APAS 5110. Internal Processes in Gases. Fall 1999.

CLASSICAL STATISTICAL MECHANICS OF IDEAL GASES

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1. Statistical Mechanics versus Thermodynamics

Statistical Mechanics is the modern microscopic theoretical foundation for the classical macroscopic phenomenology of **Thermodynamics**. I take the point of view that classical Thermodynamics, notably its axiomatic foundation, the venerable three Laws, is mostly of historical interest, so don't expect to read too much about classical Thermodynamics here.

2. Definition of Ideal Gas

An **ideal** gas is a gas in which the particles interact so weakly that their eigenstates are effectively those of isolated particles. Still, the particles interact to the extent that they are able to exchange energy and other conserved properties. The definition of ideal admits the possibility that the particles obey an exclusion principle.

The basic simplifying feature of ideal gases is that the single-particle states of the system can be treated as independent subsystems. Probabilities are multiplicative over independent subsystems (that's what independent means).

The subvolumes of an ideal gas may also be treated as independent systems, since the states of particles in one subvolume do not affect the states of particles in any other subvolume.

3. Many-Particle States versus Single-Particle States

In quantum mechanics, the **state** of a system is specified by its wavefunction. For example, to the extent that the room you are sitting in constitutes a closed system (which is obviously a lousy approximation), you could regard the room and everything in it as being in a certain state, having a certain wavefunction. Most likely, the wavefunction is not a definite eigenstate, but rather some superposition of eigenstates. In a closed system, it is always possible to find a complete orthonormal set of eigenstates of the system. The 'number of states' of the system is the number of distinct eigenstates, or if you like the dimensionality of the Hilbert space. This number of states is independent of how you choose the orthonormal basis of eigenstates, just as the number of dimensions of a vector space is independent of how you choose the basis.

Any many-particle wave function can be expressed as a suitably (anti)symmetrized sum of products of single-particle wave functions. Thus it is possible to reduce the problem of the counting of states for the entire system to the problem of counting the states of single particles. This is most particularly useful in ideal gases, where the single-particle wavefunctions are by definition the same as those of isolated particles.

When I refer to a state of a system, I shall (or should, at least) hereafter always mean the many-particle state of the entire system under consideration. When I want to refer to the states of single particles I shall say so explicitly.

4. Thermodynamic Variables and Conserved Quantities

The statistical properties of a gas in thermodynamic equilibrium (see §6 below) are specified completely by the values of additive conserved quantities, such as energy, and particle number. To each conserved quantity there corresponds a thermodynamic variable. The jargon is to call the conserved quantities extensive variables, and the associated thermodynamic variables intensive variables. In an ideal gas, extensive variables are proportional to volume, while intensive variables are independent of volume (in a nonideal gas there is in general some nonlinear dependence of extensive variables on volume, for any finite volume). Examples are:

Conserved Quantity Extensive	Thermodynamic Variable Intensive
Energy	Temperature
Number	Chemical Potential
Volume	Pressure
Momentum	Bulk Velocity
Angular Momentum	Angular Velocity

5. Thermodynamic Variables and External Parameters

In the previous section, §4, volume was construed as a conserved quantity. Actually, volume is not so much conserved, as fixed by external means, namely a box, or an infinite potential well. More generally, the eigenstates of a system may be affected by various other externally imposed parameters, for example by an externally imposed electric, magnetic, or gravitational field. Just as there is a thermodynamic variable corresponding to each conserved quantity in the system, so also there is a thermodynamic variable associated with each externally imposed parameter of the system. In some cases the thermodynamic variable has a name, for example:

External Parameter	Thermodynamic Variable
Volume	Pressure
Surface Area	Surface Tension
Magnetic Field	Magnetic Susceptibility

Note that the table above lists surface area as an external parameter. Actually, surface area is irrelevant for ideal gases, since their single-particle states are by assumption unaffected by the presence of surfaces, from which it follows that ideal gases have zero surface tension.

6. Definition of Thermodynamic Equilibrium

A closed system, with given values of the total energy, number, and other conserved or externally imposed quantities, is in **thermodynamic equilibrium** if all the (many-particle) states of the system consistent with the specified total energy, number, etc., are occupied with equal probability.

A nonclosed system is in thermodynamic equilibrium if it is part of a closed, possibly infinite in the limit, system in thermodynamic equilibrium.

Question (6.1): This definition of thermodynamic equilibrium is surely daft, since it is absurd to believe that a real system is going to cycle through all its possible states with equal probability even over the age of the universe. Discuss.

7. Microscopic Reversibility and Thermodynamic Equilibrium

The tendency of systems to approach thermodynamic equilibrium is a physical consequence of **microscopic reversibility**, also known as **detailed balance**, which states that the rate (transition probability per unit time) for one state to convert into another state equals the inverse rate. Microscopic reversibility arises from the symmetry with respect to time reversal of the quantum mechanical matrix elements that describe the transition between incoming and outgoing states.

For example, consider a system with just two possible states, A and B, which are allowed by conservation laws to transform one into the other

$$A \rightarrow B \ . \tag{7.1}$$

Microscopic reversibility says that the rate $A \rightarrow B$ equals the inverse rate $A \leftarrow B$. Therefore, if you wait long enough, the system will spend half its time in state A, and half its time in state B. But equal probabilities of being in state A or state B is just the condition of thermodynamic equilibrium.

It is ironic that the inexorably irreversible approach of systems toward thermodynamic equilibrium is ultimately a consequence of time reversibility.

Question (7.1): Read Pathria pages 4 and 32-36, or similar text. What is the relation between microscopic reversibility and Gibbs' phase space approach?

8. In Practice, When is Thermodynamic Equilibrium True?

Consider a process

$$A \rightarrow B \tag{8.1}$$

connecting two states A, B of a system. Then A and B will be in relative thermodynamic equilibrium (A and B are equally probable) if the process and its inverse are faster than any other processes connecting A or B to other states of the system.

Examples:

1. Elastic or Coulomb collisions between electrons,

$$e + e \rightarrow e + e \ , \tag{8.2}$$

(note this process is its own inverse) is usually the fastest process that redistributes energy between electrons. Elastic collisions are for example much faster than inelastic collisions,

$$e + \mathrm{X} \rightarrow e + \mathrm{X}^* \ , \tag{8.3}$$

which involve collisional excitation or deexcitation of atoms X. As a result, nonrelativistic electrons in astrophysical plasmas almost always have a thermal, otherwise known as Maxwellian, distribution of energies. Which is a profoundly useful convenience.

Question (8.1): Relativistic electrons generally do not have a thermal distribution of energies. Why not? Do the electrons in a cathode ray tube have a thermal distribution? Why?

2. At high enough density in a sufficiently ionized gas, the dominant process for populating and depopulating the levels of molecules/atoms/ions is collisional excitation and deexcitation by (a Maxwellian distribution of) electrons

$$e + \mathrm{X} \rightarrow e + \mathrm{X}^* \ . \tag{8.4}$$

Collisional (de)excitation is faster for example than any process involving radiation. As a result, the levels of molecules/atoms/ions at high density are driven into thermodynamic equilibrium with the colliding thermal electrons. Similarly, the processes of collisional ionization and its inverse, three-body recombination,

$$e + \mathrm{X} \rightarrow e + e + \mathrm{X}^+ \ , \tag{8.5}$$

dominate the ionization and recombination of a plasma at high enough density, being faster for example than photoionization or radiative recombination. This accounts for the fact that the particles in the atmospheres of stars are usually close to thermal equilibrium even though the radiation field may be far from equilibrium.

Question (8.2): In a gas at low density, the dominant process for exciting levels of molecules/atoms/ions is often collisions, whereas the dominant deexcitation process is radiative decay (emission of a photon). Do you expect the levels then to be in thermal equilibrium?

Question (8.3): In the low density interstellar hydrogen gas (HII region) surrounding a hot, UV-emitting, OB star, the main processes which cause the hydrogen to ionize and recombine are the mutually inverse processes of photoionization and radiative recombination

$$\mathrm{H} + \gamma \leftrightarrow \mathrm{H}^+ + e \ .$$

Are H and H^+ likely to be in thermodynamic equilibrium? Explain. [Hints: In this problem there are at least two things to think about: Is the radiation field in thermodynamic equilibrium? What about the fact that neutral H has many bound levels, and what about transitions between these levels? Note that it *is* reasonable to assume that elastic (Coulomb) collisions between H, H^+, and e establish a Maxwellian distribution of velocities of these particles at some temperature. You may also assume that it is a good approximation (though this is not guaranteed true) to ignore collisional processes which excite or ionize H.]

9. Temperature

Suppose you have two systems, each of which contains a very large number of particles, and each of which is in thermodynamic equilibrium. Now put the two systems together, in such a way that energy can transfer between them, but conserving the total energy $E = E_1 + E_2$. What happens? You are probably used to the classical notion that what will happen is that energy will be exchanged between the two systems until their temperatures are equal. Let's investigate more closely.

For the purposes of the argument that follows it is necessary to assume that the states of system 1 are independent of the states of system 2. This assumption is true by hypothesis for an ideal gas, and it is true in a nonideal gas if the two systems are each large enough that the interaction between them is negligible compared to the interaction of particles within each system. This is (one of the reasons) why I started out by postulating that each system contains a very large number of particles.

At any rate, according to the general argument of microscopic reversibility, §7, the system will aspire toward a condition where all the states of the combined system are occupied with equal probability. Because the states of the two systems are being assumed to be independent, the number of states Ω of the combined system such that system 1 has energy E_1 and system 2 has energy E_2, is just the product of the number of states, Ω_1 and Ω_2, of the two systems

$$\Omega(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2) \ . \tag{9.1}$$

The energy $E = E_1 + E_2$ of the system may be distributed between systems 1 and 2 in all possible ways, from one extreme in which all the energy is in system 1, to the other extreme in which all the energy is in system 2, to anything in between. However, not all divisions of energy are equally probable. The most probable division of the energy E between the two systems occurs where the number of states $\Omega(E_1, E_2)$ attains a maximum with respect to variations of the energy E_1:

$$\frac{\partial \ln \Omega(E_1, E - E_1)}{\partial E_1} = \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} + \frac{\partial \ln \Omega_2(E - E_1)}{\partial E_1} = \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} - \frac{\partial \ln \Omega_2(E_2)}{\partial E_2} = 0 \ , \tag{9.2}$$

where the third expression of equation (9.2) follows because $dE_2 = d(E - E_1) = -dE_1$ at constant total energy E. I have written the derivatives in equation (9.2) as partial derivatives because the variation with respect to energy is being done with other conserved quantities, such as number and volume, being held fixed. If the two systems are each large, as is being assumed, then the number of states $\Omega(E_1, E_2)$, subject to energy conservation $E_1 + E_2 = E$, is in practice an extremely highly peaked function of E_1, so that the probability that E_1 deviates even slightly from the most probable value is minute (see *question [21.1]*). Thus in thermodynamic equilibrium the division of energy between the two large systems is such that equation (9.2),

$$\frac{\partial \ln \Omega_1}{\partial E_1} = \frac{\partial \ln \Omega_2}{\partial E_2} \ , \tag{9.3}$$

is satisfied with high precision almost all the time. One can say that equation (9.3), the condition for the most probable state, is asymptotically exact in the limit of two infinitely large systems. This equality (9.3) of partial derivatives between two large systems in mutual thermodynamic equilibrium suggests that the partial derivatives might have something to do with the classical notion of temperature T, and indeed this is so. It turns out that the correct definition of **absolute temperature** T is

$$\frac{1}{kT} \equiv \beta \equiv \frac{\partial \ln \Omega(E)}{\partial E} \ , \tag{9.4}$$

with k Boltzmann's constant (the existence of k is a historical artifact; if temperature is measured in units of energy, then $k = 1$). That equation (9.4) is an appropriate definition of temperature will become clear below, eq. (14.1), when comparison is made to the classical equations of thermodynamics.

10. Other Thermodynamic Variables

The previous section dealt with two large systems that were allowed to exchange energy. More generally, one can consider two large systems that are allowed to exchange any other conserved quantity, such as number, momentum, etc. All the arguments of the previous section carry through essentially unchanged, and one arrives at the conclusion that, to each additive conserved quantity C, there exists a thermodynamic variable γ defined by

$$\gamma \equiv \frac{\partial \ln \Omega(C)}{\partial C} \ , \tag{10.1}$$

analogously to equation (9.4). The thermodynamic variables γ have the property that they are equal in large systems that are in mutual thermodynamic equilibrium. The partial derivative with respect to the conserved quantity C in equation (10.1) is taken with all other conserved quantities being held constant.

If there are externally imposed parameters C of the system, such as a uniform magnetic field, then again formula (10.1) defines the thermodynamic variable γ corresponding to the parameter C.

The collection of equations (10.1) for each conserved quantity or external parameter C can be written as a single equation for the total derivative of $\ln \Omega$

$$d \ln \Omega = \sum_C \gamma dC \tag{10.2}$$

the summation being taken over all the different conserved quantities or external parameters C of interest.

For example, the thermodynamic variable corresponding to conservation of number N is

$$-\frac{\mu}{kT} \equiv \alpha \equiv \frac{\partial \ln \Omega(N)}{\partial N} \ , \tag{10.3}$$

where μ is the **chemical potential**. If there are several different species of particle that are conserved, for example electrons, muons, protons, helium nuclei, ..., then there is a different chemical potential μ_{X}

$$-\frac{\mu_{\mathrm{X}}}{kT} \equiv \alpha_{\mathrm{X}} \equiv \frac{\partial \ln \Omega(N_{\mathrm{X}})}{\partial N_{\mathrm{X}}} \tag{10.4}$$

associated with the conservation of the number N_{X} of each species X.

Volume V may considered as an external parameter, but it can also be regarded as a conserved quantity; for example one can imagine two systems separated by a sliding piston, such that the two systems can exchange volume, the total volume being fixed. The thermodynamic variable associated with conservation of volume V is

$$\frac{P}{kT} \equiv \frac{\partial \ln \Omega(V)}{\partial V} \ , \tag{10.5}$$

where P is the **pressure**. The partial derivative in equation (10.5) is evaluated with all other conserved quantities, such as energy and number, being held constant.

That the definitions (10.3) and (10.5) are appropriate definitions of chemical potential μ and pressure P will become clear below, eq. (14.1), when comparison is made to the classical equations of thermodynamics. For the moment all that one can say is that they are constants that characterize systems in thermodynamic equilibrium.

Combining equations (9.4), (10.3), and (10.5) yields the total derivative of $\ln \Omega$ for a system in thermodynamic equilibrium in which energy E, number N, and volume V are considered to be the conserved properties of the system:

$$d \ln \Omega = \frac{1}{kT} dE - \frac{\mu}{kT} dN + \frac{P}{kT} dV \ . \tag{10.6}$$

Question (10.1): Take two distinct number-conserving particle types X and Y in a system in thermodynamic equilibrium. Which of the following is true/false/meaningless:

(a) $T_{\rm X} = T_{\rm Y}$;

(b) $\mu_{\rm X} = \mu_{\rm Y}$;

(c) $P_{\rm X} = P_{\rm Y}$?

Explain.

11. Linear Momentum, Bulk Velocity, and Internal Energy

If conservation of total momentum $\boldsymbol{P}$ is included, then equation (10.6) for the total derivative of $\ln \Omega$ is modified to

$$d \ln \Omega = \frac{1}{kT} dE + \boldsymbol{\gamma} \cdot d\boldsymbol{P} - \frac{\mu}{kT} dN + \frac{P}{kT} dV \ , \tag{11.1}$$

where $\boldsymbol{\gamma}$ is the (for the moment unknown) thermodynamic variable associated with the conserved momentum $\boldsymbol{P}$. However, it is always possible to transform to a frame of reference in which the total momentum is zero, $\boldsymbol{P} = 0$. In the zero momentum, or rest, frame, the system is isotropic (it looks the same in all directions) so the associated thermodynamic variable $\boldsymbol{\gamma}$, which is a vector, must also be zero in the rest frame (which direction could it possibly point in?). Thus, transformed to the rest frame, $\boldsymbol{P} = 0$, equation (11.1) goes over to

$$d \ln \Omega = \frac{1}{kT} dU - \frac{\mu}{kT} dN + \frac{P}{kT} dV \ , \tag{11.2}$$

where U is the energy of the system in the rest frame, commonly known as the **internal energy** of the system. Back in the moving frame, moving at say velocity $\boldsymbol{v}$ with respect to the rest frame, the total energy E is the sum of the internal energy U and the bulk kinetic energy $E_{\rm KE}$,

$$E = U + E_{\rm KE} \ . \tag{11.3}$$

According to a result well known from mechanics, changes in the bulk kinetic energy and momentum of a system are related by $dE_{\rm KE} = \boldsymbol{v} \cdot d\boldsymbol{P}$, which is true quite generally in the relativistic as well as the nonrelativistic domain. Thus the differential dU of the internal energy can be written

$$dU = d(E - E_{\rm KE}) = dE - \boldsymbol{v} \cdot d\boldsymbol{P} \ . \tag{11.4}$$

Inserting this result (11.4) into equation (11.2), and comparing with equation (11.1), one concludes that the thermodynamic variable $\boldsymbol{\gamma}$ associated with momentum conservation is

$$\boldsymbol{\gamma} = -\frac{\boldsymbol{v}}{kT} \ . \tag{11.6}$$

Since $\boldsymbol{\gamma}$ is a constant characteristic of the entire system, the velocity $\boldsymbol{v}$ must be a constant of the system. In other words, a system in thermodynamic equilibrium necessarily moves with a uniform bulk velocity.

In statistical mechanics it is convenient to work with internal energy U rather than the total energy E, since it is thereby possible to dispense with all appearance of momentum. You should be aware however that the fact that internal energy U can be treated as a conserved quantity arises from the conservation of both energy *and* momentum, not just energy.

12. Rotation

In the previous section it was shown that a system in thermodynamic equilibrium, in which the parts of the system can exchange linear momentum, is necessarily in uniform bulk motion. It's an obvious guess then that if the parts of the system can also exchange angular momentum, then the system should be in uniform bulk rotation as well as uniform bulk motion, and indeed this is the case. However, a rotating system is not quite so simple because, whereas the rest frame of a system in uniform bulk motion is still inertial, the corotating rest frame of a system in uniform rotation is noninertial, with an apparent centrifugal force directed away from the rotation axis. The consequence is that the internal energy of a rotating system is modified by the inclusion of a centrifugal potential energy.

Consider then a system in thermodynamic equilibrium, in which the conserved quantities of the system are taken to be energy E, momentum $\boldsymbol{P}$, and angular momentum $\boldsymbol{J}$. For simplicity, let number N and volume V be held constant, so that the dN and dV terms in the equation for $d\ln\Omega$ can be omitted. Then the total differential of the logarithm of the number of states looks like

$$d\ln\Omega = \frac{1}{kT}dE - \frac{\boldsymbol{v}}{kT}\cdot d\boldsymbol{P} - \frac{\boldsymbol{\omega}}{kT}\cdot d\boldsymbol{J} \quad ??? \tag{12.1}$$

where $\boldsymbol{\omega}$ is some constant whose physical significance has yet to be established. Equation (12.1) is written with question marks after it because it can't really be right as it stands. The trouble is that the value of the angular momentum $\boldsymbol{J}$ depends on where the origin of the coordinate system is chosen, whereas the number of states Ω should obviously be independent of the origin. It's only the angular momentum $\boldsymbol{J}$ that has this problem: the energy E and linear momentum $\boldsymbol{P}$ are independent of the origin of the coordinate system. Now the angular momentum $\boldsymbol{J}$ can always be decomposed into the intrinsic angular momentum $\boldsymbol{J}_0$ about the center of mass of the system, plus the bulk angular momentum $\boldsymbol{R}\times\boldsymbol{P}$, if the center of mass is at position $\boldsymbol{R}$ with respect to the origin:

$$\boldsymbol{J} = \boldsymbol{J}_0 + \boldsymbol{R}\times\boldsymbol{P} \ . \tag{12.2}$$

Thus to make equation (12.1) independent of the origin, one needs to use the intrinsic angular momentum $\boldsymbol{J}_0$ in place of the angular momentum $\boldsymbol{J}$. So equation (12.1) should correctly be written

$$\begin{aligned} d\ln\Omega &= \frac{1}{kT}dE - \frac{\boldsymbol{v}}{kT}\cdot d\boldsymbol{P} - \frac{\boldsymbol{\omega}}{kT}\cdot d\boldsymbol{J}_0 \\ &= \frac{1}{kT}dE - \frac{\boldsymbol{v}}{kT}\cdot d\boldsymbol{P} - \frac{\boldsymbol{\omega}}{kT}\cdot d(\boldsymbol{J} - \boldsymbol{R}\times\boldsymbol{P}) \\ &= \frac{1}{kT}dE - \frac{\boldsymbol{v} - \boldsymbol{\omega}\times\boldsymbol{R}}{kT}\cdot d\boldsymbol{P} - \frac{\boldsymbol{\omega}}{kT}\cdot d\boldsymbol{J} \ . \end{aligned} \tag{12.3}$$

Note that a term $-(\boldsymbol{\omega}/kT)\cdot\boldsymbol{P}\times d\boldsymbol{R}$ seems to have been lost in going from the second to the third expression of equation (12.3). That term is however always zero since the change $d\boldsymbol{R}$ in the center of mass of the system from one moment to the next is always parallel to its momentum $\boldsymbol{P}$. Now divide the system into a number (two or more) of large independent subsystems, labeled a, with centers of mass at positions $\boldsymbol{R}_a$. Then

$$d\ln\Omega = \sum_a d\ln\Omega_a = \sum_a \left[\frac{1}{kT_a}dE_a - \frac{\boldsymbol{v}_a - \boldsymbol{\omega}_a\times\boldsymbol{R}_a}{kT_a}\cdot d\boldsymbol{P}_a - \frac{\boldsymbol{\omega}_a}{kT_a}\cdot d\boldsymbol{J}_a\right] \ . \tag{12.4}$$

Equating (12.3) and (12.4) for arbitrary variations of the additive quantities dE_a, $d\boldsymbol{P}_a$, and $d\boldsymbol{J}_a$, one concludes that

$$kT_a = kT \ , \tag{12.5}$$

$$\frac{\boldsymbol{v}_a - \boldsymbol{\omega}_a\times\boldsymbol{R}_a}{kT_a} = \frac{\boldsymbol{v} - \boldsymbol{\omega}\times\boldsymbol{R}}{kT} \ , \tag{12.6}$$

$$\frac{\boldsymbol{\omega}_a}{kT_a} = \frac{\boldsymbol{\omega}}{kT} \ , \tag{12.7}$$

for all the subsystems a. (If you don't like the way I just said that, you can subdivide the system into just two parts and proceed as in §9.) Equation (12.5) says the temperatures T_a are equal for all subsystems, and equation (12.7) implies that $\boldsymbol{\omega}_a$ are equal for all subsystems. Equation (12.6) then implies that the velocity $\boldsymbol{v}_a$ of subsystem a is

$$\boldsymbol{v}_a = \boldsymbol{v} + \boldsymbol{\omega} \times \boldsymbol{r}_a \ , \tag{12.8}$$

where

$$\boldsymbol{r}_a \equiv \boldsymbol{R}_a - \boldsymbol{R} \tag{12.9}$$

is the center of mass of subsystem a relative to the center of mass $\boldsymbol{R}$ of the entire system. Equation (12.8) says that the velocity of subsystem a is the sum of a uniform motion at velocity $\boldsymbol{v}$ and a uniform rotation at angular velocity $\boldsymbol{\omega}$ about the center of mass of the system. All of which goes to show that the thermodynamic variable associated with conservation of angular momentum is

$$-\frac{\boldsymbol{\omega}}{kT} \ , \tag{12.10}$$

where $\boldsymbol{\omega}$ is the bulk angular velocity of the system. Since $\boldsymbol{\omega}/kT$ is a constant characteristic of the entire system, it follows that a system in thermodynamic equilibrium is necessarily in uniform angular rotation.

The above argument leaves unanswered the question, what is the internal energy U of a rotating system? The internal energy is uniquely defined by two requirements: (1) the internal energy of a subsystem is its energy evaluated in the rest frame of the subsystem; and (2) internal energy is additive over independent subsystems. It follows that the internal energy must be defined as the sum over particle kinetic plus potential energies evaluated in frames that are locally at rest. Which is to say, the internal energy must be the energy evaluated in a system comoving, at velocity $\boldsymbol{v}$, and corotating, at angular velocity $\boldsymbol{\omega}$, with the system as a whole. Suppose that the system is comprised of particles of mass m at positions $\boldsymbol{r}$ relative to the center of mass, having velocities $\boldsymbol{u}_0$ in an inertial frame, and $\boldsymbol{u}$ with respect to the comoving, corotating rest frame, so that

$$\boldsymbol{u}_0 = \boldsymbol{u} + \boldsymbol{v} + \boldsymbol{\omega} \times \boldsymbol{r} \ . \tag{12.11}$$

In the comoving, corotating rest frame, one has

$$\sum m\boldsymbol{u} = \ 0 \ , \quad \sum m\boldsymbol{r} \times \boldsymbol{u} = 0 \ , \tag{12.12}$$

and in addition

$$\sum m\boldsymbol{r} = \ 0 \ , \tag{12.13}$$

since the particle positions $\boldsymbol{r}$ are defined relative to the center of mass. In the comoving, corotating rest frame, the energy is the sum of particle kinetic energies $U_{\rm KE}$ plus the centrifugal potential energy $U_{\rm rot}$ (see e.g. Landau and Lifshitz, Mechanics, §39) plus any additional energy $U_{\rm other}$ associated with internal degrees of freedom of particles (atoms) or with external fields. Let me ignore $U_{\rm other}$ as being immaterial to the present argument, writing simply

$$U = U_{\rm KE} + U_{\rm rot} = \sum \frac{mu^2}{2} - \sum \frac{m(\boldsymbol{\omega} \times \boldsymbol{r})^2}{2} \ . \tag{12.14}$$

The centrifugal energy $U_{\rm rot} = -\sum m(\boldsymbol{\omega} \times \boldsymbol{r})^2/2$ can also be written

$$U_{\rm rot} = -\frac{\boldsymbol{\omega} \cdot \boldsymbol{J}_0}{2} \tag{12.15}$$

which follows from the result that the intrinsic angular momentum $\boldsymbol{J}_0$ is

$$\boldsymbol{J}_0 = \sum m\boldsymbol{r} \times \boldsymbol{u}_0 = \sum m\boldsymbol{r} \times (\boldsymbol{u} + \boldsymbol{v} + \boldsymbol{\omega} \times \boldsymbol{r}) = \sum m\boldsymbol{r} \times (\boldsymbol{\omega} \times \boldsymbol{r}) \ . \tag{12.16}$$

In the inertial frame, the energy E is

$$\begin{aligned}
E &= \sum \frac{m u_0^2}{2} \\
&= \sum \frac{m(\boldsymbol{u}+\boldsymbol{v}+\boldsymbol{\omega}\times\boldsymbol{r})^2}{2} \\
&= \sum \frac{m u^2}{2} + \sum \frac{m v^2}{2} + \sum \frac{m(\boldsymbol{\omega}\times\boldsymbol{r})^2}{2} + \boldsymbol{v}\cdot\sum m\boldsymbol{u} + \boldsymbol{\omega}\cdot\sum m\boldsymbol{r}\times\boldsymbol{u} + \boldsymbol{v}\cdot\boldsymbol{\omega}\times\sum m\boldsymbol{r} \\
&= \sum \frac{m u^2}{2} + \sum \frac{m v^2}{2} + \sum \frac{m(\boldsymbol{\omega}\times\boldsymbol{r})^2}{2} \\
&= U_{\mathrm{KE}} + \frac{\boldsymbol{v}\cdot\boldsymbol{P}}{2} - U_{\mathrm{rot}} \\
&= U + \frac{\boldsymbol{v}\cdot\boldsymbol{P}}{2} + \boldsymbol{\omega}\cdot\boldsymbol{J}_0 \ . \qquad (12.17)
\end{aligned}$$

According to equation (12.17), the internal energy U of a moving rotating system is given in general by

$$U = E - \frac{\boldsymbol{v}\cdot\boldsymbol{P}}{2} - \boldsymbol{\omega}\cdot\boldsymbol{J}_0 \ . \qquad (12.18)$$

Expressing $d\ln\Omega$ in terms of internal energy U rather than total energy E, one has, from equations (12.3) and (12.18),

$$d\ln\Omega = \frac{1}{kT}dU + \frac{\boldsymbol{J}_0}{kT}\cdot d\boldsymbol{\omega} - \frac{\mu}{kT}dN + \frac{P}{kT}dV \ , \qquad (12.19)$$

where for completeness the terms in dN and dV, omitted for brevity from equation (12.3), have been reinserted. Equation (12.19) is the general expression for the total derivative of $\ln\Omega$ in a system in which angular momentum $\boldsymbol{J}$ as well as energy E, momentum $\boldsymbol{P}$, number N, and volume V are considered to be the conserved properties of the system.

In a rotating system, the centrifugal force is balanced by a pressure gradient. This can be seen as follows. Equations (12.14) and (12.15) for the centrifugal energy U_{rot} can be used to rewrite equation (12.19) for $d\ln\Omega$ in the form (as in equation [12.14], the contribution U_{other} to the internal energy from internal degrees of freedom of particles [atoms] or from external fields is here omitted for simplicity)

$$d\ln\Omega = \frac{1}{kT}dU_{\mathrm{KE}} - \frac{1}{kT}\sum\frac{\partial U_{\mathrm{rot}}}{\partial\boldsymbol{r}}\cdot d\boldsymbol{r} - \frac{\mu}{kT}dN + \frac{P}{kT}dV \ , \qquad (12.20)$$

where the summation is over all particles in the system. The quantity

$$-\frac{\partial U_{\mathrm{rot}}}{\partial\boldsymbol{r}} = m(\boldsymbol{\omega}\times\boldsymbol{r})\times\boldsymbol{\omega} \qquad (12.21)$$

in equation (12.20) is the centrifugal force on the particle at position $\boldsymbol{r}$. Now suppose that the system under consideration is actually part of a much larger supersystem, such that the system is small compared to the scale over which the centrifugal acceleration $(\boldsymbol{\omega}\times\boldsymbol{r})\times\boldsymbol{\omega}$ varies. For such a small system, equation (12.20) reduces to

$$d\ln\Omega = \frac{1}{kT}dU_{\mathrm{KE}} + \frac{Nm(\boldsymbol{\omega}\times\boldsymbol{r})\times\boldsymbol{\omega}}{kT}\cdot d\boldsymbol{r} - \frac{\mu}{kT}dN + \frac{P}{kT}dV \ , \qquad (12.22)$$

where $d\boldsymbol{r}$ is now the change in the center of mass of the small system. The commutativity of partial derivatives means that the second derivative $\partial^2\ln\Omega/\partial\boldsymbol{r}\partial V$ can be written two ways,

$$\frac{\partial^2\ln\Omega}{\partial\boldsymbol{r}\partial V} = \frac{\partial}{\partial\boldsymbol{r}}\left(\frac{\partial\ln\Omega}{\partial V}\right) = \frac{\partial P/kT}{\partial\boldsymbol{r}} = \frac{1}{kT}\frac{\partial P}{\partial\boldsymbol{r}} \ , \qquad (12.23)$$

or

$$\frac{\partial^2 \ln \Omega}{\partial \boldsymbol{r} \partial V} = \frac{\partial}{\partial V} \left(\frac{\partial \ln \Omega}{\partial \boldsymbol{r}} \right) = \frac{\partial}{\partial V} \left(\frac{Nm(\boldsymbol{\omega} \times \boldsymbol{r}) \times \boldsymbol{\omega}}{kT} \right) = \frac{\rho(\boldsymbol{\omega} \times \boldsymbol{r}) \times \boldsymbol{\omega}}{kT} \ . \tag{12.24}$$

Note that in going to the final expressions of equations (12.23) and (12.24) the thermodynamic variables kT and $\boldsymbol{\omega}$ are not differentiated, since they are independent of both $\boldsymbol{r}$ and V in a system in thermodynamic equilibrium. Equating (12.23) and (12.24) shows that

$$\frac{\partial P}{\partial \boldsymbol{r}} = \rho(\boldsymbol{\omega} \times \boldsymbol{r}) \times \boldsymbol{\omega} \ , \tag{12.25}$$

which is the usual equation of hydrostatic equilibrium, with centrifugal force balanced by a pressure gradient. The situation is entirely analogous to that posed in *question (27.1)*, where the system under consideration is supposed to be subject to a large scale external gravitational force $\boldsymbol{g}$. Here, the gravitational force is replaced by a centrifugal force, with identical consequences.

In the more general case where the system is not small compared to the scale over which the centrifugal force varies, the pressure P in equations (12.19) or (12.20) is to be interpreted as the pressure at the boundary of the confining volume V, since the volume V is after all only fixed by its boundary conditions. Because the system is no longer isotropic (there's a preferred direction in the system), the pressure P will not in general be the same at all points on the boundary, so that the PdV effect of a change in the volume will depend on whereabouts on the boundary the volume is changed.

In the remainder of these notes the bulk rotation of systems will not be explicitly considered further, since almost invariably it is possible to restrict to the case of systems that are small compared to the scale over which the centrifugal force varies. The thermodynamics of such small systems, expressed in the comoving, corotating rest frame of the system, is the same as that of stationary, nonrotating systems, except for the appearance of a large scale centrifugal force which is balanced by a pressure gradient. The centrifugal force is equivalent in its effects to a gravitational force.

13. Entropy

If you read the previous four sections, you may have noticed that the logarithm of the number of states, $\ln \Omega$, whose partial derivatives with respect to conserved quantities yield thermodynamic variables, is playing a rather prominent role. Bowing to the inevitable, one defines **entropy** S as Boltzmann's constant k times $\ln \Omega$ (again, the presence of the factor k is an unnecessary historical artifact: if temperature is measured in units of energy, then $k = 1$):

$$S \equiv k \ln \Omega \ . \tag{13.1}$$

The concept of entropy, which can be considered as a measure of the degree of disorder of a system, is both peculiar and fundamental to statistical mechanics. The deceptively definite definition (13.1) tends to obscure the fact that entropy is an intrinsically statistical thing, unlike tangible things like energy and number. If you look at it too closely, entropy has a tendency, like the Cheshire cat, to vanish away till all that's left is the smile.

Question (13.1): Consider a system whose states are labeled by the numbers 0000000000 to 9999999999 inclusive. What does it mean to say that the system is in thermodynamic equilibrium? Is the state 4356932540 more probable than the state 9999999999? Is the number 4356932540 more random than the number 9999999999? What is the entropy of the system in thermodynamic equilibrium?

Entropy, as defined by equation (13.1), has a number of basic properties:

1. Entropy is additive over independent subsystems;

2. If you put two systems together, their entropy always increases;

3. Entropy is a maximum in thermodynamic equilibrium;

4. Entropy is zero if the number of states accessed by the system is one.

Property 1 and Property 4 follow immediately from the definition (13.1) of entropy. Property 2, the increase of entropy, is an ultimate consequence of a system's tendency to try and explore all its accessible states with equal probability, which is a consequence of microscopic reversibility, §7. If you put two systems together, then the number of states of the combined system in which conserved properties, such as energy, are allowed to be exchanged, is always greater than the number of states of the system in which the energies, etc., of each system are constrained to have certain fixed values. Property 3 is essentially a corollary of property 2. Note that it is possible for a system to have no maximum entropy, that is, there are an infinite number of states with finite energy, number, etc. In this case the system can never attain thermodynamic equilibrium: the system is unstable, perpetually evolving in a way that explores more and more of the states of the system.

Question (13.2): According to the argument of the above paragraph, it should be possible to lower the entropy of a system in thermodynamic equilibrium inside a box, say, by inserting an impermeable partition that divides the box into two parts. The insertion of the partition fixes the energy and number in the two sides, reducing the number of states compared to the case where energy and number may fluctuate. Is this the makings of a perpetual motion machine? Explain.

Question (13.3): If entropy is a maximum in thermodynamic equilibrium, doesn't that mean that $dS = kd\ln\Omega = 0$, rendering equation (10.6) meaningless? Explain.

14. The Two Fundamental Equations of Thermodynamics

Substituting the definition (13.1) of entropy into equation (11.2) yields

$$TdS = dU - \mu dN + PdV \ , \tag{14.1}$$

which is the familiar **first fundamental equation of classical thermodynamics**.

Now in an ideal gas the subvolumes of the system are by hypothesis independent subsystems, so that $\ln\Omega$, which is additive over independent subsystems, must be proportional to the volume V of the system. If all the thermodynamic variables, temperature T, chemical potential μ, pressure P, of the system are considered fixed, then according to equation (10.1) the additive conserved quantities of the system must also be proportional to the volume of the system. In other words $S \equiv k\ln\Omega$, U, and N are all proportional to V at fixed T, μ, and P. It then follows from equation (14.1) that, in an ideal gas,

$$TS = U - \mu N + PV \ , \tag{14.2}$$

which is the **second fundamental equation of thermodynamics**.

Question (14.1): Could I not, by accident or whim, have chosen a different set of conserved quantities and arrived at an equation different from (14.2)? For example, if I had forgotten that N is conserved, I might have written down $TS = U + PV$ without the μN term. Or, there might be some new conservation law arising from some hitherto unsuspected symmetry of the universe that I don't know about. Maybe you should allow for the possibility that surface area might be a good conserved quantity. So is equation (14.2) always right, sometimes right, or what? Explain.

15. Thermodynamics in terms of Other Variables

From the two equations (14.1) and (14.2) can be derived a whole battery of tautologous equations. Many texts devote an inordinate amount of space defining things like work functions, free energies, and enthalpies, and figuring out their partial derivatives with respect to this and that. Do not be misled. Such ponderations contain no more information than is already contained in equations (14.1) and (14.2).

You will see that equations (14.1) and (14.2) contain 7 variables, but only 3 are independent, entropy S being some function (determined by microphysics) of U, N, and V, and the thermodynamic variables T, μ, and P being determined in terms of partial derivatives of S with respect to U, N, and V. It is evident that instead of the variables U, N and V, one might prefer to express everything in terms of some other triplet of variables, such as T, P, and V. In view of all the different possible permutations it is not surprising that a large number of equations can be generated. It is pointless to try to remember all the equations. However, you do need to understand how to make the mathematical transformation of partial derivatives from one set of variables to another. The calculations of the next section, §16, provide a practical illustration of how to do this.

Question (15.1): Equation (14.1) specifies the partial derivatives of any one of S, U, N, and V with respect to the other three. Define the **free energy** $F \equiv U - TS$, and write down an equation that specifies the partial derivatives of any one of F, T, N, V with respect to the other three.

Question (15.2): Define the specific heats C_V at constant volume, and C_P at constant pressure, by

$$C_V \equiv \left.\frac{T\partial S}{\partial T}\right|_{N,V} \ , \quad C_P \equiv \left.\frac{T\partial S}{\partial T}\right|_{N,P} \ , \tag{15.1}$$

and define the **adiabatic index** γ as the ratio of specific heats

$$\gamma \equiv \frac{C_P}{C_V} \ . \tag{15.2}$$

Show that

$$\left.\frac{\partial \ln P}{\partial \ln V}\right|_{S,N} = \gamma \left.\frac{\partial \ln P}{\partial \ln V}\right|_{T,N} \ . \tag{15.3}$$

(Hint: use the method of Jacobians, eqs. (16.8)-(16.11) of the next section). An ideal Boltzmann gas satisfies $PV = NkT$ (eq. [36.37]). Show that in an **adiabatic** expansion (i.e. expansion at constant entropy S and number N), the pressure P and volume V of an ideal Boltzmann gas vary according to

$$PV^\gamma = \text{constant} \ . \tag{15.4}$$

16. Stability of Thermodynamic Equilibrium

Thermodynamic equilibrium is characterized by the property that entropy is a maximum. However, the equilibrium conditions derived in §§9–12, namely that the temperature and other thermodynamic variables should be the same for large systems in mutual equilibrium, were based only on the requirement that entropy be an extremum. For the equilibrium to be stable requires also that the entropy be a maximum.

It should be remarked here that there are in general other constraints on the thermodynamic variables, such as the positivity of temperature and pressure in most systems, which do not arise directly from the requirement that entropy be a maximum, but rather are associated with the specific character of the states of the system. These matters will be addressed in §33, after the formalism of ensembles and partition functions has been properly developed.

The discussion below deals specifically with the conditions imposed by the requirement that the thermodynamic equilibrium be stable with respect to variations in the internal energy U and the volume V, the number of particles N being taken as fixed. This is the most interesting case, and it is prototypical. Amongst other things, the calculation provides a good example of the manipulation of partial derivatives in thermodynamics. The condition for an extremum of entropy to be a maximum with respect to variations of energy and volume is that

$$\delta^2 S = \frac{\partial^2 S}{\partial U^2}(\delta U)^2 + 2\frac{\partial^2 S}{\partial U \partial V}\delta U \delta V + \frac{\partial^2 S}{\partial V^2}(\delta V)^2 < 0 \tag{16.1}$$

for arbitrary small perturbations δU and δV of the energy and volume away from thermodynamic equilibrium. The stability condition (16.1), which is quadratic in the variables δU and δV, will be true provided that the two conditions

$$\left.\frac{\partial^2 S}{\partial U^2}\right|_V < 0 \tag{16.2}$$

$$\left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 - \frac{\partial^2 S}{\partial U^2}\frac{\partial^2 S}{\partial V^2} < 0 \tag{16.3}$$

hold.

Question (16.1): In writing down the stability condition (16.1), I should properly have considered the stability between two systems allowed to exchange energy and volume, or at least the stability between the parts of a system. Show that equation (16.1) is still the correct condition.

The first stability condition (16.2) requires that

$$\left.\frac{\partial^2 S}{\partial U^2}\right|_V = \left.\frac{\partial 1/T}{\partial U}\right|_V = -\frac{1}{T^2 C_V} < 0 \ , \tag{16.4}$$

where C_V is the **specific heat at constant volume**

$$C_V \equiv \left.\frac{T\partial S}{\partial T}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V \ . \tag{16.5}$$

Equation (16.4) implies that the first condition for stability of thermodynamic equilibrium is that the specific heat at constant volume must be positive

$$C_V > 0 \ . \tag{16.6}$$

Question (16.2): Can you think of a physical system where the specific heat is negative? What do you think might happen in that case?

To reduce the second stability condition (16.3), first note that the partial derivative $\partial^2 S/\partial U \partial V$ can be written two ways:

$$\frac{\partial^2 S}{\partial U \partial V} = \left.\frac{\partial(1/T)}{\partial V}\right|_U = \left.\frac{\partial(P/T)}{\partial U}\right|_V , \tag{16.7}$$

which follows directly from the fundamental equation (14.1). Equation (16.7) is a particular example of one of **Maxwell's relations** between partial derivatives of thermodynamic quantities. Besides applying the Maxwell relation (16.7), it is convenient to transform from U, V variables to $1/T$, V variables. The transformation from one set of variables to another is most easily accomplished using Jacobians. The Jacobian is defined as the determinant of the matrix of partial derivatives, which for two variables is

$$\frac{\partial(u,v)}{\partial(x,y)} \equiv \begin{vmatrix} \partial u/\partial x & \partial v/\partial x \\ \partial u/\partial y & \partial v/\partial y \end{vmatrix} = \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x} . \tag{16.8}$$

The Jacobian has the properties

$$\frac{\partial(v,u)}{\partial(x,y)} = -\frac{\partial(u,v)}{\partial(x,y)} , \tag{16.9}$$

$$\frac{\partial(u,y)}{\partial(x,y)} = \left.\frac{\partial u}{\partial x}\right|_y , \tag{16.10}$$

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)/\partial(t,s)}{\partial(x,y)/\partial(t,s)} . \tag{16.11}$$

It is the last property, (16.11), which makes the Jacobian the handy way of transforming to new variables. The second stability condition (16.3) reduces as follows:

$$\begin{aligned} \left(\frac{\partial^2 S}{\partial U \partial V}\right)^2 - \frac{\partial^2 S}{\partial U^2}\frac{\partial^2 S}{\partial V^2} &= \left.\frac{\partial(1/T)}{\partial V}\right|_U \left.\frac{\partial(P/T)}{\partial U}\right|_V - \left.\frac{\partial(1/T)}{\partial U}\right|_V \left.\frac{\partial(P/T)}{\partial V}\right|_U \\ &= \frac{\partial(1/T, P/T)}{\partial(V,U)} \\ &= \frac{\partial(1/T, P/T)/\partial(1/T, V)}{\partial(V,U)/\partial(1/T,V)} \\ &= -\frac{\left.\frac{\partial(P/T)}{\partial V}\right|_{1/T}}{\left.\frac{\partial U}{\partial(1/T)}\right|_V} \\ &= \frac{1}{T^2 C_V}\left.\frac{\partial(P/T)}{\partial V}\right|_T < 0 . \end{aligned} \tag{16.12}$$

Since the specific heat C_V is positive, according to the first stability criterion (16.6), the second stability condition, equation (16.12), reduces to

$$\left.\frac{\partial P}{T \partial V}\right|_T < 0 . \tag{16.13}$$

With a few bizarre exceptions (33), temperature T is positive, so that the stability condition (16.13) is the same as $\partial P/\partial V|_T < 0$. Condition (16.13) is a constraint on the equation of state [that is, on the function $P(T,N,V)$] of the system: it says that pressure must decrease in an isothermal expansion.

Question (16.3): Show that

$$C_P - C_V = -\frac{(\partial P/\partial T|_V)^2}{\partial(P/T)/\partial V|_T} . \tag{16.14}$$

(Hint: my proof involves one application of one of Maxwell's relations, and one transformation of variables by the method of Jacobians). Hence (you may quote eq. [16.12]) or otherwise show that the second stability condition (16.3) is equivalent to the requirement that the adiabatic index $\gamma \equiv C_P/C_V$ is greater than unity

$$\gamma > 1 \ . \tag{16.15}$$

17. Some Examples Derivable by Scaling Arguments

The physics of any particular thermodynamic situation is contained in the function $S(U, N, V)$, or more generally $S(C)$ as a function of all the conserved properties or external parameters C of interest. The fundamental equations (14.1) and (14.2) do not specify what that information is. In general, the functional form of S must be determined from a detailed investigation of the microphysics. However, there is an interesting class of problems where one can draw conclusions about the functional form of S by simple scaling arguments, without looking too closely at precise details. The arguments below are not intended to be terribly rigorous; the idea is to give you a taste of what the thermodynamics of realistic systems looks like. Along the way we meet a hoary old problem known as the $N!$ problem.

Consider first the thermodynamics of so-called free particles. You may recall from quantum mechanics that the number of states $d\Omega_{\text{free}}$ of a free particle in an interval $d^3x d^3p$ of phase space is

$$d\Omega_{\text{free}} = \frac{g_{\text{spin}} d^3x d^3p}{h^3} \ , \tag{17.1}$$

where the g_{spin} factor is the number of different spin states of the particle, and h is Planck's constant. For nonrelativistic particles, particle momentum p is proportional to the square root of the particle energy ϵ, $p \propto \epsilon^{1/2}$, while for relativistic particles, particle momentum is proportional to particle energy, $p \propto \epsilon$. Considering that the energy available to each particle is $\epsilon \approx U/N$, one can conclude from equation (17.1), just by scaling arguments, that the number of states of each free particle must behave like

$$\Omega_{\text{free}}(\text{each particle}) \propto V(U/N)^q \ , \tag{17.2}$$

where $q = 3/2$ for nonrelativistic particles, $q = 3$ for relativistic particles. If the states of single particles are completely independent of one another (in particular, they satisfy no exclusion principle; read the paragraph containing eqs. [28.6]-[28.8] for a clarification of this point) then Ω_{free} is multiplicative over single particle states, so that

$$S_{\text{free}}(U, N, V) \equiv k \ln \Omega_{\text{free}}(U, N, V) = Nk \left\{ \text{constant} + \ln[V(U/N)^q] \right\} \quad ??? \tag{17.3}$$

You will notice that I have put question marks after equation (17.3). This is because equation (17.3) contains a piece $N \ln V$ that seems to violate the expectation that entropy should be extensive. The difficulty is attributable to the fact that in the counting of states I have effectively treated the particles of the system as distinguishable objects. If in fact the particles are indistinguishable, then the number of states must be reduced by some permutation factor. Scaling arguments imply that, if entropy is to be a truly extensive quantity, then equation (17.3) must be modified to

$$S_{\text{free}}(U, N, V) = Nk \left\{ \text{constant} + \ln[(V/N)(U/N)^q] \right\} \ . \tag{17.4}$$

You will note that the modification from (17.3) to (17.4) amounts to a reduction in entropy by $kN \ln N \approx k \ln(N!)$, which is about what you might expect for a permutation factor. This is the famous $N!$ problem. Pathria calls it the **Gibbs paradox**, and discusses it on pages 24-27. For clarification and rigorous resolution of the problem, wait till the formalism of partition functions has been developed. See especially §§28, 31, and 32.

From equation (17.4) it follows that

$$\frac{1}{T} = \left.\frac{\partial S_{\text{free}}}{\partial U}\right|_{N,V} = \frac{qNk}{U} \ , \tag{17.5}$$

$$\frac{P}{T} = \left.\frac{\partial S_{\text{free}}}{\partial V}\right|_{U,N} = \frac{Nk}{V} \ . \tag{17.6}$$

I have omitted the expression for $-\mu/T = \partial S/\partial N$ because it involves an unknown constant from equation (17.4), which my scaling arguments were insufficient to determine. Equations (17.5) and (17.6) yield the familiar equations of state for free particles

$$U = qNkT \ , \tag{17.7}$$

$$PV = NkT \ , \tag{17.8}$$

with $q = 3/2$ for nonrelativistic particles, $q = 3$ for relativistic particles. In an adiabatic experiment on a system of free particles, where the energy U and volume V are allowed to vary, but entropy S_{free} and number N are fixed, equation (17.4) implies that VU^q must remain constant. In view of the relations (17.7) and (17.8), the constancy of VU^q in an adiabatic experiment implies the familiar result

$$PV^\gamma = \text{constant} \ , \tag{17.9}$$

where the adiabatic index γ (see *question [15.2]*), is

$$\gamma = \frac{q+1}{q} \ , \tag{17.10}$$

which is equal to 5/3 for nonrelativistic free particles ($q = 3/2$), and equal to 4/3 for relativistic free particles ($q = 3$).

The above scaling arguments can be extended to the case where the particles have internal degrees of freedom that can be approximated as collections of classical simple harmonic oscillators (things on springs). In the days before quantum mechanics the only way people knew how to treat the internal degrees of freedom of atoms was to suppose that they behaved somehow like simple harmonic oscillators. This philosophy led for example to the notion of the **oscillator strength** of an atomic transition, which is essentially 'how many electronic harmonic oscillators an atomic transition is equivalent to'. Probably you will recall that in quantum mechanics a simple harmonic oscillator has discrete uniformly spaced energy levels. In the classical limit, the spacing of energy levels goes to zero, so that the energy levels form a continuum. Thus the basic feature of a classical simple harmonic oscillator (sho) is that the number of states $d\Omega_{\text{sho}}$ in an interval of energy $d\epsilon$ is a constant

$$d\Omega_{\text{sho}} \propto d\epsilon \ . \tag{17.11}$$

It follows from equation (17.11), by scaling arguments, that $\Omega_{\text{sho}} \propto U/N$ for a single harmonic oscillator, or more generally, for a particle whose internal degrees of freedom can be modeled as a system of f independent harmonic oscillators,

$$\Omega_{\text{int}}(\text{each particle}) \propto (U/N)^f \ . \tag{17.12}$$

Note that the internal states of the particle are here independent of volume, which will be true physically if the volume available to the particle is much larger than the size of the particle. The combination of the supposedly simple harmonic internal degrees of freedom of the particles, plus their translational degrees of freedom, leads to an expression for the total entropy of the N-particle system as

$$S(U,N,V) = S_{\text{free}} + S_{\text{int}} = Nk\left\{\text{constant} + \ln[(V/N)(U/N)^{q+f}]\right\} \ . \tag{17.13}$$

All the results (17.5) to (17.10) follow as before, but with q replaced by $q + f$. In particular,

$$U = (q + f)NkT \ , \tag{17.14}$$

$$PV = NkT \ . \tag{17.15}$$

The adiabatic index γ is now

$$\gamma = \frac{q + f + 1}{q + f} \ . \tag{17.16}$$

That each harmonic oscillator makes a contribution kT to the energy U, according to equation (17.14) (N particles, each comprising f oscillators, contributes $fNkT$ to U), is in accordance with a theorem known as the **equipartition theorem**. The equipartition theorem states that each quadratic term in the Hamiltonian of the system makes a contribution $kT/2$ to the energy. A harmonic oscillator has two quadratic terms, one in the momenta and one in the coordinates, yielding kT per oscillator. The number of quadratic terms in the Hamiltonian is sometimes called the number of **degrees of freedom** of the system.

Question (17.1): A **rigid rotator** has the property that it has a fixed moment of inertia I (which is in general a tensor in more than one dimension). Classically, a rigid rotator has angular momentum $J = I\omega$ and energy $\epsilon = I\omega^2/2$ where ω is the angular velocity. Quantum mechanically, the angular momentum is quantized in units of $\hbar$. Show that in the classical limit of large angular momentum the number of states of a one-dimensional rigid rotator in an interval $d\epsilon$ of energy is a power law in energy

$$d\Omega_{\text{rot}} \propto d\epsilon^f \ . \tag{17.17}$$

What is the index f of the power law? What is the corresponding result for an n-dimensional rigid rotator? What is the adiabatic index of a system of free particles each of which is an n-dimensional rigid rotator (you may quote eq. [17.16] if you wish)?

Question (17.2): The adiabatic index of air at room temperature and pressure is found to be $\gamma \approx 1.4$. Assume that the internal degrees of freedom of air molecules at room temperature arise from their rotational degrees of freedom, and assume that the molecules can be modeled as rigid rotators. Using your answer to *question (17.1)* above, what can you deduce about the nature of air molecules? What would you expect the adiabatic index of air to be:

(a) at temperatures $\lesssim 10\,\text{K}$, at which neither rotational nor vibrational levels of air molecules are excited;

(b) at temperatures $\gtrsim 1000\,\text{K}$, at which both rotational and vibrational levels of air molecules are excited?

Assume that each vibrational degree of freedom can be approximated as a simple harmonic oscillator. Diatomic molecules have 2 rotational and 1 vibrational degree of freedom, while molecules containing $N \geq 3$ atoms have 3 rotational and $3N - 6$ vibrational degrees of freedom.

18. Ensembles

So far the discussion has been confined to closed systems, or to very large systems in thermal contact. However, such considerations leave unanswered some essential questions of detail. For example, one might consider a single hydrogen atom inside a system in thermal equilibrium, say in the atmosphere of a star, and ask what is the probability that the atom is in each of its possible states? It is no longer possible to say blithely that the atom will be in its most probable state, because there's a good chance it won't be. It is to deal with such questions that one introduces the notions of canonical and grand canonical ensembles.

An **ensemble** is a collection states of a system, in which each state is supposed to occur with some specified (not necessarily equal) probability. An ensemble is a convenient mathematical fiction that formalizes the physical idea that a system evolves though many states, and that the thing of interest is not so much the exact state of the system at any instant, but rather the distribution of probabilities of finding the system in each of its many possible states. The hypothesis of thermodynamic equilibrium (defined in §6 above) defines certain special ensembles, which are termed **canonical**.

(a) Microcanonical Ensemble

A **microcanonical ensemble** is the ensemble of (many-particle) states of a system having a definite internal energy U, number of particles N, and volume V, each state being considered to occur with the same probability.

The microcanonical ensemble is characterized by U, N, V.

(b) Canonical Ensemble

A **canonical ensemble** is the ensemble of (many-particle) states of a system in contact with a vast thermal reservoir, such that the system has a definite number of particles N and volume V, but the energy of the system may be exchanged with that of the reservoir; each state of the entire system plus reservoir is considered to occur with equal probability.

The canonical ensemble is characterized by $\beta \equiv 1/kT$, N, V.

(c) Grand Canonical Ensemble

A **grand canonical ensemble** is the ensemble of (many-particle) states of a system in contact with a vast thermal reservoir, such that the system has a definite volume V, but both the number of particles and the energy of the system may be exchanged with that of the reservoir; each state of the entire system plus reservoir is considered to occur with equal probability.

The grand canonical ensemble is characterized by $\beta \equiv 1/kT$, $\alpha \equiv -\mu/kT$, V.

(d) Other Canonical Ensembles

In general, one can consider systems that are able to exchange various other conserved quantities with some vast thermal reservoir. For example, one can consider a piston, containing a fixed number of particles, lying inside a vast reservoir, such that the volume of the piston can change, but the total volume of the system plus reservoir is fixed. The set of states of the system will constitute a canonical ensemble provided that each state of the entire system plus reservoir occurs with equal probability, which is the same as saying that the entire system plus reservoir is in thermal equilibrium.

A Slightly Subtle Point Concerning Nonideal Gases

At this point it's appropriate to mention a slightly subtle point about the definition of canonical ensembles, which makes no difference in ideal gases, but it does affect nonideal gases. Although the system is supposed to be in contact with a vast reservoir, the wavefunctions of the system are considered to be evaluated subject to the boundary conditions imposed by the system volume V. If you like, the system is connected to the reservoir only by a thin pipe. Thus (grand) canonical ensembles of nonideal gases can experience, for example, surface effects arising from the finiteness of the volume V.

19. State Occupation Probabilities

The point of introducing the ensembles just defined was to allow us to determine the probability that a system (e.g. a hydrogen atom in a stellar atmosphere) is in any particular state. So let's do that.

(a) **Microcanonical Ensemble**

In a microcanonical ensemble, the probability P_j of the system being in any particular state j is by definition the same for all states, so is just the reciprocal of the number of states $\Omega(U, N, V)$ of the system:

$$P_j = \frac{1}{\Omega(U, N, V)} \ . \tag{19.1}$$

Kind of trivial, huh? Also kind of uninformative.

(b) **Canonical Ensemble**

Matters liven up in the canonical ensemble. The question is: what is the probability P_j that the system in a canonical ensemble is in a particular (many-particle) state j, with energy U_j? The hypothesis that all states of the combined system plus reservoir are equally likely implies that the probability P_j is proportional to the number of states of the system plus reservoir such that the system is in state j. Now the number of states of the system such the system is in state j is obviously just one. The only constraint on the reservoir is that its energy should be $U - U_j$, where U is the total conserved energy of the entire system plus reservoir. Thus the probability P_j of the system being in state j is proportional to the number of states $\Omega_{\rm res}(U - U_j)$ of the reservoir having energy $U - U_j$:

$$P_j \propto \Omega_{\rm res}(U - U_j) \ . \tag{19.2}$$

Since the reservoir is by hypothesis vast compared to the system, it is to be expected that the system energy U_j is very small compared to the total energy U of the system plus reservoir. This suggests that the obvious thing to do with equation (19.2) is to try to expand it as a power series in the 'small' quantity U_j. However, this must be done with due care and attention. The thing to note is that the number of states $\Omega_{\rm res}$ is multiplicative over vast, hence independent, subsystems of the vast reservoir. Hence $\ln \Omega_{\rm res}$ increases linearly with the huge volume $V_{\rm res}$ of the reservoir, $\ln \Omega_{\rm res} \propto V_{\rm res}$. For a reservoir with a given temperature, equation (9.4), energy also increases linearly with the volume of the reservoir, $U_{\rm res} \approx U \propto V_{\rm res}$. Thus, while the first derivative of $\ln \Omega_{\rm res}$ with respect to energy is a constant independent of the reservoir volume, $\partial \ln \Omega_{\rm res} / \partial U = 1/kT$, the second derivative decreases inversely with reservoir volume, $\partial^2 \ln \Omega_{\rm res} / \partial U^2 \propto 1/V_{\rm res}$, the third derivative decreases as the inverse square of reservoir volume, $\partial^3 \ln \Omega_{\rm res} / \partial U^3 \propto 1/V_{\rm res}^2$, and so on. In the limit of infinite reservoir volume, $V_{\rm res} \to \infty$, the second and higher derivatives of $\ln \Omega_{\rm res}$ with respect to energy are all zero, $\partial^n \ln \Omega_{\rm res} / \partial U^n \to 0$ as $V_{\rm res} \to \infty$ for $n \geq 2$. So, the Taylor expansion in U_j of the logarithm of equation (19.2) yields, in the limit of infinite reservoir volume,

$$\ln P_j = \ln P_0 - U_j \frac{\partial \ln \Omega_{\rm res}(U)}{\partial U} = \ln P_0 - \frac{U_j}{kT} \ , \tag{19.3}$$

where the state 0 is the ground state of the system, with zero energy, $U_0 = 0$. According to equation (19.3), the probability P_j that a system in a canonical ensemble is in state j with energy U_j is proportional to

$$P_j \propto e^{-U_j/kT} \ , \tag{19.4}$$

the famous **Boltzmann factor**.

Question (19.1): Read Pathria's comments at the top of page 53 on expanding P_j as a Taylor series in U_j. Is he right, or is he pulling wool? Try expanding P_j as a Taylor series without first taking the logarithm, and see what happens.

To effect the normalization of the probabilities P_j from equation (19.4), note that the sum of probabilities over all states j of the system must be unity, $\sum P_j = 1$. Hence

$$P_j = \frac{e^{-U_j/kT}}{Z(N)} \ , \tag{19.5}$$

where $Z(N)$ is the so-called **partition function** for N particles, defined by

$$Z(T, N, V) \equiv \sum_{\text{states } j} e^{-U_j/kT} \ , \tag{19.6}$$

the summation being over all states j of the system in the canonical ensemble.

(c) **Grand Canonical Ensemble**

The probability P_j that the system in a grand canonical ensemble is in a state j with energy U_j and number N_j is derived by essentially the same argument as for the canonical ensemble. The probability P_j is now proportional to the number of states of the reservoir having energy $U - U_j$ and number $N - N_j$

$$P_j \propto \Omega_{\text{res}}(U - U_j, N - N_j) \tag{19.7}$$

which is the grand canonical analog of canonical equation (19.2). Arguments identical to those following equation (19.2) in the canonical case lead to the grand canonical analog of equation (19.3):

$$\ln P_j = \ln P_0 - U_j \frac{\partial \ln \Omega_{\text{res}}(U, N)}{\partial U} - N_j \frac{\partial \ln \Omega_{\text{res}}(U, N)}{\partial N} = \ln P_0 - \frac{U_j}{kT} + \frac{\mu N_j}{kT} \ , \tag{19.8}$$

where the state 0 is the ground state of the system, with zero particles and zero energy, $U_j = N_j = 0$. According to equation (19.8), the probability P_j that a system in a grand canonical ensemble is in state j with energy U_j and number N_j is proportional to

$$P_j \propto e^{(-U_j + \mu N_j)/kT} \ . \tag{19.9}$$

The normalization of the probabilities P_j in equation (19.9) is again effected by the requirement that the sum of the probabilities P_j over all states of the system must be unity, $\sum P_j = 1$. Hence the probabilities P_j are

$$P_j = \frac{e^{(-U_j + \mu N_j)/kT}}{Z_G} \ , \tag{19.10}$$

where Z_G is the **grand partition function**, defined by

$$Z_G(T, \mu, V) \equiv \sum_{\text{states } j} e^{(-U_j + \mu N_j)/kT} \ , \tag{19.11}$$

the summation being over all states j of the system in the grand canonical ensemble. The relation between the grand partition function Z_G, eq. (19.11), and the N-particle partition functions $Z(N)$, eq. (19.6), is easily seen to be

$$Z_G(T, \mu, V) = \sum_{N=0}^{\infty} Z(T, N, V) e^{\mu N/kT} \ . \tag{19.12}$$

(d) **Other Canonical Ensembles**

The arguments concerning the probabilities in the case of the canonical ensemble generalize without ado to any other kind of canonical ensemble you might care to contemplate. In general, the probability

P_j of finding a system in state j in an ensemble that is able to exchange various conserved quantities C with a vast reservoir is

$$P_j = \frac{e^{-\sum \gamma C_j}}{\sum_{\text{states } j} e^{-\sum \gamma C_j}} \ , \tag{19.13}$$

where the sums $\sum \gamma C_j$ are taken over the conserved quantities C exchanged with the reservoir, and γ, equation (10.1), are the thermodynamic variables corresponding to the respective conserved quantities.

Question (19.2): Someone throws a normal 6-sided die many times. After a large number of throws, you are told that the mean of the numbers thrown so far is $\bar{N}$, which is a number between 1 and 6, not necessarily 3.5. What is the probability distribution of the numbers 1 to 6 thrown? (The probabilities are no longer the *a priori* probabilities 1/6, because you have been told some information about the system. You should find that the system is characterized by a quantity that has the character of a 'temperature', and you should find an implicit equation for the temperature. You need not solve this implicit equation explicitly, but you should show that the solution is unique. Draw a graph, with labeled axes, of the 'temperature' versus $\bar{N}$.)

20. Partition Functions

The partition functions of the (grand) canonical ensembles were introduced in the previous section, equations (19.6) and (19.11). Partition functions are so important that I can't let their introduction go by without giving them a section all of their own, so here it is. All I want to say is, partition functions play the starring role in going from microphysics to macroscopic thermodynamics.

Question (20.1): Show that the (grand) partition function defined by equation (19.6) (eq. [19.11]) is multiplicative over independent systems with the same temperature (and chemical potential). Suppose the states of molecules can be can be decomposed as a combination of free translational motion, rotational, vibrational, and electronic states, each of which modes is independent of the other (i.e. the wavefunction is a simple product of free, rotational, vibrational, and electronic states). What is the relation between the total single particle partition function $Z(1)$ and the partition functions $Z_{\text{free}}(1)$, $Z_{\text{rot}}(1)$, $Z_{\text{vib}}(1)$, and $Z_{\text{elec}}(1)$ of the individual modes?

Question (20.2): The hydrogen atom has bound state energy levels $E_n = -1/(2n^2)$ with $n = 1, 2, ...$ in atomic units $e = \hbar = m_e$, the nth level being $2n^2$-fold degenerate. Show that the one-particle partition function of the bound states of the H-atom is formally divergent. Explain the physical origin of this divergence, and what might be done to overcome it. Why is it often sufficient, in problems not requiring high accuracy, to include in the H-atom partition function only the contribution of the ground state?

Question (20.3): Discuss the population of the $n = 2$ level of hydrogen. At approximately what temperature does this population reach a maximum? Why are Balmer lines strongest in A stars? When I say strong, do I mean strong in emission or in absorption?

21. Energy and its Fluctuations

Equations (19.5) and (19.10) specify the entire distribution of probabilities of states of different energies in a (grand) canonical ensemble. From this information it is possible to deduce the moments of the energy distribution, in particular the mean energy $\bar{U}$ of the ensemble, and the variance $\langle \Delta U^2 \rangle$ of energy fluctuations.

The mean energy $\bar{U}$ of the (grand) canonical ensemble is found by differentiating the (grand) partition function with respect to $-1/kT$. For the canonical ensemble,

$$\left.\frac{\partial Z(N)}{\partial(-1/kT)}\right|_V = \sum_{\text{states } j \text{ with } N_j=N} U_j e^{-U_j/kT} = \sum_{\text{states } j \text{ with } N_j=N} U_j P_j Z(N) = \bar{U} Z(N) \ , \tag{21.1}$$

while for the grand canonical ensemble, with μ/kT and V held constant,

$$\left.\frac{\partial Z_G}{\partial(-1/kT)}\right|_{\mu/kT,V} = \sum_{\text{states } j} U_j e^{(-U_j+\mu N_j)/kT} = \sum_{\text{states } j} U_j P_j Z_G = \bar{U} Z_G \ . \tag{21.2}$$

Hence one obtains an equation for the mean energy $\bar{U}$ of the (grand) canonical ensemble as a derivative of the (grand) partition function

$$\bar{U} = \left.\frac{\partial \ln Z(N)}{\partial(-1/kT)}\right|_V = \left.\frac{\partial \ln Z_G}{\partial(-1/kT)}\right|_{\mu/kT,V} \ . \tag{21.3}$$

Equation (21.3) is the first fundamental link from the microphysics of the partition function to macroscopic thermodynamics.

Higher derivatives of the partition function with respect to $-1/kT$ yield higher moments of the energy. For example, the second derivative of the logarithm of the partition function with respect to $-1/kT$ yields the second central moment of energy. For the canonical ensemble,

$$\left.\frac{\partial^2 \ln Z(N)}{\partial(-1/kT)^2}\right|_V = \left.\frac{\partial^2 Z(N)}{Z(N)\partial(-1/kT)^2}\right|_V - \left[\left.\frac{\partial Z(N)}{Z(N)\partial(-1/kT)}\right|_V\right]^2 = U^2 - \bar{U}^2 = \langle \Delta U^2 \rangle \ . \tag{21.4}$$

The same derivation works for the grand canonical ensemble, if the derivatives are carried out with μ/kT and V held fixed. Thus the variance of energy is

$$\langle \Delta U^2 \rangle = \left.\frac{\partial^2 \ln Z(N)}{\partial(-1/kT)^2}\right|_V = \left.\frac{\partial^2 \ln Z_G}{\partial(-1/kT)^2}\right|_{\mu/kT,V} \ . \tag{21.5}$$

The third and fourth derivatives of $\ln Z$ with respect to $-1/kT$ give

$$\begin{aligned} \langle \Delta U^3 \rangle &= \left.\frac{\partial^3 \ln Z(N)}{\partial(-1/kT)^3}\right|_V = \left.\frac{\partial^3 \ln Z_G}{\partial(-1/kT)^3}\right|_{\mu/kT,V} \ , & (21.6) \\ \langle \Delta U^4 \rangle - 3\langle \Delta U^2 \rangle^2 &= \left.\frac{\partial^4 \ln Z(N)}{\partial(-1/kT)^4}\right|_V = \left.\frac{\partial^4 \ln Z_G}{\partial(-1/kT)^4}\right|_{\mu/kT,V} \ . & (21.7) \end{aligned}$$

The moments $\langle \Delta U^2 \rangle$, $\langle \Delta U^3 \rangle$, $\langle \Delta U^4 \rangle - 3\langle \Delta U^2 \rangle^2$, and so on, which are successive partial derivatives of $\ln Z$, are called **irreducible moments**. They have the property of being additive over independent subsystems, unlike the raw moments $\langle U^n \rangle$. The additivity is a consequence of the additivity of $\ln Z$ over independent subsystems.

By now you are beginning to get some idea of the power of the partition function.

Question (21.1): A gaussian, or normal, distribution is defined by the property that the third and higher irreducible moments are zero. Show that the distribution of fluctuations of energy is asymptotically gaussian for large systems, in the sense that

$$\bar{U} \gg \langle \Delta U^2 \rangle^{1/2} \gg \langle \Delta U^3 \rangle^{1/3} \gg (\langle \Delta U^4 \rangle - 3\langle \Delta U^2 \rangle^2)^{1/4} \gg \ldots \ . \tag{21.8}$$

How does the width of the gaussian change with volume in an ideal gas? (Hint: use the fact that irreducible moments are all proportional to volume, which is true as long as the subvolumes are independent of each other, which is true in particular for an ideal gas. You should find that the irreducible moments, far from going to zero, all diverge. Clarify then what is meant here by 'asymptotically gaussian'.) Justify the sentence beginning 'If the two systems are each large ...' just before equation (9.3).

By the way, if you just did the above question, then you have just proved some version of the Central Limit Theorem. Not bad after all, huh?

Question (21.2): Relate the variance of fluctuations $\langle \Delta U^2 \rangle$ of energy in the canonical ensemble to the specific heat C_V at constant volume. Interpret physically your result.

22. Number and its Fluctuations

In the canonical ensemble, the number of particles is just N, a known, set quantity. In the grand canonical ensemble the number N is variable. Its mean and higher moments can be determined by successive differentiations of $\ln Z_G$ with respect to μ/kT, in much the same manner as the moments of energy were derived in the previous section by successive differentiations of $\ln Z$ with respect to $-1/kT$.

An equation for the mean number $\bar{N}$ of particles in a grand canonical ensemble is gotten by differentiating the grand partition function with respect to μ/kT, with T and V held constant:

$$\left. \frac{\partial Z_G}{\partial(\mu/kT)} \right|_{-1/kT,V} = \sum_{\text{states } j} N_j e^{(-U_j+\mu N_j)/kT} = \sum_{\text{states } j} N_j P_j Z_G = \bar{N} Z_G \ . \tag{22.1}$$

Hence follows an equation for the mean number of particles $\bar{N}$ of the grand ensemble as a derivative of $\ln Z_G$:

$$\bar{N} = \left. \frac{\partial \ln Z_G}{\partial(\mu/kT)} \right|_{-1/kT,V} \ . \tag{22.2}$$

Equation (22.2) is the second fundamental link from the microphysics of the partition function to macroscopic thermodynamics.

Higher moments of number are obtained from higher derivatives of $\ln Z_G$ with respect to μ/kT:

$$\begin{aligned} \langle \Delta N^2 \rangle &= \left. \frac{\partial^2 \ln Z_G}{\partial(\mu/kT)^2} \right|_{-1/kT,V} , & (22.3) \\ \langle \Delta N^3 \rangle &= \left. \frac{\partial^3 \ln Z_G}{\partial(\mu/kT)^3} \right|_{-1/kT,V} , & (22.4) \\ \langle \Delta N^4 \rangle - 3\langle \Delta N^2 \rangle^2 &= \left. \frac{\partial^4 \ln Z_G}{\partial(\mu/kT)^4} \right|_{-1/kT,V} , & (22.5) \end{aligned}$$

and so on, exactly paralleling equations (21.5) to (21.7) for the moments of energy. The irreducible moments $\langle \Delta N^2 \rangle$, $\langle \Delta N^3 \rangle$, and $\langle \Delta N^4 \rangle - 3\langle \Delta N^2 \rangle^2$ are again additive over independent subsystems.

23. Joint Fluctuations of Energy and Number

The fluctuations of energy and number are in general correlated. For example, the cross-correlation $\langle \Delta U \Delta N \rangle$ of energy and number in the grand canonical ensemble is obtained by a technique that by now is becoming familiar, namely by differentiating $\ln Z_G$ once with respect to $-1/kT$, then once with respect to μ/kT:

$$\begin{aligned} \frac{\partial^2 \ln Z_G}{\partial(-1/kT)\partial(\mu/kT)} &= \frac{\partial^2 Z_G}{Z_G \partial(-1/kT)\partial(\mu/kT)} - \frac{\partial Z_G}{Z_G \partial(-1/kT)} \frac{\partial Z_G}{Z_G \partial(\mu/kT)} \\ &= UN - \bar{U}\bar{N} = \langle \Delta U \Delta N \rangle \ . \end{aligned} \tag{23.1}$$

Now you know, so let's move on.

24. Volume

The third fundamental link (the first two being eqs. [21.3] and [22.2]) from the microphysics of the partition function to macroscopic thermodynamics is established by considering the derivative of the partition function with respect to volume. In the (grand) canonical ensembles the volume V of the system is a definite quantity, which is not exchanged with the reservoir. However, just as one imagines thermodynamic operations that change the energy, number, and volume of a microcanonical ensemble, so also it is possible to imagine thermodynamic operations that change the volume of the system in the (grand) canonical ensembles.

For the canonical ensemble, it suffices to recognize that changing the volume V, with number of particles N and temperature T fixed, has an effect on the system, which can be construed as a change in the energy levels of the states of the ensemble (see §34, eq. [34.9] ff.), so that the derivative of the partition function with respect to volume is not necessarily zero. While it is customary in textbooks at this point to make arguments about how all this is related to the notion of pressure and work being done, I shall simply write down the partial derivative of $\ln Z(N)$ with respect to volume V as

$$\left. \frac{\partial \ln Z(N)}{\partial V} \right|_{-1/kT} = \frac{P}{kT} \ , \tag{24.1}$$

which I regard as the definition of **pressure** P in a canonical ensemble. That the definition is appropriate becomes clear when comparison is made to the classical equations of thermodynamics.

For the grand canonical ensemble I again write down the partial derivative of $\ln Z_G$ with respect to volume V as

$$\left. \frac{\partial \ln Z_G}{\partial V} \right|_{-1/kT, \mu/kT} = \frac{P}{kT} \ , \tag{24.2}$$

which I regard as the definition of **pressure** P in a grand canonical ensemble. A more physical explanation of what's going on here appears in §34.

Notwithstanding the apparent similarity of equations (24.1) and (24.2) between the canonical and grand canonical ensembles, matters are more interesting in the grand case. As you know, partition functions are multiplicative over independent systems in mutual thermodynamic equilibrium. In particular, the logarithm of the partition function is additive over the subvolumes of an ideal gas in thermodynamic equilibrium. In other words the logarithm of the grand partition function $\ln Z_G$ of an ideal gas is proportional to volume in a system with a given T, μ,

$$\ln Z_G = \frac{PV}{kT} \ , \tag{24.3}$$

where the constant of proportionality, P/kT, follows from equation (24.2). The same statement cannot be made about the partition function Z of the canonical ensemble, for in that case the increase of volume called for in equation (24.1) is carried out with N rather than μ held fixed, so that the 'new' volume will not in general be in thermodynamic equilibrium with the 'old' volume.

25. Entropy Revisited

The definition (13.1) of entropy S as Boltzmann's constant times the logarithm of the number of states, $k \ln \Omega$, is fine for a microcanonical ensemble, but it's not quite good enough for the canonical or grand canonical ensembles, where it's not so obvious how to count different states that occur with different probability. However, each state of the entire system plus reservoir occurs with equal probability, so the entropy

$$S_{\text{tot}} = k \ln \Omega_{\text{tot}} \tag{25.1}$$

of the whole system plus reservoir is well-defined. Now entropy is additive over independent systems, so it seems a good idea to impose the requirement of additivity on the entropies of the system and the reservoir. In other words, entropy needs to be defined so that it is the sum of its parts, the entropy S of the system plus the entropy S_{res} of the reservoir:

$$S_{\text{tot}} = S + S_{\text{res}} \ . \tag{25.2}$$

If the energy (and number) in the reservoir were exactly fixed, life would be very simple: the entropy of the reservoir would be $S_{\text{res}} = k \ln \Omega_{\text{res}}(U_{\text{res}}, N_{\text{res}})$. In reality the energy (and number) in the reservoir fluctuate slightly, because of the small amount of energy (and number) which the reservoir exchanges with the system. The obvious thing to do then is to define the entropy of the reservoir as an average over the fluctuating energy (and number)

$$S_{\text{res}} \equiv k \ln \Omega_{\text{res}}(U_{\text{res}}, N_{\text{res}}) = k \sum_{\text{states } j} P_j \ln[\Omega_{\text{res}}(U - U_j, N - N_j)] \ , \tag{25.3}$$

where the summation is over all states j of the system, and U, N represent the fixed total energy and particle number of the entire system plus reservoir. The notion of defining entropy by an average becomes especially plausible when you consider that the thermodynamics of (grand) canonical ensembles involves the average energy $\bar{U}$ (and average number $\bar{N}$) of the system, in place of the fixed energy U and number N of a microcanonical ensemble (see eqs. [21.3] and [22.2]). But now according to equation (19.2) or (19.7), the probability P_j that the system is any one state j is proportional to $\Omega_{\text{res}}(U - U_j, N - N_j)$. In fact, considering that the total number of states of the system plus reservoir is $\Omega_{\text{tot}} = \sum_j \Omega_{\text{res}}(U - U_j, N - N_j)$ it must be that

$$P_j = \frac{\Omega_{\text{res}}(U - U_j, N - N_j)}{\Omega_{\text{tot}}} \ . \tag{25.4}$$

Substituting equation (25.4) into equation (25.3), and using equations (25.1) and (25.2), yields

$$S = S_{\text{tot}} - S_{\text{res}} = k \ln \Omega_{\text{tot}} - k \sum_{\text{states } j} P_j \ln[P_j \Omega_{\text{tot}}] = -k \sum_{\text{states } j} P_j \ln P_j \ . \tag{25.5}$$

Equation (25.5) is so important that it is worth writing down again all by itself:

$$S = -k \sum_{\text{states } j} P_j \ln P_j \ . \tag{25.6}$$

Equation (25.6) is often taken as the definition of entropy in a general ensemble, since it works quite generally in situations where the definition $S = k \ln \Omega$ is inadequate. The definition (25.6) of entropy is a fundament of the mathematical discipline of Information Theory. The demonstration that entropy defined by equation (25.6) inevitably increases in closed Hamiltonian systems, Boltzmann's famous H-theorem, was one of the profound achievements of statistical mechanics in the nineteenth century.

Question (25.1): Show directly that the entropy defined by equation (25.6) is additive over independent systems, that it reduces to the definition $S = k \ln \Omega$ in the case of a microcanonical ensemble, and that it is zero if the system accesses only a single state j.

In the case of the canonical ensemble, inserting the probabilities (19.5) into the expression (25.6) for entropy yields

$$\frac{S}{k} = - \sum_{\text{states } j} \frac{e^{-U_j/kT}}{Z(N)} \ln \left[\frac{e^{-U_j/kT}}{Z(N)} \right] = \ln Z(N) + \frac{\bar{U}}{kT} \ . \tag{25.7}$$

In the case of the grand canonical ensemble, the probabilities (19.10) inserted into the expression (25.6) for entropy yield

$$\frac{S}{k} = - \sum_{\text{states } j} \frac{e^{(-U_j+\mu N_j)/kT}}{Z_G} \ln \left[\frac{e^{(-U_j+\mu N_j)/kT}}{Z_G} \right] = \ln Z_G - \frac{\mu \bar{N}}{kT} + \frac{\bar{U}}{kT} \ . \tag{25.8}$$

26. Free Energy Minimization

Entropy (25.6) strives to attain a maximum in a closed system. However, (grand) canonical ensembles are not closed systems, being able to exchange energy (and number) with a vast reservoir. Therefore the entropy of the system is not generally a maximum in thermodynamic equilibrium. Only the total entropy of the system plus reservoir is maximized in thermodynamic equilibrium.

In a canonical ensemble, the aspiration of the system to maximize its entropy is constrained by the requirement that its temperature equal that of the vast reservoir, $T = T_{\text{res}}$. This means that any variation of the entropy of the system is accompanied by an exchange of energy with the reservoir in such a way that

$$\delta S = \delta \bar{U} \frac{\partial S}{\partial \bar{U}} = \frac{\delta \bar{U}}{T} = \frac{\delta \bar{U}}{T_{\text{res}}} \tag{26.1}$$

for small variations about equilibrium. In other words,

$$\delta S - \frac{1}{T} \delta \bar{U} = \delta \left(S - \frac{\bar{U}}{T} \right) = 0 \ , \tag{26.2}$$

which is to say that the entropy of the canonical ensemble is not maximized, but rather the quantity $\bar{S} - \bar{U}/T$ is maximized. Equivalently, the **free energy** F

$$F \equiv \bar{U} - TS \tag{26.3}$$

is minimized. It should be remarked that the principle of free energy minimization is more limited than the principle of entropy maximization, since the former can be applied only to systems that are already partially equilibrated in the sense of having a definite temperature. By contrast, entropy is defined, by equation (25.6), for arbitrary ensembles.

The principle of free energy minimization is useful for practical computations of thermodynamic equilibrium in complicated mixtures of reacting species (see §35, paragraph containing eqs. [35.13]-[35.15]). That is, one writes down the free energy of a system as a function of temperature T, volume V, and the numbers N_{X} of the various particle species X of interest, and then finds numerically the minimum of the free energy with respect to variations of the numbers N_{X}.

Question (26.1): What quantity is maximized/minimized in a grand canonical ensemble?

27. Summary of Thermodynamical Equations for the (Grand) Canonical Ensembles

(a) Canonical Ensemble

The properties of the partition function $Z(N)$ of the canonical ensemble, as defined by equation (19.6), can be summarized in two equations (gotten from eqs. [21.3], [24.1], and [25.7]):

$$\begin{aligned} d\ln Z(N) &= \bar{U} d\left(\frac{-1}{kT}\right) + \frac{P}{kT} dV \ , & (27.1) \\ \ln Z(N) &= \frac{S}{k} - \frac{\bar{U}}{kT} \ , & (27.2) \end{aligned}$$

from which follow all the familiar equations of thermodynamics for systems where N is fixed. In particular, eliminating $\ln Z(N)$ between equations (27.1) and (27.2) leads to the familiar equation (14.1) of thermodynamics, except with $dN = 0$ since N is fixed. Equations (27.1) and (27.2) are true in both ideal and nonideal gases, since none of the relevant arguments in §§18–25 invoked ideality. Equation (27.2) can be written

$$-kT \ln Z(N) = \bar{U} - TS \ , \tag{27.3}$$

which is the free energy of the canonical ensemble.

(b) Grand Canonical Ensemble

The properties of the grand partition function Z_G of the grand canonical ensemble, as defined by equation (19.11), can be summarized in three equations (gotten from eqs. [21.3], [22.2], [24.2], [25.8], and [24.3]):

$$\begin{aligned} d\ln Z_G &= \bar{U} d\left(\frac{-1}{kT}\right) + \bar{N} d\left(\frac{\mu}{kT}\right) + \frac{P}{kT} dV \ , & (27.4) \\ \ln Z_G &= \frac{S}{k} - \frac{\bar{U}}{kT} + \frac{\mu \bar{N}}{kT} \ , & (27.5) \\ \ln Z_G &= \frac{PV}{kT} \ , & (27.6) \end{aligned}$$

from which flow the two familiar fundamental equations (14.1) and (14.2) of thermodynamics in which number N is also allowed to vary. Equations (27.4) and (27.5) are true in both ideal and nonideal gases, but equation (27.6) is only true in ideal gases (see the argument in the paragraph containing eq. [24.3]).

The classical thermodynamic quantity (27.5) corresponding to $\ln Z_G$ is so important that you'd think it, or something near it, like $kT \ln Z_G$, would have a suitably impressive name, but it doesn't. Pathria calls $\ln Z_G$ the q-potential. A close relative is the so-called **Gibbs free energy** $G \equiv U - TS + PV$, which is kT times the logarithm of the partition function that you would get if you considered an ensemble in which the number of particles N is fixed, but energy U and volume V are allowed to vary by exchange with a vast thermal reservoir. In some sense, the q-potential is to the Gibbs free energy as Eulerian mechanics is to Lagrangian mechanics, as a Hamiltonian is to a Lagrangian, as the Schroedinger or Dirac equations are to the Feynman path integral formalism.

Question (27.1): Consider a system of particles of mass m immersed in a uniform externally applied gravitational field $\boldsymbol{g}$. Is thermodynamic equilibrium still possible? Argue that the presence of the gravitational field makes the energies of the states of a parcel of gas a function of its height $\boldsymbol{r}$. Show that the partial derivative of the grand partition function, equation (19.11), of a parcel of gas with respect to its height $\boldsymbol{r}$ is

$$\left.\frac{\partial \ln Z_G}{\partial \boldsymbol{r}}\right|_{T,\mu,V} = \frac{\bar{N} m \boldsymbol{g}}{kT} \ . \tag{27.7}$$

Hence show that an ideal gas in thermodynamic equilibrium must satisfy the usual equation of hydrostatic equilibrium

$$\nabla P = \rho \boldsymbol{g} \ , \tag{27.8}$$

where $\rho \equiv m\bar{N}/V$ is the mass density (assume equation [27.6]). Do T or μ vary with height?

Question (27.2): A one-dimensional quantum mechanical simple harmonic oscillator has equally spaced energy levels $\epsilon_n = \hbar\omega(n + 1/2)$, with one state per energy level.

(a) For a single particle in the SHO, determine explicit expressions for partition function, the mean energy, and the specific heat.

(b) The classical limit corresponds to $\hbar \to 0$. Find the classical limits of your results for (a).

28. Partition Function of an Ideal Fermi-Dirac Gas

The key property of a system in statistical mechanics is its partition function. Once you know the partition function of a system, working out the thermodynamics is just a matter of applying equations (27.1) and (27.2) or (27.4) to (27.6) of the previous section.

A Fermi-Dirac, or Fermi, gas has the property that the particles of the system are indistinguishable, and no two particles can occupy exactly the same single-particle state. The single-particle partition function $Z(1)$ of the system is, as always,

$$Z(1) \equiv \sum_{\text{states } i \text{ with } N_i = 1} e^{-\epsilon_i/kT} \ , \tag{28.1}$$

where I've written the energy as ϵ rather than U to remind you that it's the energy of a single particle. If the system is ideal and is described by Fermi statistics, how is the partition function $Z(2)$ for say two particles related to the single-particle partition function? It's

$$\begin{aligned} Z(2) \ &\equiv \sum_{\text{states } j \text{ with } N_j = 2} e^{-U_j/kT} = \frac{1}{2!} \sum_{\text{states } i \neq j \text{ with } N_i = 1} \ \sum_{\text{states } j \text{ with } N_j = 1} e^{-\epsilon_i/kT} e^{-\epsilon_j/kT} \\ &= \frac{1}{2!} \left(Z(1)^2 - \sum_{\text{states } i \text{ with } N_i = 1} e^{-2\epsilon_i/kT} \right) \ . \end{aligned} \tag{27.7}$$

The factor $1/2!$ in equation (28.2) comes in because the two-particle state ij is indistinguishable from ji. The last term $-\sum e^{-2\epsilon_i/kT}$ in equation (28.2) arises because the $Z(1)^2$ term includes states where both particles are in the same state i; such states are not allowed by the exclusion principle in Fermi statistics, so the contribution must be subtracted off. In general, the N-particle partition function $Z(N)$ in an ideal Fermi gas looks like

$$Z(N) = \frac{1}{N!} \sum_{\text{states } i_1 \neq i_2,\ldots,i_N \text{ with } N_{i_1} = 1} \ \sum_{\text{states } i_2 \neq i_3,\ldots,i_N \text{ with } N_{i_2} = 1} \cdots \sum_{\text{states } i_N \text{ with } N_{i_N} = 1} e^{-\epsilon_1/kT} e^{-\epsilon_2/kT} \ldots e^{-\epsilon_N/kT} \ . \tag{28.3}$$

In other words, $Z(N)$ is a mess for a Fermi gas. In the particular case where there are g single-particle states that all happen to have exactly the same energy ϵ ('equivalent' states), then $Z(N)$ for an ideal Fermi gas would go over to

$$Z(N) = \frac{g!}{N!(g-N)!} e^{-\epsilon N/kT} \quad \text{(Case of } g \text{ 1-particle states with same energy)} \ , \tag{28.4}$$

but equation (28.4) is not true in general, because in general single-particle states have various energies ϵ. You can if you want write the 2-particle partition function $Z(2)$, equation (28.2), as (letting $Z(T)$ denote the single-particle partition function Z as a function of T)

$$Z(2) = \frac{1}{2!}[Z(T)^2 - Z(T/2)] \ . \tag{28.5}$$

If you really insist, you can also construct formulae like equation (28.5) for $Z(N)$, but I'll tell you right now there's a better way. The general conclusion is that $Z(N)$ is not the nicest thing to work with in a Fermi gas.

The grand partition function Z_G on the other hand makes life a lot easier, because the grand partition function is multiplicative over single-particle states. This is because in the grand canonical ensemble, knowing that a certain single-particle state does or does not contain a particle provides no information about any other single-particle state. By contrast, in the canonical ensemble, where the number N of particles is fixed, knowing that there is a particle in a particular single-particle state immediately tells you information about the state of the rest of the system, namely that the rest of the system must contain $N-1$ particles. So consider a particular single-particle state i. In Fermi statistics, the single-particle state can contain either zero or one particle. The partition functions for zero and one particles are, trivially,

$$Z_i(0) = \ 1 \ , \quad Z_i(1) = e^{-\epsilon_i/kT} \ . \tag{28.6}$$

The grand partition function $Z_{G,i}$ for the particular single-particle state i is then

$$Z_{G,i} = \sum_{N=0}^{1} Z_i(N) e^{\mu N/kT} = 1 + e^{(-\epsilon_i+\mu)/kT} \ . \tag{28.7}$$

That the grand partition function is multiplicative over single-particle states is the same thing as saying that the logarithm of the grand partition function is additive over single-particle states. Thus the logarithm of the grand partition function of an ideal Fermi gas is

$$\ln Z_G = \sum_{\text{1-particle states } i} \ln \left[1 + e^{(-\epsilon_i+\mu)/kT} \right] \ , \qquad \text{(Fermi-Dirac)} \tag{28.8}$$

which is a lot simpler than $Z(N)$. Equation (28.8) for the grand partition function also gives you a prescription for figuring out what $Z(N)$ is. If you expand Z_G as a power series in $e^{\mu/kT}$, then the coefficients are, according to equation (19.12), just the N-particle partition functions $Z(N)$. I invite you to try it.

29. Partition Function of an Ideal Bose-Einstein Gas

A Bose-Einstein, or Bose, gas has the property that the particles of the system are indistinguishable, and any number of particles can occupy the same single-particle state. The case of Bose-Einstein goes much the same as Fermi-Dirac. The single-particle partition function Z is defined in the usual way, equation (28.1). The 2-particle partition function $Z(2)$ is

$$Z(2) \equiv \sum_{\text{states } j \text{ with } N_j=2} e^{-U_j/kT} = \frac{1}{2!} \left(Z(1)^2 + \sum_{\text{states } i \text{ with } N_i=1} e^{-2\epsilon_i/kT} \right) \ . \tag{29.1}$$

The factor $1/2!$ in equation (29.1) is because the two-particle state ij is the same as ji. The last term $\sum e^{-2\epsilon_i/kT}$ in equation (29.1) has to be added in because the $Z(1)^2/2!$ term includes only half the correct contribution to the two-particle state where both particles are in the same single-particle state i. Once again you can see that $Z(N)$ is going to be a mess for a Bose gas. In the particular case where there are g single-particle states that all happen to have exactly the same energy ϵ ('equivalent' states), then $Z(N)$ for an ideal Bose gas would go over to

$$Z(N) = \frac{(g+N-1)!}{N!(g-1)!} e^{-\epsilon N/kT} \quad \text{(Case of } g \text{ 1-particle states with same energy)} \ , \tag{29.2}$$

but equation (29.2) is not true in general.

As in the Fermi case, dealing with the grand partition function makes life a lot easier, because the grand partition function is multiplicative over single-particle states. For N particles in the single-particle state i, the partition function is

$$Z_i(N) = e^{-N\epsilon_i/kT} \ , \tag{29.3}$$

so the grand partition function $Z_{G,i}$ for the single-particle state i is

$$Z_{G,i} = \sum_{N=0}^{\infty} Z_i(N) e^{\mu N/kT} = \frac{1}{1 - e^{(-\epsilon_i+\mu)/kT}} \ . \tag{29.4}$$

The logarithm of the grand partition function is additive over single-particle states, so the logarithm of the grand partition function of an ideal Bose gas is

$$\ln Z_G = \sum_{\text{1-particle states } i} - \ln \left[1 - e^{(-\epsilon_i+\mu)/kT} \right] \quad \text{(Bose-Einstein)} \ . \tag{29.5}$$

Question (29.1): Superfluid ^{4}He is sometimes described as a Bose gas. How is it that a gas whose elementary particles are fermions, hence obey an exclusion principle, can show bosonic behavior, in which a large number of particles can occupy the same single-particle state?

30. Partition Function of an Ideal Planck Gas

A Planck gas is the special case of a Bose gas in which number of particles is not conserved. The obvious example is the case of a gas of photons. Since the number of particles is variable, it is more appropriate to use the grand canonical ensemble than the canonical ensemble. However, since number is not conserved, there is no thermodynamic variable μ corresponding to number conservation. The partition function is obtained from the Bose case (29.5) simply by setting $\mu = 0$:

$$\ln Z_G = \sum_{\text{1-particle states } i} - \ln \left[1 - e^{-\epsilon_i/kT} \right] \quad \text{(Planck)} \ . \tag{30.1}$$

31. Partition Function of an Ideal Boltzmann Gas

Boltzmann statistics is properly obtained as the nondegenerate limit of Fermi or Bose statistics when the number of particles per single-particle state is very much less than one. In this case, the N-particle partition function $Z(N)$ does take a simple form:

$$\begin{aligned} Z(N) &\equiv \sum_{\text{states } j \text{ with } N_j=N} e^{-U_j/kT} \\ &= \frac{1}{N!} \sum_{\text{states } i_1 \text{ with } N_{i_1}=1} \ \sum_{\text{states } i_2 \text{ with } N_{i_2}=1} \cdots \sum_{\text{states } i_N \text{ with } N_{i_N}=1} e^{-\epsilon_1/kT} e^{-\epsilon_2/kT} \ldots e^{-\epsilon_N/kT} \\ &= \frac{1}{N!} Z(1)^N \ . \end{aligned} \tag{31.1}$$

The extra terms that appeared in the Fermi and Bose N-particle partition functions, such as in the 2-particle partition functions (28.2) or (29.1), can be ignored in the Boltzmann case because the probability of two particles occupying (or trying to occupy) the same single-particle state is negligibly small.

The grand partition function of a Boltzmann gas is properly derived as the limit of the Fermi or Bose grand partition functions in the limit of small occupation numbers. Since the probability that a single-particle state i is occupied by N particles goes like $e^{N(-\epsilon_i+\mu)/kT}$, the condition of small occupation numbers for arbitrary single-particle states, in particular for the ground single-particle state 0 where $\epsilon_0 = 0$, is

$$e^{\mu/kT} \ll 1 \ . \tag{31.2}$$

In this limit (31.2) of small occupation numbers, the ideal Fermi and Bose grand partition functions, eqs. (28.8) and (29.5), go over to the grand partition function of an ideal Boltzmann gas,

$$\ln Z_G = \sum_{\text{1-particle states } i} e^{(-\epsilon_i+\mu)/kT} = Z(1)e^{\mu/kT} \qquad \text{(Boltzmann)} \ . \tag{31.3}$$

If the grand partition function Z_G from equation (31.3) is expanded as a power series in $e^{\mu/kT}$, then one recovers a second time the result (31.1) for the N-particle partition functions $Z(N)$ in an ideal Boltzmann gas.

32. Partition Function of an Ideal Gas of Distinguishable Particles

It is possible to consider formally a gas of distinguishable particles, even though such a gas would not normally appear in nature. Since each particle is of a different 'type', it is more appropriate to use the canonical ensemble, in which the particle number is fixed, rather than the grand canonical ensemble, which involves a reservoir presumably containing one each of an infinite number of particle types. The grand canonical ensemble can nevertheless be used, as long as it is understood that equation (27.6) is no longer valid.

For a gas of distinguishable particles the N-particle partition function $Z(N)$ is

$$\begin{aligned} Z(N) &\equiv \sum_{\text{states } j \text{ with } N_j=N} e^{-U_j/kT} \\ &= \sum_{\text{states } i_1 \text{ with } N_{i_1}=1} \ \sum_{\text{states } i_2 \text{ with } N_{i_2}=1} \ldots \sum_{\text{states } i_N \text{ with } N_{i_N}=1} e^{-\epsilon_1/kT} e^{-\epsilon_2/kT} \ldots e^{-\epsilon_N/kT} \\ &= Z(1)^N \ , \end{aligned} \tag{32.1}$$

which differs from the Boltzmann case (31.1) by a factor of $N!$.

Nevertheless, in the real world there are different species of particle, that are indeed distinguishable. But distinguishable by whom? E. T. Jaynes (https://bayes.wustl.edu/etj/articles/gibbs.paradox.pdf) proffers the following scenario. Suppose that there are two isotopes of argon that are so similar that to one experimenter they appear identical. However, a second experimenter knows the secret difference between the two isotopes. The second experimenter has crafted two membranes, each of which is impenetrable by one isotope but transparent to the other. The second experimenter prepares a volume with two equal compartments, one containing only the first isotope, the second containing only the second. The two compartments are arranged to contain the same number of particles at the same temperature and pressure. The only distinction between the two compartments is that they carry different isotopes. The first experimenter, not knowing that the compartments contain different isotopes, assigns an entropy to the system that is $N \ln 2$ larger (in energy units $k = 1$, with N the total combined number of particles) than the entropy assigned by the second. The first experimenter opens a hole in the barrier between the compartments, allowing the isotopes to mix thoroughly, and then closes the hole. The first experimenter, believing the isotopes to be identical, claims that the entropy has remained unchanged. The second experimenter, who knows the isotopes are different, concludes that the entropy has increased by the mixing entropy $N \ln 2$. At this point the first and second experimenters agree on the entropy of the mixed system. But while the first experimenter concludes that the entropy has remained the same, the second experimenter concludes that the entropy has increased.

Redo the experiment with the second experimenter at the helm. Once again, the initial volume contains two equal compartments that differ only in that they carry different isotopes. Instead of opening a hole in the barrier between the compartments, the second experimenter replaces the barrier with two adjacent membranes, one impenetrable to the first isotope, serving to confine the first isotope, the other impenetrable to the second isotope, serving to confine the second isotope. Each membrane is attached to a piston. The first membrane, which is transparent to the second isotope, feels only the pressure from the first isotope on one side. Likewise the second membrane feels only the pressure from the second isotope, on the opposite side. The second experimenter, holding the pistons, allows the two membranes to move, slowly, adiabatically, away from each other. As the membranes recede from each other, the volume divides into three parts: the volume between the two membranes fills with a mixture of both isotopes, while the volumes at the two sides each contain a pure isotope. Each isotope, bounded by its personal membrane, fills an increasing volume (part mixed, part pure) that in due course expands to fill the entire volume. At the end of the experiment, both isotopes fill the entire volume, and are fully mixed. But because the expansion has been adiabatic, PdV work has been done, and the temperature has decreased thanks to adiabatic cooling. The second experimenter concludes that, because the experiment was adiabatic, the entropy has remained constant during the experiment. The first experimenter is mystified by the experiment. Initially, the system contains two equal compartments with equal pressure on either side. The system appears to be in thermodynamic equilibrium. But as the first experimenter watches, the two membranes spontaneously, miraculously, move apart, with a high density region appearing between the two membranes, and regions of lower density on either side. The temperature of the system decreases, while the membranes push pistons, providing useful work to the outside. The entropy of the system decreases, apparently violating the second law of thermodynamics. A perpetual motion machine!? At the end of the experiment, both experimenters agree on the entropy of the mixed system. But while the second experimenter concludes that the entropy has remained the same, the first experimenter concludes that entropy has decreased.

Jaynes' point is that two different observers can consistently count entropy differently depending on whether or not they can distinguish particles. As long as the first experimenter has no way to distinguish particles, they count entropy as that of indistinguishable particles. But when the second experimenter shows their experiment to the first, and shares the secret of the distinguishable isotopes, the second experimenter revises their measure of entropy, and is able to extract work from what originally appeared to be a system in thermodynamic equilibrium at maximum entropy.

Experiment indicates that fundamental particles such as photons are fundamentally indistinguishable. In that case it is fundamentally impossible to lower the entropy of a closed system that has reached thermodynamic equilibrium.

Question (32.1): If you watch a 3D movie at the cinema, you will be provided with a pair of 3D glasses whose two lenses transmit respectively only right-handed and only left-handed circularly polarized light. The two lenses provide a practical realization of Jaynes' membranes. Yet photons are fundamentally indistinguishable. Do the 3D lenses provide a way to extract entropy from a system of photons in thermodynamic equilibrium? *Answer.* No. A system of photons in thermodynamic equilibrium has each spin state, right- and left-handed polarization, equally occupied. It is possible to extract entropy from a system of photons with unequally occupied spins, but that system is not in thermodynamic equilibrium.

33. Constraints on Thermodynamic Variables

Conditions for thermodynamic equilibrium to be stable were derived in §16. However, there exist other constraints on temperature, chemical potential, and pressure which arise not so much from the requirement of stability, but rather from certain properties of the states of the system.

(a) **Temperature**

Probabilities of states j in (grand) canonical ensembles go like $P_j \propto e^{-U_j/kT}$. Thus systems at positive temperature have the property that states of higher energy are less probable than states of lesser energy. Conversely, systems at negative temperature have the property that states of higher energy are more probable than states of lesser energy. Therefore, if there is no upper bound to the energy of the possible states of the system, then temperature must be positive, since a negative temperature would require an infinite amount of energy. Conversely, if there is an upper bound to the energy of states, then the temperature may be negative.

In realistic systems, where the free motions of particles permits them an unbounded amount of energy, temperature must be positive. However, it is possible to imagine, even to construct, systems in which particles have no free motion, being confined for example to the lattice of a crystal. In such a system each particle may only have a finite number of single-particle energy states, which might for example be associated with the interaction of the particle spin with an external magnetic field. Such systems can have negative temperatures if it can be arranged that the more energetic of the spin single-particle states are more highly populated than the less energetic. It is to be noted that although the state of the system at negative temperature is more energetic than at positive temperature, it is impossible to achieve negative temperatures by heating the system. At best, heating can increase the energy to the point where all single-particle states are equally occupied regardless of energy, corresponding to infinite temperature. More devious means must be used to achieve a population inversion and hence a negative temperature. In the example just mentioned, where the energy levels arise from the interaction of spin with an external magnetic field, a negative temperature might be attained by reversing the direction of the magnetic field, so that the spin single-particle states of lesser energy suddenly become the spin single-particle states of higher energy. Ultimately, systems with negative temperature are unstable in nature, because they drive inevitably toward thermodynamic equilibrium with the external medium, which, having unbounded energy states, must have a positive temperature.

(b) **Chemical Potential**

In an ideal Bose gas, convergence of the single-particle grand partition function, eq. (29.4),

$$Z_{G,i} = \sum_{N=0}^{\infty} e^{N(-\epsilon_i+\mu)/kT} \tag{33.1}$$

for any single-particle state i, in particular for the ground single-particle state 0 where $\epsilon_0 = 0$, requires that the chemical potential be zero or negative

$$\frac{\mu}{kT} \leq 0 \ . \tag{33.2}$$

The zero of energy in equation (33.2) is defined as the energy of the lowest energy state, the ground state.

In an ideal Fermi gas, the grand partition function converges for any value of μ/kT. Large negative values of μ/kT correspond to the nondegenerate limit, where the mean number of particles per single-particle state is much less than one. Conversely, large positive values of μ/kT correspond to the degenerate limit, where the number of particles per single-particle state approaches unity in single particle states with energy ϵ_i less than μ.

(c) **Pressure**

According to the standard relation $\partial S/\partial V = P/T$, eq. (14.1), a gas with negative P/T can increase its entropy by reducing its volume. In an ideal gas, therefore, the pressure (more strictly, P/T) must always be positive, since under a condition of negative pressure the gas would contract spontaneously. Examination of the grand partition functions $\ln Z_G = PV/kT$ of ideal Fermi and Bose gases, eqs. (28.8) and (29.5), shows that indeed P/T is invariably positive in these cases.

Negative pressures are however possible in nonideal gases, and routine in solids. In a nonideal gas inside a finite container, the contraction of the gas requires the creation of surfaces that may require more energy to form than is gained from the contraction of the gas. Thus thermodynamic equilibrium may occur even at negative pressure. As for a solid, like a wire say, chances are you can put it under quite a bit of tension (negative pressure) before it busts.

34. Occupancy

The **occupation number**, or **occupancy**, of a single-particle state i in a grand canonical ensemble is by definition the mean number $\bar{N}_i$ of particles in that state. Occupation numbers can offer an intuitively appealing and physically elegant alternative to more commonly used measures such as photon intensity (Krolik and McKee 1978, ApJ Supp, 37, 459, is a fine example). For the purpose of this section, occupancy numbers provide an opportunity to review the equations of thermodynamics from a slightly different, less rigorous, but more intuitive, angle.

In a Fermi gas, a single-particle state i can contain either zero or one particle, so the occupation number $\bar{N}_i$ is, from the probabilities (19.9),

$$\bar{N}_i = \sum_{N=0}^{1} N P_i(N) = \frac{e^{(-\epsilon_i+\mu)/kT}}{1 + e^{(-\epsilon_i+\mu)/kT}} = \frac{1}{e^{(\epsilon_i-\mu)/kT} + 1} \ . \tag{34.1}$$

The same result is obtained more formally by differentiating the grand partition function $Z_{G,i}$ of the single-particle Fermi state i, equation (28.7), with respect to μ/kT, according to the fundamental equation (27.6):

$$\bar{N}_i = \left.\frac{\partial \ln Z_{G,i}}{\partial(\mu/kT)}\right|_{-1/kT,V} = \frac{1}{e^{(\epsilon_i-\mu)/kT} + 1} \ . \tag{34.2}$$

A similar calculation for a Bose gas, where the number of particles in a single-particle state i can vary from zero to infinity, yields the occupation number $\bar{N}_i$

$$\bar{N}_i = \sum_{N=0}^{\infty} N P_i(N) = \frac{\sum_{N=0}^{\infty} N e^{(-\epsilon_i+\mu)N/kT}}{\sum_{N=0}^{\infty} e^{(-\epsilon_i+\mu)N/kT}} = \frac{1}{e^{(\epsilon_i-\mu)/kT} - 1} \ . \tag{34.3}$$

Again, the same result is obtained more formally as the partial derivative with respect to μ/kT of the grand partition function function $Z_{G,i}$ of the single-particle Bose state i, equation (29.4). A Boltzmann gas corresponds to the limit of small occupation numbers $\bar{N}_i$ for all single-particle states i in a Fermi or Bose gas. The limit of small occupation numbers is attained when $e^{\mu/kT} \ll 1$, or equivalently when $\mu/kT \to -\infty$. The occupation number $\bar{N}_i$ in a Boltzmann gas is then

$$\bar{N}_i = e^{(-\epsilon_i+\mu)/kT} \ . \tag{34.4}$$

The occupation numbers $\bar{N}_i$ of the Fermi, Bose, and Boltzmann gases, equations (34.1), (34.3), and (34.4), can be summarized in the single formula

$$\bar{N}_i = \frac{1}{e^{(\epsilon_i-\mu)/kT} + \begin{cases} 1 \\ 0 \\ -1 \end{cases}} \ , \tag{34.5}$$

where the numbers 1, 0, and -1 correspond respectively to Fermi, Boltzmann, and Bose gases.

The mean energy $\bar{U}_i$ of a single-particle state is, obviously,

$$\bar{U}_i = \sum_N \epsilon_i N P_i(N) = \epsilon_i \bar{N} \ , \tag{34.6}$$

which can also be derived formally by differentiating the grand partition function $Z_{G,i}$ of the single-particle state i with respect to $-1/kT$, according to equation (27.6).

The total number $\bar{N}$ and energy $\bar{U}$ in a grand canonical ensemble can be written as sums over the single-particle state occupation numbers

$$\bar{N} = \sum_i \bar{N}_i \ , \tag{34.7}$$

$$\bar{U} = \sum_i \epsilon_i \bar{N}_i \ , \tag{34.8}$$

which look kind of obvious. You can check that the formal partition function approach gives the same results.

Pressure is a little bit more subtle. Consider the notion of defining the pressure P_i of a single-particle state (not to be confused with probability P_i). According to the fundamental equation (27.6), P_i should be given by

$$\begin{aligned} \frac{P_i}{kT} &= \left.\frac{\partial \ln Z_{G,i}}{\partial V}\right|_{-1/kT,\mu/kT} = \frac{1}{Z_{G,i}} \left.\frac{\partial}{\partial V}\right|_{-1/kT,\mu/kT} \sum_N e^{(-\epsilon_i+\mu)N/kT} \\ &= -\left.\frac{\partial \epsilon_i}{\partial V}\right|_{-1/kT,\mu/kT} \frac{1}{kT Z_{G,i}} \sum_N N e^{(-\epsilon_i+\mu)N/kT} = -\frac{\partial \epsilon_i}{\partial V}\frac{\bar{N}_i}{kT} \ , \end{aligned} \tag{34.9}$$

so that the pressure P_i associated with the single-particle state i is

$$P_i = -\frac{\partial \epsilon_i}{\partial V}\bar{N}_i \ . \tag{34.10}$$

The question which equation (34.10) raises is, what is $\partial\epsilon_i/\partial V$? The change in the energy level ϵ_i caused by a change in the volume V is to be evaluated with T and μ held constant, but in fact the energy ϵ_i does not depend on T or μ in any case: the energy level is determined by the boundary conditions of the problem, which is to say that ϵ_i is, in the present case, only a function of volume V. As long as the gas is ideal, only the translational states of particles are affected by the volume V; the internal energy levels of particles (atoms) are unchanged. For the translational states, the number of states in an interval of phase volume is $g_{\rm spin} d^3x d^3p/h^3$, so it must be that when the volume V is changed the momentum of the states changes as

$$V p^3 = \text{constant} \ , \tag{34.11}$$

at least on average. If the scaling relation (34.11) is taken to be literally true for individual free states, then from the relativistic formula $(\epsilon_{\rm free} + mc^2)^2 - p^2c^2 = m^2c^4$ it follows that

$$-\frac{\partial \epsilon_{\rm free}}{\partial V} = -\frac{pc^2}{\epsilon_{\rm free} + mc^2}\frac{\partial p}{\partial V} = -\frac{v\partial p}{\partial V} = \frac{vp}{3V} \ , \tag{34.12}$$

where v is the velocity of the particle. Equation (34.12) reduces in the nonrelativistic case to

$$-\frac{\partial \epsilon_{\rm free}}{\partial V} = \frac{2\epsilon_{\rm free}}{3V} \qquad (\epsilon_{\rm free} \ll mc^2) \ , \tag{34.13}$$

and in the highly relativistic case to

$$-\frac{\partial \epsilon_{\rm free}}{\partial V} = \frac{\epsilon_{\rm free}}{3V} \qquad (\epsilon_{\rm free} \gg mc^2) \ . \tag{34.14}$$

Actually, equations (34.12)-(34.14) are not necessarily true for every translational energy level, but they are true on average. The total pressure P is a sum over the pressures P_i of single-particle states, which from equations (34.10) and (34.12) is

$$P = \sum_i P_i = \frac{1}{3V} \sum_i v_i p_i \bar{N}_i \ . \tag{34.15}$$

Equation (34.15) is the general formula for the pressure of an ideal gas of free particles. In the nonrelativistic case the total pressure P, equation (34.15), is

$$P = \frac{1}{3V} \sum_i 2\epsilon_{\mathrm{free},i} \bar{N}_i = \frac{2\bar{U}_{\mathrm{free}}}{3V} \ , \tag{34.16}$$

while in the relativistic case the total pressure P is

$$P = \frac{1}{3V} \sum_i \epsilon_{\mathrm{free},i} \bar{N}_i = \frac{\bar{U}_{\mathrm{free}}}{3V} \ , \tag{34.17}$$

which agree with the results (17.14) and (17.15) for an ideal gas obtained previously by other scaling arguments. The above arguments about the pressure were not entirely rigorous, because of the sloppy application of the scaling law (34.11). However, the same results (34.16) and (34.17) for the total pressure P can be derived more formally, in the usual way, by differentiating the grand partition function with respect to volume, according to the fundamental equation (27.6).

In the following two questions you may use the fact that the number of single-particle states in an interval of phase space is $g_{\mathrm{spin}} d^3x d^3p / h^3$.

Question (34.1): Derive the Maxwell-Boltzmann distribution, that is, the distribution of number densities of particles with velocity v in an ideal Boltzmann gas of nonrelativistic free particles of mass m and total number density n_{tot} in thermodynamic equilibrium at a temperature T:

$$dn = n_{\mathrm{tot}} \frac{4}{\pi^{1/2}} \left(\frac{m}{2kT} \right)^{3/2} e^{-mv^2/2kT} v^2 dv \ . \tag{34.18}$$

Question (34.2): Derive the Planck distribution of intensity B_ν (energy per unit time per unit area per unit frequency per steradian)

$$B_\nu d\nu = \frac{2h\nu^3 d\nu}{c^2 (e^{h\nu/kT} - 1)} \tag{34.19}$$

for a gas of photons in thermodynamic equilibrium.

35. Equilibria Between Reacting Species

In a system containing many different particles species X, the first fundamental equation (14.1) of thermodynamics looks like

$$T dS = dU - \sum_{\mathrm{X}} \mu_{\mathrm{X}} dN_{\mathrm{X}} + P dV \ . \tag{35.1}$$

Typically, there are processes, or reactions, that transform some sets of particles into other sets of particles. For example, a hydrogen atom may be converted by ionization into a proton and an electron, and conversely, a proton and an electron may recombine to form a hydrogen atom:

$$H \leftrightarrow p + e \ . \tag{35.2}$$

As a result, the numbers N_{X} of each particle species X are not conserved individually, but rather, only the numbers N_{A} of fundamental constituents A are conserved. In the example (35.2), the numbers N_{H} of hydrogen atoms, N_p of free protons, and N_e of free electrons are not individually conserved, but the total number of protons, free and bound, which is $N_p + N_{\mathrm{H}}$, and the total number of electrons, free and bound, which is $N_e + N_{\mathrm{H}}$, are conserved. This implies that the chemical potentials μ_{X} in equation (35.1) are not all independent; rather, only the chemical potentials μ_{A} of the fundamental conserved constituents are independent. If the number of fundamental particles of type A that compose particle X is written n_{AX}, then the total number of fundamental particles of type A is

$$N_{\mathrm{A}} = \sum_{\mathrm{X}} n_{\mathrm{AX}} N_{\mathrm{X}} \ . \tag{35.3}$$

Thus the fundamental equation (14.1) of thermodynamics can also be written

$$TdS = dU - \sum_{\mathrm{A}} \mu_{\mathrm{A}} d \left(\sum_{\mathrm{X}} n_{\mathrm{AX}} N_{\mathrm{X}} \right) + PdV \ , \tag{35.4}$$

which properly reflects the conservation of each of the fundamental particle types A. The equivalence of equations (35.1) and (35.4) implies that the chemical potential μ_{X} of particle X is related to the chemical potentials of its constituents by

$$\mu_{\mathrm{X}} = \sum_{\mathrm{A}} n_{\mathrm{AX}} \mu_{\mathrm{A}} \ . \tag{35.5}$$

In the example (35.2), the chemical potential of the hydrogen atom H, which is composed of a proton p and an electron e, is the sum of the chemical potentials of the proton and the electron

$$\mu_{\mathrm{H}} = \mu_p + \mu_e \ . \tag{35.6}$$

The mean number $\bar{N}_{\mathrm{X}}$ of reacting species X in thermodynamic equilibrium is determined in the usual way by differentiating the logarithm of the grand partition function with respect to μ_{X}/kT, eq. (22.2),

$$\bar{N}_{\mathrm{X}} = \left. \frac{\partial \ln Z_G}{\partial(\mu_{\mathrm{X}}/kT)} \right|_{-1/kT, \mu_Y/kT} \ , \tag{35.7}$$

where the partial derivative with respect to μ_{X}/kT is carried out with the chemical potentials μ_Y of all other particles $Y \neq X$ formally held fixed. Equation (35.7) expresses the mean number $\bar{N}_{\mathrm{X}}$ of particles X as a function of the chemical potentials μ_{X} (and T, V). If the relation (35.5) for the chemical potential μ_{X} in terms of the chemical potentials μ_{A} of its fundamental constituents A is now imposed, then equations (35.7) for all X comprise a set of implicit relations between the numbers $\bar{N}_{\mathrm{X}}$ of the various reacting particle species. In the case of an ideal Boltzmann gas, considered in the next paragraph, it is possible to eliminate the chemical potentials so as to obtain explicit, rather than implicit, relations between the numbers N_{X}, but this is not in general possible.

So consider the case of an ideal Boltzmann gas. In an ideal gas, the grand partition function Z_G of the whole system is multiplicative over the grand partition functions $Z_{G,X}$ of each of the particle species X

$$\ln Z_G = \sum_{\mathrm{X}} \ln Z_{G,X} \ . \tag{35.8}$$

Substituting into equation (35.8) the expression (31.3) for the grand partition function of an ideal Boltzmann gas yields

$$\ln Z_G = \sum_{\mathrm{X}} Z_{\mathrm{X}}(1) e^{\mu_{\mathrm{X}}/kT} \ , \tag{35.9}$$

where $Z_{\mathrm{X}}(1)$ is the single-particle partition function of the species X. The number $\bar{N}_{\mathrm{X}}$ of particle species X follows by differentiating the grand partition function (35.9) with respect to μ_{X}/kT

$$\bar{N}_{\mathrm{X}} = \frac{\partial \ln Z_G}{\partial(\mu_{\mathrm{X}}/kT)} = Z_{\mathrm{X}}(1) e^{\mu_{\mathrm{X}}/kT} \ . \tag{35.10}$$

Equation (35.10) can be inverted to yield the chemical potential μ_{X} in terms of the number N_{X}

$$\mu_{\mathrm{X}}/kT = \ln \left(\frac{\bar{N}_{\mathrm{X}}}{Z_{\mathrm{X}}(1)} \right) \ . \tag{35.11}$$

Imposing the relation (35.5) for the chemical potential μ_{X} then implies

$$\frac{\bar{N}_{\mathrm{X}}}{Z_{\mathrm{X}}(1)} = \prod_{\mathrm{A}} \left(\frac{\bar{N}_{\mathrm{A}}}{Z_{\mathrm{A}}(1)} \right)^{n_{\mathrm{AX}}} \ , \tag{35.12}$$

which is the **Saha equation** in its most general form. The Saha equation (35.12) determines the numbers of the different particle species in an ideal Boltzmann gas in thermodynamic equilibrium.

In a nonideal or non-Boltzmann gas, it is not usually possible to obtain explicit relations between the numbers N_{X} of particle species in thermodynamic equilibrium. A procedure widely used in the literature to determine the numbers N_{X} is called *free energy minimization* (see §26). In this procedure one considers a canonical ensemble, in which the temperature T, volume V, and numbers of fundamental particles N_{A} are fixed. The numbers N_{X} of particle species are then varied numerically, at fixed T, V, and N_{A}, until the free energy $\bar{U} - TS$ is a minimum. It is not difficult to see that the minimization of free energy is equivalent to the condition (35.5) on the chemical potentials of reacting species in thermodynamic equilibrium. Reexpressed as an equation for the total derivative of the free energy $\bar{U} - TS$, the first fundamental equation (14.1) of thermodynamics looks like

$$d(\bar{U} - TS) = -SdT + \sum_{\mathrm{X}} \mu_{\mathrm{X}} dN_{\mathrm{X}} - PdV \ . \tag{35.13}$$

In particular, the partial derivative of free energy with respect to number N_{X} is

$$\left. \frac{\partial(\bar{U} - TS)}{\partial N_{\mathrm{X}}} \right|_{T, N_{\mathrm{Y}}(\mathrm{Y} \neq X), V} = \mu_{\mathrm{X}} \ . \tag{35.14}$$

The minimum of the free energy $\bar{U} - TS$ at fixed N_{A} is achieved when the abundances N_{X} are such that

$$\frac{\partial(\bar{U} - TS)}{\partial N_{\mathrm{X}}} - \sum_{\mathrm{A}} n_{\mathrm{AX}} \frac{\partial(\bar{U} - TS)}{\partial N_{\mathrm{A}}} = 0 \tag{35.15}$$

is satisfied for all species X. Equation (35.15) is exactly the same condition as the relation (35.5) between the chemical potentials of reacting species.

Question (35.1): Show that the number densities of an ideal nonrelativistic Boltzmann gas of H-atoms, protons, and electrons in thermodynamic equilibrium satisfy (notation: $n \equiv \bar{N}/V$)

$$\frac{n_p n_e}{n_{\mathrm{H}}} = \frac{g_p g_e}{Z_{\mathrm{H,int}}} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \ , \tag{35.16}$$

where $Z_{\mathrm{H,int}}$ is the internal partition function of a hydrogen atom. Argue that if only the ground state of hydrogen is considered, and if the zero-point of energy of H is taken equal to that of the just-ionized atom, then

$$Z_{\mathrm{H,int}} = g_{\mathrm{H}} e^{\chi_{\mathrm{H}}/kT} \ , \tag{35.17}$$

where $\chi_{\rm H}$ is the ionization potential of hydrogen. What are the numbers g_e, g_p, and $g_{\rm H}$ of spin states?

Question (35.2): The most tightly bound of all nuclei is ^{56}Fe. Once a star has synthesized its way to ^{56}Fe, no more nuclear energy is left. A star in such a condition gets its energy from gravitational contraction, which causes the star to heat up. Eventually, the temperature gets high enough to dissociate ^{56}Fe into α particles (^{4}He nuclei) and neutrons by

$$^{56}\text{Fe} \rightarrow 13\alpha + 4n \tag{35.18}$$

which costs 124.4129 MeV dissociation energy per ^{56}Fe. Write down the Saha equation that describes the equilibrium between ^{56}Fe, α particles, and neutrons. If the original (low temperature) composition of the star was entirely ^{56}Fe, argue that $n_n/n_\alpha = 4/13$ (assume that the reaction [35.18] is very much faster than any weak interaction that converts neutrons to protons or vice versa). Show that the temperature at which ^{56}Fe dissociates is about 4 MeV, with a weak dependence on density.

Question (35.3): Derive implicit relations between the equilibrium number densities of an ideal gas of H-atoms, protons, and electrons when degeneracy of the electrons is becoming important (i.e., treat the H-atoms and protons as ideal Boltzmann gases, but the electrons as a Fermi gas). Include only the ground state of the H-atom, and assume that the ground state energy remains unperturbed even at high electron density. Interpret your results physically. Is the approximation of an unperturbed ground state of the H-atom likely to be a good one? Does the energy of the continuum relative to the ground state, the ionization potential, increase or decrease as the electron density increases?

36. Summary of Equations of State of Ideal Gases

For reference, this section gives equations for the number density $n \equiv \bar{N}/V$, pressure P, and energy density $\bar{U}/V$ in ideal Fermi, Bose, and Boltzmann gases of particles, in the nonrelativistic and relativistic limits. The results are obtained using the fundamental equation (27.6), and the grand partition functions (28.8), (29.5), and (31.3). The most commonly encountered cases in astrophysics are: the nonrelativistic Boltzmann gas, equations (36.8)-(36.10), or equations (36.37)-(36.39) if internal degrees of freedom of particles are also to be included; the nonrelativistic degenerate Fermi gas, equations (36.11)-(36.13); and the Planck gas, equations (36.26)-(36.28).

The general form of the grand partition function of an ideal gas of free particles is

$$\ln Z_G = \sum_{\text{1-particle free states } i} \ln Z_{G,i} = V \int \left\{ \begin{array}{c} \ln[1 + e^{(-\epsilon+\mu)/kT}] \\ e^{(-\epsilon+\mu)/kT} \\ -\ln[1 - e^{(-\epsilon+\mu)/kT}] \end{array} \right\} \frac{g_{\rm spin} 4\pi p^2 dp}{h^3} \ , \tag{36.1}$$

where the upper, middle, and lower rows in the integrand correspond respectively to the cases of Fermi, Boltzmann, and Bose gases. The quantity $g_{\rm spin}$ is the number of spin states of the particle. For nonrelativistic free particles of mass m, the momentum p and the energy ϵ are related by

$$\epsilon = \frac{p^2}{2m} \qquad (\epsilon \ll mc^2) \tag{36.2}$$

while for highly relativistic particles

$$\epsilon = pc \qquad (\epsilon \gg mc^2) \ . \tag{36.3}$$

The quantities $F_n^+(\alpha)$ and $F_n^-(\alpha)$ used below denote the Fermi-Dirac (+) and Bose-Einstein (−) integrals

$$F_n^\pm(\alpha) \equiv \int_0^\infty \frac{x^{n-1} dx}{e^{x+\alpha} \pm 1} \ . \tag{36.4}$$

Salient properties of these integrals are summarized in the Appendix to this section.

(a) **Nonrelativistic Free Particles**

The number density n, pressure P, and energy density $\bar{U}/V$ of an ideal gas of nonrelativistic free fermions or bosons are

$$n \equiv \frac{\bar{N}}{V} = \frac{g_{\rm spin} 2\pi (2mkT)^{3/2}}{h^3} F^{\pm}_{3/2}(-\mu/kT) \ , \tag{36.5}$$

$$P = \frac{g_{\rm spin} 4\pi (2m)^{3/2} (kT)^{5/2}}{3h^3} F^{\pm}_{5/2}(-\mu/kT) = nkT \frac{2F^{\pm}_{5/2}(-\mu/kT)}{3F^{\pm}_{3/2}(-\mu/kT)} \ , \tag{36.6}$$

$$\bar{U} = \frac{3PV}{2} \ , \tag{36.7}$$

where the + sign on $F^{\pm}_n$ is for fermions, the − sign for bosons.

In the nondegenerate, Boltzmann limit, $\mu/kT \ll 0$, the number density n, pressure P, and energy density $\bar{U}/V$ from equations (36.5)-(36.7) go over to

$$n \equiv \frac{\bar{N}}{V} = \frac{g_{\rm spin} (2\pi mkT)^{3/2}}{h^3} e^{\mu/kT} \ , \tag{36.8}$$

$$P = \frac{g_{\rm spin} (2\pi m)^{3/2} (kT)^{5/2}}{h^3} e^{\mu/kT} = nkT \ , \tag{36.9}$$

$$\bar{U} = \frac{3PV}{2} = \frac{3\bar{N}kT}{2} \ . \tag{36.10}$$

In the degenerate limit of a Fermi gas, $\mu/kT \gg 0$, the number density n, pressure P, and energy density $\bar{U}/V$ from equations (36.5)-(36.7) go to

$$n \equiv \frac{\bar{N}}{V} = \frac{g_{\rm spin} 4\pi (2m\mu)^{3/2}}{3h^3} \ , \tag{36.11}$$

$$P = \frac{g_{\rm spin} 8\pi (2m)^{3/2} \mu^{5/2}}{15h^3} = \frac{2n\mu}{5} = \frac{h^2 3^{2/3} n^{5/3}}{5m(g_{\rm spin} 4\pi)^{2/3}} \ , \tag{36.12}$$

$$\bar{U} = \frac{3PV}{2} \ . \tag{36.13}$$

The case where $\mu/kT = 0$, corresponding to the case where the number of particles is not conserved, is also of special interest. In this case, the number density n, pressure P, and energy density $\bar{U}/V$ from equations (36.5)-(36.7) are

$$n \equiv \frac{\bar{N}}{V} = \frac{g_{\rm spin} 2\pi (2mkT)^{3/2}}{h^3} F^{\pm}_{3/2}(0) \ , \tag{36.14}$$

$$P = \frac{g_{\rm spin} 4\pi (2m)^{3/2} (kT)^{5/2}}{3h^3} F^{\pm}_{5/2}(0) = nkT \frac{2F^{\pm}_{5/2}(0)}{3F^{\pm}_{3/2}(0)} = \frac{h^2 n^{5/3}}{3m(g_{\rm spin} 2\pi)^{2/3}} \frac{F^{\pm}_{5/2}(0)}{[F^{\pm}_{3/2}(0)]^{5/3}} \ , \tag{36.15}$$

$$\bar{U} = \frac{3PV}{2} \ . \tag{36.16}$$

where again the + sign on $F^{\pm}$ is for fermions, the − sign for bosons.

(b) **Relativistic Free Particles**

The number density $\bar{N}/V$, pressure P, and energy density $\bar{U}/V$ of an ideal gas of relativistic free fermions or bosons are

$$n \equiv \frac{\bar{N}}{V} = \frac{g_{\rm spin} 4\pi (kT)^3}{c^3 h^3} F^{\pm}_3(-\mu/kT) \ , \tag{36.17}$$

$$P = \frac{g_{\rm spin} 4\pi (kT)^4}{3c^3h^3} F_4^{\pm}(-\mu/kT) = nkT \frac{F_4^{\pm}(-\mu/kT)}{3F_3^{\pm}(-\mu/kT)} \ , \tag{36.18}$$

$$\bar{U} = 3PV \ , \tag{36.19}$$

where the + sign on $F_n^{\pm}$ is for fermions, the − sign for bosons.

In the nondegenerate, Boltzmann limit, $\mu/kT \to -\infty$, the number density n, pressure P, and energy density $\bar{U}/V$ from equations (36.17)-(36.19) go over to

$$n \equiv \frac{\bar{N}}{V} = \frac{g_{\rm spin} 8\pi (kT)^3}{c^3h^3} e^{\mu/kT} \ , \tag{36.20}$$

$$P = \frac{g_{\rm spin} 8\pi (kT)^4}{c^3h^3} e^{\mu/kT} = nkT \ , \tag{36.21}$$

$$\bar{U} = 3PV = 3\bar{N}kT \ . \tag{36.22}$$

In the degenerate limit of a Fermi gas, $\mu/kT \gg 0$, the number density n, pressure P, and energy density $\bar{U}/V$ from equations (36.17)-(36.19) go to

$$n \equiv \frac{\bar{N}}{V} = \frac{g_{\rm spin} 4\pi \mu^3}{3c^3h^3} \ , \tag{36.23}$$

$$P = \frac{g_{\rm spin} \pi \mu^4}{3c^3h^3} = \frac{n\mu}{4} = \frac{3^{1/3} chn^{4/3}}{4(g_{\rm spin} 4\pi)^{1/3}} \ , \tag{36.24}$$

$$\bar{U} = 3PV \ . \tag{36.25}$$

If the number of particles is not conserved, then $\mu/kT = 0$, in which case the number density n, pressure P, and energy density $\bar{U}/V$ from equations (36.17)-(36.19) are

$$n \equiv \frac{\bar{N}}{V} = \frac{g_{\rm spin} 4\pi (kT)^3}{c^3h^3} F_3^{\pm}(0) \ , \tag{36.26}$$

$$P = \frac{g_{\rm spin} 4\pi (kT)^4}{3c^3h^3} F_4^{\pm}(0) = nkT \frac{F_4^{\pm}(0)}{3F_3^{\pm}(0)} = \frac{chn^{4/3}}{3(g_{\rm spin} 4\pi)^{1/3}} \frac{F_4^{\pm}(0)}{[F_3^{\pm}(0)]^{4/3}} \ , \tag{36.27}$$

$$\bar{U} = 3PV \ . \tag{36.28}$$

Equations (36.26)-(36.28) include the case of photons, which are bosons, and have $g_{\rm spin} = 2$. Photons are so ubiquitous that one commonly writes radiation density (36.28) as

$$\frac{\bar{U}}{V} = aT^4 \ , \tag{36.29}$$

where the constant a is, from equation (36.27) with (A36.12),

$$a = \frac{8\pi k^4}{c^3h^3} F_4^{-}(0) = \frac{8\pi^5 k^4}{15c^3h^3} \ . \tag{36.30}$$

Radiation pressure (36.27) is

$$P = \frac{aT^4}{3} \ . \tag{36.31}$$

It is not hard to figure out that the energy flux of photons (energy per unit area per unit time) passing in one direction through a plane is $c\bar{U}/(4V)$. From this follows the **Stefan-Boltzmann law** for the luminosity L emitted from a surface area A of photons in thermodynamic equilibrium at temperature T,

$$L = A\sigma T^4 \ , \tag{36.32}$$

where σ is the **Stefan-Boltzmann constant**

$$\sigma = \frac{ac}{4} = \frac{2\pi^5 k^4}{15c^2h^3} \ . \tag{36.33}$$

(c) Particles with Internal Degrees of Freedom

Atoms and molecules have internal as well as translational degrees of freedom. If the gas is ideal, then invariably the atoms and molecules are well described as Boltzmann particles. For if the density becomes so high that the electron gas begins to become degenerate, then you can be sure that the energy levels of the atoms and molecules are strongly perturbed, and that the gas is no longer ideal. Note from equation (36.8) that the density n at which nonrelativistic particles of mass m become degenerate is proportional to $m^{3/2}$, so that the lighter electrons become degenerate at lower densities than the more massive nuclei.

The grand partition of an ideal Boltzmann gas of particles with internal degrees of freedom is

$$\ln Z_G = Z_{\text{int}}(1) Z_{\text{free}}(1) e^{\mu/kT} \ , \tag{36.34}$$

where $Z_{\text{int}}(1)$ is the single-particle partition function of the internal states of the particle,

$$Z_{\text{int}}(1) = \sum_{\text{internal states } i} e^{-\epsilon_i/kT} \ , \tag{36.35}$$

and $Z_{\text{free}}(1)$ is the single-particle partition function of the translational degrees of freedom, assumed here to be nonrelativistic,

$$Z_{\text{free}}(1) = V \int e^{-\epsilon/kT} \frac{g_{\text{spin}} 4\pi p^2 dp}{h^3} = \frac{V g_{\text{spin}} (2\pi mkT)^{3/2}}{h^3} \ . \tag{36.36}$$

The number density n, pressure P, and energy density $\bar{U}/V$ of the ideal Boltzmann gas of nonrelativistic particles with internal degrees of freedom are then modified from equations (36.5)-(36.7) to

$$n \equiv \frac{\bar{N}}{V} = \frac{Z_{\text{int}}(1) Z_{\text{free}}(1) e^{\mu/kT}}{V} = Z_{\text{int}} \frac{g_{\text{spin}} (2\pi mkT)^{3/2}}{h^3} e^{\mu/kT} \ , \tag{36.37}$$

$$P = nkT \ , \tag{36.38}$$

$$\bar{U} = \frac{3PV}{2} + \bar{U}_{\text{int}} \ , \tag{36.39}$$

where $\bar{U}_{\text{int}}$ is the mean energy of the internal degrees of freedom of a single particle

$$\bar{U}_{\text{int}} = \sum_{\text{internal states } i} \epsilon_i e^{-\epsilon_i/kT} \ . \tag{36.40}$$

(d) More than One Particle Type

If there is more than one type of particle X (which may be Fermi, Bose, Boltzmann or any mix thereof), then number density n, pressure P, and energy density $\bar{U}/V$ are additive over particle types, $n = \sum n_{\text{X}}$, $P = \sum P_{\text{X}}$, and $\bar{U} = \sum \bar{U}_{\text{X}}$, provided that they are expressed in terms of temperature T and chemical potential μ. If the particle species X react, then the relation (35.5) between the chemical potentials μ_{X} must be imposed.

Question (36.1): Write down the grand partition function of an ideal Fermi gas of relativistic free particles and antiparticles (what is the relation between the chemical potential μ of the particle and that μ' of its antiparticle?). Hence obtain expressions for the numbers $\bar{N}$ and $\bar{N}'$ of particles and antiparticles, the internal energy $\bar{U}$, and the pressure P of the gas in terms of the temperature T, chemical potential μ, and volume V (you should find expressions involving the Fermi-Dirac integrals F_n^+). Determine the forms of the equations in the degenerate limit, and in the case where the number of particles equals the number of antiparticles. In these last two cases, try to obtain expressions for the pressure P in terms of the density $n \equiv \bar{N}/V$ and/or temperature T.

Appendix to Section 36: Fermi-Dirac and Bose-Einstein Integrals

This Appendix sets out various properties of the Fermi-Dirac (+) and Bose-Einstein (−) integrals

$$F_n^{\pm}(\alpha) \equiv \int_0^\infty \frac{x^{n-1}dx}{e^{x+\alpha} \pm 1} \ . \tag{A36.1}$$

The derivative of the integrals F_n^+ and F_n^- is

$$\frac{\partial F_n^{\pm}(\alpha)}{\partial \alpha} = -(n-1)F_{n-1}^{\pm}(\alpha) \qquad (n > 1) \ , \tag{A36.2}$$

which can be proven by an integration by parts.

In the limit $\alpha \to \infty$, corresponding to the Boltzmann, or nondegenerate, limit, the integrals F_n^+ and F_n^- go over to

$$F_n^+(\alpha) = F_n^-(\alpha) = e^{-\alpha}\Gamma(n) \qquad (\alpha \to \infty) \ , \tag{A36.3}$$

where Γ is the gamma function. Series expansions, good for $\alpha \geq 0$, are

$$\begin{aligned} F_n^+(\alpha) &= \Gamma(n)\left(e^{-\alpha} - \frac{e^{-2\alpha}}{2^n} + \frac{e^{-3\alpha}}{3^n} - ...\right) \ , \\ F_n^-(\alpha) &= \Gamma(n)\left(e^{-\alpha} + \frac{e^{-2\alpha}}{2^n} + \frac{e^{-3\alpha}}{3^n} - ...\right) \ . \end{aligned} \tag{A36.4}$$

In the opposite limit $\alpha \to -\infty$, corresponding to the degenerate limit, the Fermi-Dirac integral F_n^+ goes to

$$F_n^+(\alpha) = \frac{|\alpha|^n}{n} \qquad (\alpha \to -\infty) \ . \tag{A36.5}$$

The Bose-Einstein integral F_n^- is of physical relevance only for $\alpha \geq 0$. An asymptotic expansion of the Fermi-Dirac integral F_n^+, good for $\alpha < 0$, is

$$\begin{aligned} F_n^+(\alpha) &= \frac{(-\alpha)^n}{n}\left[1 + \sum_{j=1}^{\infty} n(n-1)...(n+1-2j)2(1-2^{1-2j})\zeta(2j)\alpha^{-2j}\right] \\ &= \frac{(-\alpha)^n}{n}\left[1 + \sum_{j=1}^{\infty} \frac{n(n-1)...(n+1-2j)}{(2j)!}(2^{2j}-2)|B_{2j}|\left(\frac{\pi}{\alpha}\right)^{2j}\right] \\ &= \frac{(-\alpha)^n}{n}\left[1 + n(n-1)\frac{\pi^2}{6\alpha^2} + n(n-1)(n-2)(n-3)\frac{7\pi^4}{360\alpha^4} + ...\right] \ , \end{aligned} \tag{A36.6}$$

where $\zeta(n)$ is the Riemann zeta-function

$$\zeta(n) = 1 + \frac{1}{2^n} + \frac{1}{3^n} + ... \ , \tag{A36.7}$$

and B_n are Bernoulli numbers. Equation (A36.6) is a particular case of the more general result, known as Sommerfeld's lemma, that for a function $\phi(x)$ that is sufficiently well-behaved, and regular at $x = 0$,

$$\int_0^\infty \frac{(d\phi/dx)\,dx}{e^{x+\alpha} \pm 1} = \phi(-\alpha) + \sum_{j=1}^{\infty} \left.\frac{d^{2j}\phi}{dx^{2j}}\right|_{x=-\alpha} 2(1-2^{1-2j})\zeta(2j)\alpha^{-2j}$$

$$= \phi(-\alpha) + \left.\frac{d^2\phi}{dx^2}\right|_{-\alpha} \frac{\pi^2}{6\alpha^2} + \left.\frac{d^4\phi}{dx^4}\right|_{-\alpha} \frac{7\pi^4}{360\alpha^4} + \ldots \; . \qquad (A36.8)$$

The case $\alpha = 0$ corresponds to non-number-conserving particles, such as photons, or particle-antiparticle pairs. A useful and easily proven relation between the Fermi-Dirac and Bose-Einstein integrals for $\alpha = 0$ is

$$F_n^+(0) = (1 - 2^{1-n}) F_n^-(0) \qquad (n > 1) \; . \qquad (A36.9)$$

The Bose-Einstein integral $F_n^-(0)$ is

$$F_n^-(0) = \Gamma(n)\zeta(n) \; , \qquad (A36.10)$$

where $\zeta(n)$ is the Riemann zeta-function (A36.7). For even integral n,

$$F_n^-(0) = \frac{(2\pi)^n}{2n} |B_n| \qquad (n \text{ even}) \; , \qquad (A36.11)$$

where B_n are Bernoulli numbers. For example,

$$F_2^-(0) = \frac{\pi^2}{6} \; , \quad F_4^-(0) = \frac{\pi^4}{15} \; , \quad F_6^-(0) = \frac{8\pi^6}{63} \; . \qquad (A36.12)$$