical particles is symmetric with respect to interchange of particles:

$$\begin{aligned}&H(\ldots,\mathbf{q}_j,\ldots,\mathbf{q}_k,\ldots,\mathbf{p}_j,\ldots,\mathbf{p}_k,\ldots) \\ =\ &H(\ldots,\mathbf{q}_k,\ldots,\mathbf{q}_j,\ldots,\mathbf{p}_k,\ldots,\mathbf{p}_j,\ldots)\end{aligned}$$

Since phase space points obtained by exchanging identical particles are physically equivalent, the probability density $\rho(\mathbf{x})$ can be assumed to be symmetric with respect to particle exchange

$$\begin{aligned}&\rho(\ldots,\mathbf{q}_j,\ldots,\mathbf{q}_k,\ldots,\mathbf{p}_j,\ldots,\mathbf{p}_k,\ldots) \\ =\ &\rho(\ldots,\mathbf{q}_k,\ldots,\mathbf{q}_j,\ldots,\mathbf{p}_k,\ldots,\mathbf{p}_j,\ldots)\end{aligned}$$

The reduced phase space has total volume smaller by a factor $N!$. This symmetry also implies that given a solution of the Schrodinger equation

$$\Psi(\ldots,\mathbf{q}_j,\ldots,\mathbf{q}_k,\ldots,t)$$

then

$$\epsilon\Psi(\ldots,\mathbf{q}_k,\ldots,\mathbf{q}_j,\ldots,t)$$

for any constant ϵ is also a solution. Quantum mechanics insists on only a single solution, however, by enforcing the condition that these are equal (for interchange of any two particles), where $\epsilon = 1$ corresponds to particles with integer spin J (called bosons) and $\epsilon = -1$ corresponds to particles with half-integer spin (called fermions). Other values of ϵ would produce a factor after two exchanges, which is inconsistent (in three dimensions). Electrons, protons and neutrons all have spin 1/2, atoms are bosons (fermions) if they have an even (odd) number of these constituents, respectively. Photons (particles of light) have zero mass and spin 1; they satisfy a different wave equation and have 2 (rather than $2J+1=3$) spin states, which are called polarizations.

Example: The Schrodinger equation for three identical particles has a solution of the form

$$\psi(\mathbf{q}_1,s_1,\mathbf{q}_2,s_2,\mathbf{q}_3,s_3)$$

Write down the relevant wave function, taking account of the (anti)-symmetry. The solution is a sum over permutations with a minus sign for odd permutations in the case of fermions:

$$\frac{1}{C}\{[\psi(1,2,3)+\psi(2,3,1)+\psi(3,1,2)] \\ +\epsilon[\psi(3,2,1)+\psi(2,1,3)+\psi(1,3,2)]\}$$

The normalisation C cannot be evaluated explicitly, since we have no knowledge of the relevant inner products.

If, however, the particles are non-interacting, we have

$$\psi = \prod_k \phi_{j_k}(\mathbf{q}_k,s_k)$$

If the particles are fermions then they must all be in different states, otherwise the antisymmetry would lead to complete cancellation. Since the states are orthonormal, we conclude the the normalisation factor is $C=\sqrt{6}$.

If the particles are bosons we have a few cases to consider. All particles could be in the same state j, ie $n_j = 3$. The state is thus

$$\frac{6}{C}\phi_j(1)\phi_j(2)\phi_j(3)$$

and the normalisation is $C = 6$. We could have two particles in state j and one in state l, ie $n_j = 2, n_l = 1$. The state is thus

$$\frac{2}{C}[\phi_j(1)\phi_j(2)\phi_l(3)+\phi_j(2)\phi_j(3)\phi_l(1)+\phi_j(3)\phi_j(1)\phi_l(2)]$$

and the normalisation is $C = 2\sqrt{3}$. If all particles are in different states, the normalisation is $C=\sqrt{6}$ as in the fermion case.

In general we have the (anti)-symmetrised state

$$\psi_{A/S} = (N!\prod n_j!)^{-1/2}\sum_P \epsilon_P \prod_k \phi_{j_k}(\mathbf{q}_{Pk},s_{Pk})$$

where the normalisation factor generalises this example, P stands for permutations, and ϵ_P is -1 for fermions and odd permutations, $+1$ otherwise. In the case of fermions, we must have $n_j \in \{0,1\}$.

Example: Write down a fully (anti-)symmetrised state for a system of five non-interacting particles in which three particles in a single-particle state $j=1$ and two particles in a state $j=2$.

Note that because there is more than one particle per state, the particles must be bosons, hence all the wavefunctions are included with a positive sign. We have $N=5$, $n_1=3$, $n_2=2$ so the normalisation prefactor in this case is

$$(N!\prod n_j!)^{-1/2} = \frac{1}{\sqrt{5!3!2!}} = \frac{\sqrt{10}}{120}$$

If we write $\phi_j(1)$ for $\phi_j(\mathbf{q}_1,s_1)$ for brevity, and note that the $5! = 120$ permutations group into 10 terms, we have

$$\psi_{A/S} = \frac{1}{\sqrt{10}}\times \\ [\phi_1(1)\phi_1(2)\phi_1(3)\phi_2(4)\phi_2(5)+\phi_1(1)\phi_1(2)\phi_1(4)\phi_2(3)\phi_2(5) \\ +\phi_1(1)\phi_1(2)\phi_1(5)\phi_2(3)\phi_2(4)+\phi_1(1)\phi_1(3)\phi_1(4)\phi_2(2)\phi_2(5) \\ +\phi_1(1)\phi_1(3)\phi_1(5)\phi_2(2)\phi_2(4)+\phi_1(1)\phi_1(4)\phi_1(5)\phi_2(2)\phi_2(3) \\ +\phi_1(2)\phi_1(3)\phi_1(4)\phi_2(1)\phi_2(5)+\phi_1(2)\phi_1(3)\phi_1(5)\phi_2(1)\phi_2(4) \\ +\phi_1(2)\phi_1(4)\phi_1(5)\phi_2(1)\phi_2(3)+\phi_1(3)\phi_1(4)\phi_1(5)\phi_2(1)\phi_2(2)]$$

We can now adjust Weyl's law to account for quantum statistics. The spin degrees of freedom give an extra factor $(2J+1)^N$ to the classical phase space density. For fermions and in the "classical" regime, ie phase space per particle much larger than h^{3N}, $n_j = 0,1$, so the classical $N!$ is reproduced. Note that Weyl's formula for the full system only applies at high energy (classical regime) anyway. However we can use Weyl's formula for 1-particle states, together with correct fermionic or bosonic statistics to treat ideal systems in the quantum regime.

In the classical limit, we can ignore the (anti)-symmetrisation and use the product state, with a factor $N!$ put in by hand. This turns out to be simpler, and a good approximation since the particles are well separated in phase space and quantum interference effects (see below) are rare.

All this is summarized in table 3.

Statistics	n_j
Bose-Einstein	Unbounded
Fermi-Dirac	0 or 1
Maxwell-Boltzmann	Average $\ll 1$

Table 3: The occupation number (particles per state) is limited to 1 for fermions by the antisymmetry of the wave function. Classical (MB) statistics are valid only in the limit of occupation number much less than 1.

4.3 Quantum ensembles

There are two distinct notions of probability in quantum statistical mechanics. A quantum state has intrinsic uncertainty, for example we saw that the probability density of finding a system at a given point in configuration space above is $|\psi(\mathbf{q})|^2$. Thus the outcome of a measurement may not be known even if we know the state with certainty. An exception to this is that for an eigenstate (eg of energy) the relevant observable is fixed exactly. Also, interference experiments add two states together, but this probability density is not additive - such interference can be constructive (greater than the sum of the individual probabilities) or destructive (less).

We are concerned with the situation in which we do not even know what state the system is in; all we have is a set of probabilities that the system will be in a particular state. The latter obeys the classical rules of probability, and is superimposed on any intrinsic quantum uncertainty. We say that the state of the system is "mixed", a combination of exactly specified "pure" states. Thus we write for some observable $\hat{f}$

$$\langle \hat{f} \rangle = \sum_k \rho_k \langle \psi_k | \hat{f} \psi_k \rangle$$

where ψ_k is an arbitrary set of (pure) states, and

$$\sum_k \rho_k = 1$$

Now we expand in an orthonormal basis (typically the energy eigenstates) ϕ_j,

$$\psi_k = \sum_j a_{kj} \phi_j \qquad a_{kj} = \langle \phi_j | \psi_k \rangle$$

and find

$$\begin{aligned} \langle \hat{f} \rangle &= \sum_{jkl} \rho_k \langle \phi_j | \psi_k \rangle^* \langle \phi_l | \psi_k \rangle \langle \phi_j | \hat{f} \phi_l \rangle \\ &= \sum_{jkl} \rho_k \langle \phi_l | \psi_k \rangle \langle \psi_k | \phi_j \rangle \langle \phi_j | \hat{f} \phi_l \rangle \\ &= \sum_{jl} \hat{\rho}_{lj} \hat{f}_{jl} \\ &= \mathrm{tr}(\hat{\rho} \hat{f}) \end{aligned}$$

where the matrix elements of an operator $\hat{A}$ are

$$\hat{A}_{jl} = \langle \phi_j | \hat{A} \phi_l \rangle$$

the density operator $\hat{\rho}$ is the weighted sum of projection operators

$$\hat{\rho} = \sum_k \rho_k | \psi_k \rangle \langle \psi_k |$$

and tr denotes trace, ie a sum of the diagonal matrix elements.

The weighting in quantum statistical mechanics is the same as classically, so we have for the microcanonical ensemble

$$\rho_k = \begin{cases} 1/\Omega & E_k \in [E, E+\delta] \\ 0 & \text{otherwise} \end{cases}$$

$$\hat{\rho} = \frac{\delta(\hat{H} - E\hat{1})}{\mathrm{tr}[\delta(\hat{H} - E\hat{1})]}$$

the latter is rather pathological. For the canonical ensemble

$$\rho_k = \frac{e^{-\beta E_k}}{\sum_k e^{-\beta E_k}}$$

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\mathrm{tr} e^{-\beta \hat{H}}}$$

where exp is defined using the Taylor series, and the trace in the denominator is the partition function:

$$Z(N, V, T) = \sum_k e^{-\beta E_k} = \mathrm{tr}(e^{\beta \hat{H}})$$

Expectation values are:

$$\langle \hat{f} \rangle = \frac{\mathrm{tr}(e^{-\beta \hat{H}} \hat{f})}{\mathrm{tr}(e^{-\beta \hat{H}})}$$

and the entropy is

$$S = \langle -k \ln \hat{\rho} \rangle = -k \mathrm{tr}(\hat{\rho} \ln \hat{\rho})$$

where the logarithm is the inverse of the exponential operation. All the equations we used in the classical case, eg

$$E = -\frac{\partial}{\partial \beta} \ln Z(N, V, T)$$

remain true. For the grand canonical ensemble we have

$$\rho_k = \frac{e^{-\beta(E_k - \mu N)}}{\sum_{k,N} e^{-\beta(E_k - \mu N)}}$$

$$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\mathrm{tr}[e^{-\beta(\hat{H} - \mu \hat{N})}]}$$

$$\mathcal{Z} = \sum_{k,N} e^{-\beta(E_k - \mu N)} = \mathrm{tr}(e^{-\beta(\hat{H} - \mu \hat{N})})$$

where $\hat{N}$ is the operator for which the eigenvalue is the number of particles where this is definite; our space is now the direct sum of the spaces for fixed particle number.

Example: Show that $\langle \hat{1} \rangle = 1$ for the density matrix expectations, where $\hat{1}$ is the identity operator.

Solution:

$$\begin{aligned} \langle \hat{1} \rangle &= \mathrm{tr}(\hat{\rho} \hat{1}) \\ &= \mathrm{tr}(\hat{\rho}) \\ &= \sum_j \langle \phi_j | \hat{\rho} | \phi_j \rangle \\ &= \sum_{jk} \rho_k \langle \phi_j | \psi_k \rangle \langle \psi_k | \phi_j \rangle \\ &= \sum_{jk} \rho_k \langle \psi_k | a_{kj} \phi_j \rangle \\ &= \sum_k \rho_k \langle \psi_k | \psi_k \rangle \\ &= \sum_k \rho_k \\ &= 1 \end{aligned}$$

4.4 GCE for ideal quantum systems

Just as in the classical case, it turns out that the grand canonical ensemble is the easiest for calculations in the quantum case. As above, we represent the states in terms of occupation numbers $\{n_j\}$, ie there are n_j particles in 1-particle state j. Then we have

$$N = \sum_j n_j$$

$$E = \sum_j n_j \epsilon_j$$

In the grand canonical ensemble we need to sum both over N and j; this is achieved by summing over $\{n_j\}$ without having to fix either of the above equations as a constraint. Thus

$$\mathcal{Z}(\mu, V, \beta) = \sum_{\{n_j\}} e^{-\beta \sum_j n_j(\epsilon_j - \mu)}$$

is valid for both Bose-Einstein (BE) and Fermi-Dirac (FD) statistics, if in the latter we sum only over $n_j = 0, 1$. In the case of classical Maxwell-Boltzmann (MB) statistics we do not (anti-)symmetrise, so each set of occupation numbers corresponds to $N!/\prod_j n_j!$ states; we include the $N!$ Gibbs factor by hand, and obtain a formula for all three cases

$$\mathcal{Z}(\mu, V, \beta) = \sum_{\{n_j\}} g\{n_j\} e^{-\beta \sum_j n_j(\epsilon_j - \mu)}$$

where the "statistical weight" $g\{n_j\}$ is given by

$$g\{n_j\} = \begin{cases} 1 & \text{BE} \\ 1 & \text{FD with all } n_j\text{=0,1; zero otherwise} \\ \prod_j n_j!^{-1} & \text{MB} \end{cases}$$

Now the exponential of a sum is a product of exponentials. We find

$$\begin{aligned} \mathcal{Z}_{BE} &= \sum_{n_1, n_2, \ldots = 0}^{\infty} \prod_j e^{-\beta n_j(\epsilon_j - \mu)} \\ &= \prod_j \sum_{n=0}^{\infty} e^{-\beta n(\epsilon_j - \mu)} \\ &= \prod_j \frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}} \end{aligned}$$

summing the geometric series. Similarly

$$\begin{aligned} \mathcal{Z}_{FD} &= \sum_{n_1, n_2, \ldots = 0}^{1} \prod_j e^{-\beta n_j(\epsilon_j - \mu)} \\ &= \prod_j \sum_{n=0}^{1} e^{-\beta n(\epsilon_j - \mu)} \\ &= \prod_j [1 + e^{-\beta(\epsilon_j - \mu)}] \end{aligned}$$

We can also do the Maxwell-Boltzmann case:

$$\begin{aligned} \mathcal{Z}_{MB} &= \sum_{n_1, n_2, \ldots = 0}^{\infty} \frac{1}{n_1! n_2! \ldots} \prod_j e^{-\beta n_j(\epsilon_j - \mu)} \\ &= \prod_j \sum_{n=0}^{\infty} \frac{1}{n!} e^{-\beta n(\epsilon_j - \mu)} \\ &= \prod_j \exp(\exp(-\beta(\epsilon_j - \mu))) \end{aligned}$$

To compute thermodynamic state variables we use the classical formulas, including

$$\frac{pV}{kT} = \ln \mathcal{Z} = \frac{1}{a} \sum_j \ln(1 + a e^{-\beta(\epsilon_j - \mu)})$$

where

$$a = \begin{cases} -1 & BE \\ 0 & MB \\ 1 & FD \end{cases}$$

where $a = 0$ is understood as the limit. Then we have for example

$$N(\mu, V, \beta) = kT \frac{\partial}{\partial \mu} \ln \mathcal{Z} \Big|_{T,V} = \sum_j \frac{1}{e^{\beta(\epsilon_j - \mu)} + a}$$

$$E(\mu, V, \beta) = -kT \frac{\partial}{\partial \beta} \ln \mathcal{Z} \Big|_{z,V} = \sum_j \frac{\epsilon_j}{e^{\beta(\epsilon_j - \mu)} + a}$$

Notice that for the energy, the derivative is at constant $z = e^{\beta\mu}$. These expressions are very suggestive - it looks like the average occupation number of a state j is given in general by

$$\frac{1}{e^{\beta(\epsilon_j - \mu)} + a}$$

In fact this is easy to show: first observe that

$$\langle n_j \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_j} \ln \mathcal{Z} \Big|_{z, V, \epsilon_{l \neq j}}$$

then differentiate.

We can easily sketch $\langle n_j \rangle$ as a function of $\beta(\epsilon_j - \mu)$, ie the difference in energies between the level and the chemical potential, normalised by the temperature. It decreases exponentially for positive argument in all cases. For FD it approaches 1 at large negative argument, for MB it increases exponentially and for BE it diverges at zero. This means that the chemical potential of a Bose system is always less than the lowest energy level.

4.5 Bose and Fermi integrals

We will apply the preceding theory to a number of examples. However converting the above sums to integrals using Weyl's law we obtain some special functions that need to be discussed first. These integrals are of the form

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1} dx}{z^{-1} e^x - 1}$$

$$f_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}dx}{z^{-1}e^x+1}$$

where clearly x is $\beta\epsilon$, z is fugacity, $g_n(z)$ with $0 \leq z \leq 1$ is for the Bose case and $f_n(z)$ with $z \geq 0$ is for the Fermi case. They are really two sides of the same function, $f_n(z) = -g_n(-z)$, so we can treat them both together.

Expanding the first integrand as a geometric series we find

$$\begin{aligned} g_n(z) &= \frac{1}{\Gamma(n)}\sum_{k=1}^\infty z^k \int_0^\infty x^{n-1}e^{-kx}dx \\ &= \frac{1}{\Gamma(n)}\sum_{k=1}^\infty \frac{z^k}{k^n}\int_0^\infty y^{n-1}e^{-y}dy \\ &= \sum_{k=1}^\infty \frac{z^k}{k^n} \end{aligned}$$

Similarly

$$f_n(z) = \sum_{k=1}^\infty (-1)^{k-1}\frac{z^k}{k^n}$$

The g function is clearly increasing in z and decreasing in n. The series converges for $z < 1$, diverges for $z > 1$, and at $z = 1$ it is

$$g_n(1) = \zeta(n)$$

the Riemann zeta function, convergent for $n > 1$. Exact values are $\zeta(1) = \infty$, $\zeta(2) = \pi^2/6 \approx 1.645$, $\zeta(4) = \pi^4/90 \approx 1.082$. We can also express $f_n(1)$ in terms of the ζ function. We split it into odd and even terms

$$f_n(1) = \sum_{k=1}^\infty \frac{(-1)^{k+1}}{k^n} = \zeta_o(n) - \zeta_e(n)$$

while

$$\zeta(n) = \zeta_o(n) + \zeta_e(n)$$

However the even integers are just twice all the integers, so

$$\zeta_e(n) = \frac{\zeta(n)}{2^n}$$

so substituting and solving for ζ_o we find

$$\zeta_o(n) = (1-2^{-n})\zeta(n)$$

$$f_n(1) = (1-2^{1-n})\zeta(n)$$

From the sum we can recognise particular values of n (although for $n = 0$ the integral diverges):

$$g_0(z) = \frac{z}{1-z} \qquad f_0(z) = \frac{z}{1+z}$$

$$g_1(z) = -\ln(1-z) \qquad f_1(z) = \ln(1+z)$$

so $g_n(z)$ is often denoted $Li_n(z)$ and called a polylogarithm. Finally, the derivatives can be expressed in terms of the same functions. Differentiating the series yields

$$\frac{\partial}{\partial z}g_n(z) = \frac{1}{z}g_{n-1}(z)$$

$$\frac{\partial}{\partial z}f_n(z) = \frac{1}{z}f_{n-1}(z)$$

The integral expression shows immediately that $f_n(z)$ is positive, and this shows that its derivative is also positive.

4.6 Blackbody radiation

Blackbody radiation is the gas of photons in equilibrium with any object at nonzero temperature. Photons (particles of light) are massless bosons with two spin states (polarisations) that can be created or destroyed consistent with conservation of energy or momentum. Being massless, they move at a fixed speed $c = 299792458ms^{-1}$ and have energy

$$E = hf = \frac{hc}{\lambda} = |\mathbf{p}|c$$

where f is the frequency, λ is wavelength and c is the speed of light as discussed previously. Since N is not conserved, there is no chemical potential, or in terms of the above formalism, $\mu = 0, z = 1$.

We use Weyl's law to replace the sum over 1-particle states by an integral over energy:

$$\sum = 2\int \frac{d^3qd^3p}{h^3} = \frac{8\pi V}{h^3}\int_0^\infty p^2dp = \frac{8\pi V}{h^3c^3}\int_0^\infty \epsilon^2 d\epsilon$$

which corresponds to a 1-particle density of states $g(\epsilon) = 8\pi V\epsilon^2/h^3c^3$. The "2" comes from the two spin/polarisation states of the photon. Thus we have

$$\begin{aligned} \frac{pV}{kT} = \ln \mathcal{Z} &= -\frac{8\pi V}{h^3c^3}\int_0^\infty \ln(1-e^{-\beta\epsilon})\epsilon^2 d\epsilon \\ &= \frac{8\pi V}{h^3c^3}\frac{\beta}{3}\int_0^\infty \frac{\epsilon^3 d\epsilon}{e^{\beta\epsilon}-1} \end{aligned}$$

integrating by parts. Similarly we have

$$N = \frac{8\pi V}{h^3c^3}\int_0^\infty \frac{\epsilon^2 d\epsilon}{e^{\beta\epsilon}-1}$$

$$E = \frac{8\pi V}{h^3c^3}\int_0^\infty \frac{\epsilon^3 d\epsilon}{e^{\beta\epsilon}-1}$$

In terms of the previously calculated integrals we have

$$\frac{E}{V} = 3p = \frac{48\pi(kT)^4}{(hc)^3}g_4(1) = \frac{48\pi(kT)^4}{(hc)^3}\frac{\pi^4}{90}$$

$$\frac{N}{V} = \frac{16\pi(kT)^3}{(hc)^3}g_3(1) = \frac{16\pi(kT)^3}{(hc)^3}\zeta(3)$$

Now since $\mu = 0$ we have

$$E = TS - pV + \mu N$$

so

$$\frac{S}{V} = \frac{E}{VT} + \frac{p}{T} = \frac{64\pi^5}{90h^3c^3}(kT)^3k$$

and the adiabatic law (constant entropy) is

$$VT^3 = \text{const}, \qquad pT^{-4} = \text{const}, \qquad pV^{4/3} = \text{const}$$

We actually have information not just on the total number N but the number in each energy interval.

$$dN(\epsilon) = \frac{8\pi V}{h^3c^3}\frac{\epsilon^2 d\epsilon}{e^{\beta\epsilon}-1}$$

or in terms of the frequency of the photons $f = \epsilon/h$

$$dn(f) = \frac{8\pi}{c^3}\frac{f^2 df}{e^{\beta hf}-1}$$

where $n = N/V$ is the number density. Suppose the light escapes through a small hole. We have from problem 6.5 that the number of particles escaping per unit area per unit time is

$$R = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Now N/V is known for each frequency interval, and $\langle v\rangle = c$, so

$$R(f) = \frac{2\pi}{c^2}\frac{f^2}{e^{\beta hf}-1}$$

and the power flux density, ie energy per unit area, time and frequency interval is

$$Q_{black}(f) = hfR(f) = \frac{2\pi h}{c^2}\frac{f^3}{e^{\beta hf}-1}$$

This is called Planck's radiation formula. The maximum power flux is obtained by differentiating this and setting it equal to zero:

$$e^{\beta hf}(3-\beta hf) - 3 = 0$$

which has solution approximately

$$hf_{max} \approx 2.821kT$$

ie proportional to temperature. The total power flux is

$$\int_0^\infty hfR(f)df = \frac{2\pi(kT)^4}{h^3c^2}\int_0^\infty \frac{x^3dx}{e^x-1}$$

substituting $x = \beta hf$. The integral is $\Gamma(4)g_4(1) = 6\zeta(4) = \pi^4/15$. Thus the total flux is

$$Q_{tot} = \sigma T^4 \qquad \sigma = \frac{2\pi^5k^4}{15h^3c^2} = 5.67\times 10^{-8}Wm^{-2}K^{-4}$$

which is called the Stefan-Boltzmann law.

Suppose we have a surface that absorbs a fraction A of the light hitting it. It is in equilibrium with light radiation at temperature T. The surface absorbs an amount $A\sigma T^4$ per unit area, and so it must emit this much to remain in equilibrium. We could put a barrier between the light and the surface, which transmits radiation at a certain frequency and reflects all other radiation. Thus the thermal radiation is in general

$$Q(\omega,T) = A(\omega,T)Q_{black}(\omega,T)$$

where for "black" objects $A = 1$ the power flux is as we computed above, hence the term black body radiation.

Temp(K)	Example	EM spectrum
10^9	Fusion reactor	Gamma radiation
6000	The sun	Visible
300	Room temperature	Infra-red
3	Cosmic background	Microwave

Table 4: Examples of frequency-temperature relation

Properties of the Planck radiation formula: As we saw above, the frequency of maximum intensity is proportional to temperature. In practice this corresponds to the ranges shown in table 4. Also,

$$Q_{black}(f) \sim f^2 \qquad f\to 0$$

$$Q_{black}(f) \sim e^{-hf/kT} \qquad f\to\infty$$

$$\frac{\partial}{\partial T}Q_{black}(f) = \frac{2\pi h^2 f^4}{kc^2T^2}\frac{e^{hf/kT}}{(e^{hf/kT}-1)^2} > 0$$

Example: Temperature of the Earth. The sun, radius R_S and temperature T_S emits blackbody radiation, with total power $4\pi R_S^2\sigma T_S^4$. At the Earth's orbit (radius D_E) the power per unit area is $(R_S/D_E)^2\sigma T_S^4$ and is absorbed by the Earth of radius R_E and cross-sectional area πR_E^2. Thus the total power absorbed by the Earth is $A_E\sigma T_S^4\pi(R_SR_E/D_E)^2$. The Earth in turn radiates an amount $4\pi A_ER_E^2\sigma T_E^4$. For equilibrium we need

$$T_E^4 = \frac{1}{4}\frac{R_S^2}{D_E^2}T_S^4$$

Putting the numbers in: $T_S = 6000K$, $R_S = 7\times 10^8m$, $D_S = 1.5\times 10^{11}m$ we find

$$T_E = 290K$$

which is not far wrong. In fact the absorption coefficient does not cancel, since the Earth receives radiation mostly in the visible region of the spectrum, but emits it in the infrared. The greenhouse effect is due to absorption of infrared in the atmosphere, which reduces emission from the surface but has little effect on the incoming light.

Example: Efficiency of incandescent lights. The element receives virtually all of the electrical energy, however it emits throughout the spectrum, not just in the visible range. The efficiency is then

$$\eta = \frac{\int_{f_{min}}^{f_{max}} Q_{black}(f)df}{\int_0^\infty Q_{black}(f)df}$$

Now the integral is difficult analytically; we can solve it numerically, or since the threshold of the visible range is high compared to the temperature, ignore the 1. We find, integrating by parts three times and using the exact formula (with the 1) for the denominator as above,

$$\frac{\int_x^\infty}{\int_0^\infty} \approx \frac{15}{\pi^4}e^{-x}(x^3+3x^2+6x+6)$$

with

$$x = \beta hf = \frac{hc}{\lambda kT} \frac{14390 K\mu m}{\lambda T}$$

The limits of visible light are about $\lambda = 0.7\mu m$ for red and $\lambda = 0.4\mu m$ for violet. Incandescent lights are limited by the melting point of tungsten at about $3500K$. If we substitute this above we find

$$\eta(3500) = 0.15$$

$$\eta(2500) = 0.03$$

The remaining energy is emitted as invisible infrared, which we feel as "heat". Other effects: it is not exactly black body radiation, the brightness perceived by the eye is wavelength dependent. Efficiency can be improved by increasing the temperature (up to the melting point of tungsten) at the expense of shorter life, and by a coating which reflects back some of the infrared.

4.7 Bose-Einstein condensation

Now we turn to the non-relativistic Bose gas, which is relevant to clusters of trapped atoms, superfluid helium and pairs of electrons in "normal" superconductors; however the behaviour in all of these is modified by the presence of interactions. We start from the partition function

$$\ln \mathcal{Z}(z, V, T) = -\sum_j \ln(1 - z\exp(-\beta\epsilon_j))$$

from which comes the average occupation numbers of single-particle states

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}$$

and notice as before that this diverges for $\mu = \epsilon_j$. This has two effects: firstly that $\mu \leq 0$ always, and that the lowest state of (almost) zero energy can have such a large occupation number that it must be treated separately, ie this term in the sum is not properly represented by an integral over a continuous energy variable. Thus we have from Weyl's law

$$\begin{aligned} \sum_j &= \{\epsilon = 0\} + \int \frac{d^3q d^3p}{h^3} \\ &= \{\epsilon = 0\} + \frac{4\pi V}{h^3} \int_0^\infty p^2 dp \\ &= \{\epsilon = 0\} + \frac{2\pi V}{h^3}(2m)^{3/2} \int_0^\infty \epsilon^{1/2} d\epsilon \end{aligned}$$

giving a density of states

$$g(\epsilon) = \frac{2\pi V}{h^3}(2m)^{3/2}\epsilon^{1/2}$$

where we could multiply the whole expression by the spin degeneracy $2j+1$ and we used the nonrelativistic $\epsilon = p^2/2m$. We find

$$\begin{aligned} \ln \mathcal{Z} &= -\ln(1-z) - \frac{2\pi V}{h^3}(2m)^{3/2} \int_0^\infty \epsilon^{1/2} \ln(1 - ze^{\beta\epsilon}) d\epsilon \\ &= -\ln(1-z) + \frac{2\pi V}{h^3}(2m)^{3/2} \frac{2\beta}{3} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{z^{-1}e^{\beta\epsilon} - 1} \\ &= \frac{V}{\lambda_T^3} g_{5/2}(z) - \ln(1-z) \end{aligned}$$

where

$$\lambda_T = \sqrt{\frac{h^2}{2\pi mkT}}$$

as before. Similarly the total number of particles is given by the sum (turned to integral) of the occupation numbers

$$\begin{aligned} N &= \frac{z}{1-z} + \frac{2\pi V}{h^3}(2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{z^{-1}e^{\beta\epsilon} - 1} \\ &= \frac{z}{1-z} + \frac{V}{\lambda_T^3} g_{3/2}(z) \\ &= N_0 + N_\epsilon \end{aligned}$$

where the first term gives the number of particles in the lowest state. We now need to invert this to find z as a function of N.

Now $g_{3/2}(z)$ is continuous and increasing. So it is bounded by $g_{3/2}(0) = 0$ and $g_{3/2}(1) = \zeta(3/2) \approx 2.612$. Thus at fixed V and T there is a maximum bound on N_ϵ. If there are any more particles they must be in N_0. The fact that there are a macroscopic fraction of particles in the lowest state is called Bose condensation. This means that

$$z = \frac{N_0}{1 + N_0}$$

is very close to 1 if N_0 is macroscopic. In this case we can compute

$$N_0 \approx N - \frac{V}{\lambda_T^3}\zeta(3/2)$$

and hence z. On the other hand, if there are not enough particles to reach this bound, we have to solve

$$N \approx \frac{V}{\lambda_T^3} g_{3/2}(z)$$

for z noting that N_0 is now negligible. Writing $x = N\lambda_T^3/V$ we have in the thermodynamic limit (extensive quantities large):

$$z = \begin{cases} 1 & x \geq \zeta(3/2) \\ g_{3/2}^{-1}(x) & x < \zeta(3/2) \end{cases}$$

For real (non-infinite) systems there is a smooth transition region between these regimes.

It is also helpful to consider a system at constant N with varying T. The equation

$$N = V\left(\frac{2\pi mkT_c}{h^2}\right)^{3/2} \zeta(3/2)$$

defines the critical temperature

$$T_c = \left(\frac{N}{V}\right)^{2/3} \frac{h^2}{2\pi k m \zeta(3/2)^{2/3}}$$

at which the transition occurs. In terms of this temperature we have

$$\begin{aligned} \frac{N_\epsilon}{N} &= \left\{ \begin{array}{cc} 1 & T > T_c \\ (T/T_c)^{3/2} & T < T_c \end{array} \right. \\ \frac{N_0}{N} &= \left\{ \begin{array}{cc} 0 & T > T_c \\ 1 - (T/T_c)^{3/2} & T < T_c \end{array} \right. \end{aligned}$$

This is an example of a phase transition, in momentum space.

The other thermodynamic quantities can now be calculated from the partition function. For example

$$\frac{pV}{kT} = \ln \mathcal{Z} = \frac{V}{\lambda_T^3} g_{5/2}(z) - \ln(1-z)$$

$$E = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}\bigg|_{z,V} = \frac{3}{2} kT \frac{V}{\lambda_T^3} g_{5/2}(z)$$

So we have

$$p = \frac{2}{3}\frac{E}{V}$$

as in the classical ideal gas, but now generally valid.

At small x we have

$$x = g_{3/2}(z) = z + \frac{z^2}{2^{3/2}} + \ldots$$

so

$$z \approx x = \frac{N\lambda_T^3}{V}$$

which is the classical ideal gas.

$$\frac{pV}{kT} = \ln \mathcal{Z} = \frac{V}{\lambda_T^3} g_{5/2}(z) - \ln(1-z)$$

Here, $\ln(1-z) \ll N$ can be ignored, and again $g_{5/2}(z) \approx z$ so we have

$$pV = NkT$$

as expected.

At larger x but $z < 1$ we can substitute the expression for N and find

$$pV = NkT \frac{g_{5/2}(z)}{g_{3/2}(z)}$$

In the condensation regime we have

$$z = \frac{N_0}{1+N_0}$$

so $\ln(1-z)$ appearing in the partition function is logarithmic in N and can be neglected. Thus we find

$$p = \frac{kT}{\lambda_T} g_{5/2}(z) = \frac{kT}{\lambda_T} \zeta(5/2)$$

which depends on T but not N or V: the extra particles in the condensate have zero energy and do not contribute to the pressure or energy. $\zeta(5/2) \approx 1.341$. If we substitute here the critical temperature, we find the relation between p and V for the phase transition:

$$pV^{5/3} = \frac{h^2 N^{5/3}}{2\pi m} \frac{\zeta(5/2)}{\zeta(3/2)^{5/3}} = \text{const}$$

Example: Liquid Helium-4 undergoes a transition to a state containing a "normal" component plus a zero viscosity superfluid which can be modelled as ideal BEC (albeit some differences due to interactions). The mass of a helium atom is $4u$ and the density of liquid helium is $125kgm^{-3}$. Estimate the transition temperature and the fraction of particles in the superfluid at half the transition temperature.

Solution: We have above

$$T_c = \left(\frac{N}{V}\right)^{2/3} \frac{h^2}{2\pi k m \zeta(3/2)^{2/3}}$$

The particle density is

$$\frac{N}{V} = \frac{125 \times 6.022 \times 10^2 6}{4} = 1.882 \times 10^{28} m^{-3}$$

the mass is

$$m = 4u = 6.642 \times 10^{-27} kg$$

giving

$$T_c = 2.84K$$

which is not far from the experimentally measured $T_c = 2.17K$. At half the transition temperature we have

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2} \approx 0.65$$

4.8 The ideal Fermi gas

A gas of fermions is also relevant to a number of applications, namely electrons in metals, protons and neutrons in nuclei, and in the relativistic case, electrons in white dwarf stars and neutrons in neutron stars. All these situations are well approximated by the low temperature (ie quantum) limit of the theory. Fermions are different to bosons in that only one can occupy each state, thus even at zero temperature they are forced to occupy high energy states and can exert sufficient pressure to hold up a star.

There is no ground state occupation to be concerned with, so we simply replace the sums for $\mathcal{Z}$ and N by integrals

$$\begin{aligned} \ln \mathcal{Z}(z,V,T) &= \int_0^\infty g(\epsilon) \ln(1 + z e^{-\beta\epsilon}) d\epsilon \\ N(z,V,T) &= \int_0^\infty \frac{g(\epsilon) d\epsilon}{z^{-1} e^{\beta\epsilon} + 1} \\ g(\epsilon) &= g \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} \end{aligned}$$

where $g = 2j + 1$ is the spin degeneracy factor, $j = 1/2$ for electrons, protons and neutrons. Substituting the density of states $g(\epsilon)$ and in the $\mathcal{Z}$ case integrating by parts, we find

$$\ln \mathcal{Z} = \frac{pV}{kT} = \frac{gV}{\lambda_T^3} f_{5/2}(z)$$

$$N = \frac{gV}{\lambda_T^3} f_{3/2}(z)$$

and by analogy with before we have

$$\begin{aligned} E &= -\frac{\partial}{\partial \beta} ln\mathcal{Z}\bigg|_{z,V} \\ &= \frac{3}{2} kT \frac{gV}{\lambda_T^3} f_{5/2}(z) \\ &= \frac{3}{2} NkT \frac{f_{5/2}(z)}{f_{3/2}(z)} \end{aligned}$$

which clearly gives the classical limit when $z \ll 1$. We also have as before

$$p = \frac{2E}{3V}$$

so this is completely general for the non-relativistic ideal gas.

Let us now consider the case of very low temperature (actually a good approximation for metals at room temperature), also called a degenerate Fermi gas. In the integral above for N, we notice that the denominator has a term $z^{-1}e^{\beta\epsilon} = e^{(\epsilon-\mu)/kT}$. This will be very large if $\epsilon > \mu$, corresponding to a very small number of particles with these energies. It will be very small if $\epsilon < \mu$, giving a finite contribution $g(\epsilon)$. In other words, the fermions, being forced to occupy different states, fill the lowest energy states until the requisite number of particles has been achieved. The value of μ at zero temperature for a given particle number density N/V is called the Fermi energy, ϵ_F. We can easily calculate this:

$$\begin{aligned} N &= \int_0^{\epsilon_F} g(\epsilon) d\epsilon \\ &= g\frac{2\pi V}{h^3}(2m)^{3/2} \int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon \\ &= \frac{4\pi g V}{3} \left(\frac{2m\epsilon_F}{h^2}\right)^{3/2} \end{aligned}$$

Thus

$$\epsilon_F = \frac{h^2}{2m}\left(\frac{3N}{4\pi g V}\right)^{2/3}$$

Also

$$\begin{aligned} E &= \int_0^{\epsilon_F} g(\epsilon)\epsilon d\epsilon \\ &= \frac{4\pi g V}{5}\left(\frac{2m}{h^2}\right)^{3/2} \epsilon_F^{5/2} \\ &= \frac{1}{5}\frac{h^2}{2m}(4\pi g V)^{-2/3}(3N)^{5/3} \\ &= \frac{3}{5} N\epsilon_F \end{aligned}$$

which is not zero, even though the temperature is zero.

Example: Calculate the Fermi energy for copper, and compare it with kT at 298K. Also calculate the contribution to the pressure from the free electrons. You are given that copper has one free electron per atom, atomic mass $63.5u$ and mass density $8920kgm^{-3}$. We have

$$\frac{N}{V} = \frac{6.02 \times 10^{26} \times 8920}{63.5} = 8.46 \times 10^{28} m^{-3}$$

and also $g = 2j + 1 = 2$ and $m = 9.11 \times 10^{-31} kg$ for electrons, giving

$$\epsilon_F = 1.13 \times 10^{-18} J$$

which we can compare with

$$kT = 4.11 \times 10^{-21} J$$

thus zero temperature is a good approximation in this case. The pressure is

$$p = \frac{2E}{3V} = \frac{2}{5}\frac{N}{V}\epsilon_F = 3.81 \times 10^{10} Pa$$

which at $38GPa$ is much larger than the yield strength of copper $0.2GPa$. This enormous pressure is counteracted by the attraction of the positive ions.