Chapter 10: Statistical Thermodynamics

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10.1 The Statistics of Equilibrium States

The discussion in the previous chapter suggests that the macroscopic quantities that appear in classical thermodynamics are to be associated with the phase averages, ⟨R⟩, of dynamical variables, R(q,p), where

\[ \langle R \rangle = \sum R(q,p)\rho(q,p)dqdp \]  \hspace{1cm} 10.1

and ρ(q,p) is the density of states in phase space. Since the phase average of any dynamical variable can be calculated, at least in principle, when the density of states is known, the function ρ(q,p) determines the value of any macroscopic quantity.
The distribution function of an arbitrary ensemble of systems is a function of time as well as a function of the position in phase space. Each member of the ensemble evolves along some trajectory that moves it constantly from point to point in phase space, so the fraction of the members of the ensemble, \( \rho \), whose states lie instantaneously in the differential volume, \( dqdp \), at the point \((q,p)\) depends on the time:

\[
\rho = \rho(q,p,t)
\]

The macroscopic properties of an ensemble are generally functions of time as well. Since the value of the dynamical variable, \( R(q,p) \), is, by definition, determined by the point \((q,p)\), and the phase space is fixed by the dimension of the system, the time dependence of the macroscopic properties is given by the integral equation

\[
\frac{d\langle R \rangle}{dt} = \int \sum R(q,p) \left[ \frac{\partial \rho}{\partial t} \right] dqdp
\]

where the partial derivative of \( \rho \) is taken at fixed \((q,p)\). At equilibrium all macroscopic quantities are independent of time. It is hence a condition of equilibrium that

\[
\frac{\partial}{\partial t} [\rho(q,p,t)] = 0
\]

or

\[
\rho = \rho(q,p)
\]

That is,

*the representative ensemble of an equilibrium state has a constant value of the distribution function, \( \rho(q,p) \).*

It is a very short step from these observations to the recognition that the equilibrium distribution function, \( \rho(q,p) \), is equivalent to the fundamental equation. The natural variables of the distribution function, \((q,p)\), are the constitutive coordinates of the system. All equilibrium properties are determined by the fundamental equation through integral equations of the form 10.1. The stationary values of the distribution function, for which \( \partial \rho/\partial t = 0 \), determine the equilibrium states of the system. These are precisely the properties of the fundamental equation of the macroscopic system. It follows that

*the fundamental equation of a macroscopic system of classical particles is determined by its equilibrium distribution function, \( \rho(q,p) \).*

The remainder of this chapter is devoted to the evaluation of the equilibrium distribution function for systems that are subject to various sets of macroscopic constraints. As we shall see, the distribution function can be evaluated for any admissible combination of constraints on the macroscopic geometric coordinates and their conjugate...
forces, and leads in each case to an equation for the thermodynamic potential that
governs the behavior of a macroscopic system that is subject to those constraints. In each
case the representative ensemble for the system is made up of systems that satisfy the
macroscopic constraints that are imposed. The simplest and most familiar cases are the
isolated system, which is represented by a \textit{microcanonical ensemble} of states and leads to
the definition of the entropy function, $S(E,\{N\})$, the isothermal system, which is
represented by a \textit{canonical ensemble} of states and leads to the definition of the Helmholtz
free energy, $F(T,\{N\})$, and the open system, which is represented by a \textit{grand canonical ensemble} of states and leads to the definition of the work function,
$\Omega(T,\{u\},\{\mu\})$. A general method is developed that is capable of treating arbitrary sets of
admissible constraints and leads to the definition of the appropriate thermodynamic potentials, just as the Legendre transform permits the definition of the appropriate
thermodynamic potentials in the macroscopic case.

To evaluate the equilibrium distribution function we use three of its properties: it
is independent of time, as shown above, its logarithm is additive, as shown in the
previous chapter, and it is a constant of the motion along a trajectory. This last property
of the distribution function is Liouville's Theorem, which is proved in the following
section.

\section{10.2 Liouville's Theorem}

Consider a system of classical particles that may or may not be in equilibrium.
Suppose that we are given (or have somehow found) an appropriate representative en-
semble. The phase space of the system is then filled with points that correspond to the
instantaneous states of the systems that make up its representative ensemble. At any
instant of time these are distributed through $\Sigma^N$ with the fractional density, $\rho(q,p,t)$, which
may depend on the time since each system in the representative ensemble is in motion
along its particular trajectory.

The whole ensemble can be pictured as a fluid of non-interacting particles in
motion through the 6N-dimensional phase space, where each particle, or \textit{phase point}, is
the instantaneous state of one of the systems in the ensemble. The 6N coordinates of the
phase space are the 3N spatial coordinates, $q_i$, and the 3N conjugate momenta, $p_i$, which
we shall take to be orthogonal. Let $\mathbf{e}_q^i$ be a unit vector along the coordinate $q_i$ and let
$\mathbf{e}_p^i$ be a unit vector along $p_i$. Orthogonality requires that
\begin{align*}
\mathbf{e}_q^i \cdot \mathbf{e}_q^j &= \delta_{ij} \\
\mathbf{e}_p^i \cdot \mathbf{e}_p^j &= \delta_{ij} \\
\mathbf{e}_q^i \cdot \mathbf{e}_p^j &= 0
\end{align*}

The velocity, $\mathbf{v}$, with which a system moves through phase space is the 6N-dimensional vector

\pagebreak
\[ \mathbf{v} = \sum_{i=1}^{3N} q_i \mathbf{e}_q^i + \sum_{i=1}^{3N} p_i \mathbf{e}_p^i \]  

Since the total number of phase points is conserved the system obeys a 6N-dimensional equation of continuity, which can be derived as follows. Consider a 6N-dimensional volume, \( V \), in phase space. The total number of phase points inside \( V \) at the time, \( t \), is

\[ N(V, t) = N_0 \int_V \rho(q, p, t) dq dp \]  

where \( N_0 \) is the total number of systems in the ensemble. The change in \( N(V) \) in the time interval from \( t \) to \( t + \delta t \) is

\[ \left[ \frac{dN}{dt} \right] \delta t = N_0 \left[ \int_V \frac{\partial \rho}{\partial t} dq dp \right] \delta t \]  

Since phase points cannot be created the only way that phase points can be added or subtracted from the volume \( V \) is to flow across its boundary, \( S \). Let \( dS \) be a differential element of the surface, \( S \), and let the 6N-dimensional unit vector, \( \mathbf{n} \), be the outward normal vector to \( dS \). All phase points that are located within a distance

\[ v_n = \mathbf{v} \cdot \mathbf{n} \]  

of \( dS \) flow across it in unit time. It follows that the net number of phase points that are added to \( V \) in the time interval between \( t \) and \( t + \delta t \) is

\[ \left[ \frac{dN}{dt} \right] \delta t = -N_0 \left[ \int_S \rho(\mathbf{v} \cdot \mathbf{n}) dS \right] \]  

The surface integral on the right hand side of equation 10.11 can be converted into an integral over the volume by applying the divergence theorem:

\[ \int_S (\mathbf{A} \cdot \mathbf{n}) dS = \int_V (\nabla \cdot \mathbf{A}) dV \]  

where \( \mathbf{A} \) is a vector and \( \nabla \) is the divergence operator. Given an n-dimensional space with coordinates \( x_1, ..., x_n \),

\[ \nabla = \sum_{i=1}^{n} \mathbf{e}_i \frac{\partial}{\partial x_i} \]  

where \( \mathbf{e}_i \) is a unit vector in the direction of the coordinate \( x_i \). In the specific case of the 6N-dimensional phase space, \( \Sigma^N \), the divergence operator is
\[ \nabla \Sigma = \sum_{i=1}^{3N} e_i^i \frac{\partial}{\partial q_i} + \sum_{i=1}^{3N} e_i^i \frac{\partial}{\partial p_i} \]  

10.14

and equation 10.11 can be rewritten

\[ \left[ \frac{dN}{dt} \right] \delta t = - N_0 \left[ \int_V \left[ \nabla \Sigma^* (\rho v) \right] dV \right] \delta t \]  

10.15

Combining equations 10.15 and equation 10.9 gives

\[ N_0 \left[ \int_V \left[ \frac{\partial \rho}{\partial t} + \nabla \Sigma^* (\rho v) \right] dV \right] \delta t = 0 \]  

10.16

Since this equation must hold for any choice of the volume, V, it holds in particular when \( V \) is so small that the value of the integrand can be assumed constant within it. We are hence led to the equation of continuity in phase space:

\[ \frac{\partial \rho}{\partial t} = - \nabla \Sigma^* (\rho v) \]  

10.17

The equation of continuity in phase space can be simplified by differentiating the parenthetical term on the right hand side to give

\[ \frac{\partial \rho}{\partial t} = - v \cdot \nabla \Sigma (\rho) - \rho (\nabla \Sigma^* v) \]  

10.18

When the second term on the right is written out in full we have, from equations 10.7 and 10.14,

\[ \rho (\nabla \Sigma^* v) = \rho \sum_{i=1}^{3N} \left[ \frac{\partial q_i}{\partial q_i} + \frac{\partial p_i}{\partial p_i} \right] \]  

10.19

But from the Hamiltonian equations of motion, 10.3-4,

\[ \frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial p_i \partial q_i} = - \frac{\partial \dot{p}_i}{\partial p_i} \]  

10.20

which shows that the right hand side of equation 10.19 vanishes. Hence equation 10.18 simplifies to

\[ \frac{\partial \rho}{\partial t} + v \cdot \nabla \Sigma (\rho) = 0 \]  

10.21
The left hand side of equation 10.21 has an important physical meaning that is often used in dynamics. It is the material derivative of \( \rho(q,p,t) \), the time derivative of the distribution function as seen by an observer who moves with the local velocity, \( \mathbf{v} \), of the center of mass of the phase points located at \( (q,p) \), and is written

\[
\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \Sigma(\rho) \tag{10.22}
\]

To see this note that an observer who follows a differential element of phase space that moves with the local velocity, \( \mathbf{v} \), along the mean trajectory will observe a change in the density, \( \rho \), from two sources: the flow of phase points into the volume element across the boundaries and the change in local density due to the fact that the volume element as a whole is translating through space.

Equation 10.21 shows that the material derivative of the distribution function vanishes

\[
\frac{d\rho}{dt} = 0 \tag{10.23}
\]

that is, the distribution function has the same value at every point \( (q,p) \) along a given trajectory of the system. Equation 10.23 has the consequence that the distribution function is a constant of the motion along any trajectory, just as the energy, linear and angular momentum are. This result is known as Liouville's Theorem:

*the distribution function \( \rho(q,p) \) is a constant of the motion.*

Note that Liouville's Theorem holds whether or not the system is in equilibrium.

### 10.3 THE EQUILIBRIUM DISTRIBUTION FUNCTION

The distribution function has the general form

\[
\rho = \rho(q,p,t) \tag{10.24}
\]

We wish to evaluate it for a system at equilibrium in terms of the macroscopic constitutive variables that govern the equilibrium behavior of that system. We do so in three steps, introducing first the constraints imposed by equilibrium, then the constraints imposed by Liouville's Theorem, and finally the constraints imposed by the additive property of its logarithm.
10.3.1 Equilibrium

As shown in Section 10.1 when the system is at equilibrium its distribution function cannot depend explicitly on the time. Hence $\frac{\partial \rho}{\partial t} = 0$ and the distribution function simplifies to the form

$$\rho = \rho(q,p)$$

10.25

10.3.2 Liouville's Theorem

According to Liouville's Theorem the distribution function is a constant along any given trajectory of the system. This means that it cannot be an explicit function of any variable that changes along the trajectory. Since $\{q\}$ and $\{p\}$ fall into this category, $\rho$ can only depend on those combinations of $\{q\}$ and $\{p\}$ that remain constant along the trajectory. The constants of the motion on a given trajectory through a stationary system are the energy, $E$, and the deformation coordinates, $\{u\}$ and $\{N\}$ ($E$, $V$ and $N$ in the case of a one-component fluid). When the system is not isolated these quantities are not the same for all trajectories, but must be constant on any given trajectory. It follows that the most general form the distribution function can have is

$$\rho = \rho(E,\{u\},\{N\},\{\phi\})$$

10.26

where the set $\{\phi\}$ includes other integrals of the motion.

The set of variables $\{\phi\}$ on the right-hand side of equation 10.26 includes constants of the motion whose values are not fixed by the macroscopic variables, either the deformation coordinates or their conjugate forces. But the only information that is available for a given system is the values of its macroscopic coordinates. The microscopic, or internal coordinates are unknown. The actual trajectory that the system follows is, hence, randomly chosen from among those that have given values of the external coordinates. The trajectories must be assigned equal probability whatever the values of the constants of the motion in the set $\{\phi\}$ if these values are not set by macroscopic constraints. It follows that the systems in the representative ensemble must be equally distributed over trajectories that have given values of $E$, $\{u\}$ and $\{N\}$ whatever the values of the other constants of the motion may be. This condition, which is often called the principle of equal a priori probability, has the consequence that the distribution function cannot depend on the set $\{\phi\}$ of internal coordinates, and, hence, that

$$\rho = \rho(E,\{u\},\{N\})$$

10.27

10.3.3 The additivity of $\ln(\rho)$

We showed in the previous chapter that if two systems are joined together their distribution functions multiply, so the logarithms of their distribution functions add. This result is easily generalized to an arbitrary number of systems.
Let a macroscopic system be constructed by joining \( n \) subsystems in an unconstrained contact. Let each of the subsystems be large enough that the subsystems interact weakly. To phrase a simple example, let the subsystems contain one-component fluids. The distribution function for the \( i^{th} \) subsystem is then

\[
\rho^i = \rho^i(E^i, V^i, N^i)
\]

where \( E^i, V^i \) and \( N^i \) are its energy, volume and mole number. A point \((q, p)\) in the phase space of the composite system identifies a state in which the \( i^{th} \) subsystem is in a state \((q^i, p^i)\), where \( q^i \) and \( p^i \) are its individual coordinates and momenta. Since the coordinates and momenta of the different subsystems are independent, there is one member of the representative ensemble of the composite system for every independent way of choosing one member from each of the representative ensembles of the subsystems. Hence

\[
\rho(q, p) = \prod_{i=1}^{n} \rho^i(q^i, p^i) = \prod_{i=1}^{n} \rho^i(E^i, V^i, N^i)
\]

where \( \rho(q, p) \) is the distribution function for the composite system. The logarithms of the density functions add:

\[
\ln[\rho(q, p)] = \sum_{i=1}^{n} \ln[\rho^i(E^i, V^i, N^i)]
\]

Since the distribution functions of the subsystems are functions of their energy, volume and mole number only, it follows from equation 10.29 or 10.30 that the composite distribution function must be a function of the same variables. But since the subsystems have an unrestricted contact with one another, it is impossible to tell which particular subsystems were joined together once the composite system is made. The same composite system can be constructed from many independent sets of subsystems, provided that they have the same total values of \( E, V \) and \( N \). It follows that the distribution function of the composite system must depend only on the total values of \( E, V \) and \( N \), and not on the manner in which these quantities are divided among some arbitrary set of subsystems. Hence

\[
\rho(q, p) = \rho(E, V, N)
\]

and equation 10.30 can be rewritten

\[
\ln[\rho(E, V, N)] = \sum_{i=1}^{n} \ln[\rho^i(E^i, V^i, N^i)]
\]

Since \( E, V \) and \( N \) are additive quantities this relation can only hold if \( \ln(\rho) \) is a linear, homogeneous function of its variables, that is, if
\[ \ln[\rho(E,V,N)] = \alpha - \beta E + \gamma N + \pi V \]  10.33

where \( \alpha, \beta, \gamma \) and \( \pi \) are constants, and \( \beta, \gamma, \) and \( \pi \) have the same value in all parts of the system that interact to exchange the quantities \( E, N \) and \( V \).

To complete the evaluation of the distribution function we need only find the values of the constants \( \alpha, \beta, \gamma \) and \( \pi \). The sign on the constant \( \beta \) is taken to be negative so that \( \beta \), which will be shown to be the reciprocal temperature, is positive.

The same reasoning can be applied to a material that has the general set of constitutive coordinates \( (E,\{u\},\{N\}) \). Provided that these coordinates are additive quantities the result is

\[ \ln[\rho(E,\{u\},\{N\})] = \alpha - \beta E + \sum_k \gamma_k N_k + \sum_k \pi_k q_k \]  10.34

If the system is in motion with net linear momentum, \( \mathbf{P} \), and angular momentum, \( \mathbf{L} \), its distribution function also contains terms that are linear in these variables since they are macroscopic constants of the motion. Hence

\[ \ln[\rho(E,\{u\},\{N\},\mathbf{P},\mathbf{L})] = \ln[\rho(E,\{u\},\{N\})] + \delta \cdot \mathbf{P} + \lambda \cdot \mathbf{L} \]  10.35

where \( \rho(E,\{u\},\{N\}) \) is the distribution function for the system at rest.

### 10.4 THE MICROCANONICAL ENSEMBLE: ENTROPY

#### 10.4.1 The microcanonical ensemble

The simplest system that is physically realistic is an isolated system that contains a one-component fluid. This system is represented by an ensemble whose members follow all trajectories that are consistent with given values of \( E, V \) and \( N \). Such an ensemble is called a microcanonical ensemble. To be consistent with equation 10.33 its distribution function, the microcanonical distribution, must have a constant value on the \((6N-7)\)-dimensional hypersurface in its \(6N\)-dimensional phase space that contains states with the given values of \( E \) within the volume \( V \):

\[ \ln[\rho(E,V,N)] = -S \]  10.36

where we have used the symbol, \( S \), for convenience. We shall show below that \( S \) is equivalent to the entropy of the system.

Equation 10.36 has a simple alternative interpretation. The distribution function, \( \rho(q,p) \), is the probability that a randomly chosen member of the ensemble would be found
in the state \((q,p)\). The constancy of \(\rho(q,p)\) means that all possible states are equally likely. Since we chose the dimensions of \(q\) and \(p\) so that there is one state per unit volume of phase space, the distribution function is related to the total number of states of the system, \(\omega(E,V,N)\), by the equation

\[
\rho(q,p) = \frac{1}{\omega(E,V,N)}
\]

It then follows from equation 10.36 that

\[
S(E,V,N) = \ln[\omega(E,V,N)]
\]

### 10.4.2 Surface and spatial forms of the distribution function

The systems in a microcanonical distribution have given values of the total energy, \(E\), volume, \(V\), and mole number, \(N\), and are usually taken to be at rest. Their states are uniformly distributed over a portion of a \((6N-7)\)-dimensional hypersurface in the \(6N\)-dimensional space that is spanned by the coordinates \(\{q\}\) and \(\{p\}\). The microcanonical distribution function that describes this situation can be written in either of two ways, each of which is convenient for some problems.

The simplest form was implicitly used above, where assumed the hypersurface and wrote the distribution function for the probability of states on that hypersurface. In this picture

\[
\rho(E,V,N) = e^{-S(E,V,N)}
\]

The normalization condition on the distribution function is

\[
\int_\Sigma \rho(q,p)dqdp = [e^{-S}] \int_\Sigma dqdp = \omega e^{-S} = 1
\]

where the range of integration is confined to that part of the hypersurface of energy, \(E\), that has zero net momentum and all spatial coordinates, \(\{q\}\), within the volume, \(V\). The expected value of any dynamical variable, \(R(q,p)\), is

\[
\langle R \rangle = \int_\Sigma R(q,p)\rho(q,p)dqdp = \frac{1}{\omega} \int_\Sigma R(q,p)dqdp
\]

where the range of integration is restricted as above.

However, it is sometimes convenient to write the distribution function so that its variables \((q,p)\) range over the whole of \(\Sigma^N\). Letting the total energy be \(E^o\) and the total volume be \(V^o\), the density function in \(6N\)-dimensional phase space can be written

\[
\rho(q,p) = [e^{-S(E,V,N)}]\delta(E-E^o)\delta(P)\delta(L)\theta(V^o)
\]
The function $\delta(x-x^\circ)$ in this equation is the *Dirac $\delta$-function*, which has the property that, given an arbitrary function, $f(x)$,

$$\int_a^b f(x)\delta(x-x^\circ)\,dx = f(x^\circ) \tag{10.43}$$

if $x^\circ$ is in the range of integration $a \leq x \leq b$, and is zero otherwise. The Dirac $\delta$-function selects a particular value of a variable from an integration over a range of values of the variable. The function $\theta(V)$ is a step function that has the value, 1, if all spatial coordinates are inside the volume, $V$, and is zero otherwise. A function of this type is sometimes called a *Heavyside function*. With this notation the expected value of the dynamical variable, $R(q,p)$, is

$$\langle R \rangle = \int \Sigma R(q,p)\rho dq dp$$

$$\quad = \frac{1}{\omega} \int \Sigma R(q,p)\delta(E-E^\circ)\delta(P)\delta(L)\theta(V^\circ)\,dq dp \tag{10.44}$$

We shall normally use the simpler, surface form of the distribution function given by equation 10.39. Whatever restrictions pertain to the total energy, momentum, volume, mole number, or other macroscopic variables are implicitly incorporated into the range of integration over the constant energy surface in phase space.

### 10.4.3 The statistical entropy

We can now show that the parameter, $S$, the *statistical entropy*, is equivalent to the thermodynamic entropy. This is done by demonstrating that the statistical entropy has the properties of the thermodynamic entropy: it is a state function, its value in an isolated system can only increase, and it is the fundamental equation for an isolated system.

First, the statistical entropy of an isolated system is a state function whose value is uniquely determined by the values of its geometric coordinates. This statement follows immediately from equation 10.38 and the definition of the microcanonical ensemble. The ensemble contains all states that are consistent with the constraints on the isolated system, which are simply the values of its geometric coordinates. For a one-component fluid,

$$S = \ln[\omega(E,V,N)] = \tilde{S}(E,V,N) \tag{10.45}$$

since the number of states, $\omega$, is fixed by $E$, $V$ and $N$.

Second, the statistical entropy of an isolated system can only increase. To prove this let an isolated system be constructed by joining two isolated systems to one another.
A state of the composite system is a distinguishable combination of a state of system 1 and a state of system 2, so the number of states of the composite system, $\omega$, is

$$\omega = \omega^1 \omega^2$$  

and

$$S = S^1 + S^2$$

which shows, incidentally, that the statistical entropy is additive. Now relax the constraints so that the two systems interact with one another. All of the states that were possible when the subsystems were mutually isolated are still possible, so the entropy of the system in the unconstrained condition is at least as great as it was when the system was constrained. But there may be additional states that involve some redistribution of material or energy between the two subsystems and only become possible after the constraint is broken. Hence, writing $\omega'$ and $S'$ for the number of states and the entropy in the unconstrained state,

$$\omega' \geq \omega$$  

$$S' \geq S$$

Since any change in an isolated system can be modeled by a manipulation of internal constraints that restrict the interaction between parts of the system, the statistical entropy can only increase. It follows as a corollary that the statistical entropy of an isolated system has its maximum value when the system is in equilibrium.

Finally, note that the statistical entropy has an integrated form that is formally identical to that of the thermodynamic entropy. From equations 10.34 and 10.36, for a one-component fluid,

$$S - \alpha = \tilde{S}(E,V,N) = \beta E - \gamma N - \pi V$$

where $\alpha$ is a constant.

It can be shown that the right hand side of 10.50 is the integrated form of the statistical entropy. To accomplish this let the system be divided into $n$ identical subsystems, and assume that the system is homogeneous so that the subsystems are in identical states. The total energy, volume and mole number are just $nE^o$, $nV^o$ and $nN^o$, where $E^o$, $V^o$ and $N^o$ are the quantities in the subsystems. Since the entropy is also additive,

$$\tilde{S}(E,V,N) = \tilde{S}(nE^o, nV^o, nN^o) = n\tilde{S}(E^o, V^o, N^o)$$

Equation 10.51 shows that the statistical entropy is a linear homogeneous function of its variables. Differentiating the second two forms of equation 10.51 with respect to the
variable, \( n \), as in the similar derivation of the integrated form of the macroscopic entropy function, we have

\[
\tilde{S} = \left[ \frac{\partial \tilde{S}}{\partial E} \right] E + \left[ \frac{\partial \tilde{S}}{\partial V} \right] V + \left[ \frac{\partial \tilde{S}}{\partial N} \right] N
\]

10.52

which is consistent with equation 10.50 if and only if

\[ \alpha = 0 \]

10.53

and the constants \( \beta, \gamma \) and \( \pi \) are proportional to the thermodynamic forces that are determined by the partial derivatives of the entropy function:

\[
\beta = \left[ \frac{\partial \tilde{S}}{\partial E} \right] = \frac{1}{T}
\]

10.54

\[
\gamma = -\left[ \frac{\partial \tilde{S}}{\partial N} \right] = \frac{\mu}{T}
\]

10.55

\[
\pi = -\left[ \frac{\partial \tilde{S}}{\partial V} \right] = -\frac{P}{T}
\]

10.56

where \( T \) is the absolute temperature, \( \mu \) is the chemical potential, and \( P \) is the pressure.

These results show that

\[ S = \tilde{S}(E,V,N) \]

10.57

is the fundamental equation for an isolated system whether \( S \) is regarded as the classical or statistical entropy. Hence the two are identical.

Moreover, the uniformity of the constants \( \beta, \gamma \) and \( \pi \) implies the uniformity of the thermodynamic forces, \( T, \mu \) and \( P \), and reproduces the conditions of thermal, chemical and mechanical equilibrium within a homogeneous one-component fluid.

These results are readily generalized to other classes of materials. Given the deformation coordinates \( E, \{u\} \) and \( \{N\} \) and the definition of the statistical entropy,

\[
S = S(E,\{u\},\{N\}) = -\ln[p(E,\{q\},\{N\})]
\]

\[ = \ln[\omega(E,\{u\},\{N\})] \]

10.58

equation 10.34 has the consequence that
\[ S = \beta E - \sum_k \gamma_k N_k - \sum_k \pi_k q_k \]  
\[ \beta = \left[ \frac{\partial \tilde{S}}{\partial E} \right] = \frac{1}{T} \]  
\[ \gamma_k = - \left[ \frac{\partial \tilde{S}}{\partial N_k} \right] = \frac{\mu_k}{T} \]  
\[ \pi_k = - \left[ \frac{\partial \tilde{S}}{\partial q_k} \right] = \frac{p_k}{T} \]  

and \( p_k \) is the force conjugate to the mechanical coordinate, \( q_k \).

### 10.5 THE CANONICAL ENSEMBLE: HELMHOLTZ FREE ENERGY

#### 10.5.1 The canonical ensemble

Next consider the case of a system at rest with a fixed chemical and mechanical content that interacts thermally with its environment. When the system contains a one-component fluid its wall fixes the volume and mole number, but leaves the energy undetermined. If the environment is a thermal reservoir that is very large compared to the system then the energy of the system can have any value whatever. The system is represented by a *canonical ensemble*, whose members include systems in all states \( (q, p) \) that fall in the volume \( V \) with any value of the energy but no net momentum.

The *canonical distribution function* for a one-component fluid can be written immediately from equation 10.33:

\[ \ln[\rho(\beta, V, N)] = \xi(\beta, V, N) - \beta E \]  

where the value of \( \beta \) is fixed by the environment and we have used the symbol \( \xi(\beta, V, N) \) to represent the constant terms in equation 10.33. The function \( \xi(\beta, V, N) \) can be evaluated from the condition that \( \rho(\beta, V, N) \) be normalized:

\[ \int_{\Sigma} \rho(\beta, V, N) dq dp = e^{\xi} \int_{\Sigma} e^{-\beta E(q, p)} dq dp = 1 \]  

#### 10.5.2 The canonical partition function

The *canonical partition function* of a one-component fluid, \( Z(\beta, V, N) \), is defined by the equation
\[ Z(\beta,V,N) = Z(\beta) = \int_{\Sigma} e^{-\beta E(q,p)} \, dqdp \]  

where we write the canonical partition function as \( Z(\beta) \) for notational convenience. The integral is taken over the \((6N-6)\)-dimensional hypersurface of zero net momentum in phase space, and over the portion of that surface that is contained within the volume, \( V \). From equation 10.64,

\[ \xi(\beta,V,N) = -\ln[Z(\beta)] \]

which confirms the functional dependence assigned to \( \xi \). The expected value of any dynamical variable in the canonical ensemble can then be written as a weighted integral over phase space

\[
\langle R \rangle = \int_{\Sigma} R(q,p)\rho dqdp
= \left[ \frac{1}{Z(\beta)} \right] \int_{\Sigma} R(q,p)e^{-\beta E(q,p)} \, dqdp
\]

**10.5.3 The Helmholtz free energy of a one-component fluid**

To find the classical thermodynamic potential of the canonical ensemble we require the value of its entropy. Since we know how to measure the entropy of an isolated system we can measure the entropy of the canonical ensemble by the following hypothetical experiment. Isolate the canonical system from its thermal reservoir at some random time. Its energy is then fixed at whatever value, \( E \), it happens to have at that instant and its entropy is

\[ S = -\ln[\rho(E,V,N)] \]

The expected value of these measurements is

\[ \langle S \rangle = -\langle \ln[\rho(E,V,N)] \rangle \]

which we shall define to be the *statistical entropy of the canonical ensemble*:

\[ S(\beta,V,N) = -\int_{\Sigma} [\rho \ln(\rho)] \, dqdp \]

The definition of the statistical entropy leads immediately to a statistical definition of the Helmholtz free energy. Substituting the value of \( \rho \) in the canonical ensemble from equation 10.63

\[ S(\beta,V,N) = -\int_{\Sigma} [\xi(\beta,V,N) - \beta E] \rho dqdp \]
\[ = -\bar{\xi}(\beta,V,N) + \beta\langle E \rangle \]  

Comparing this equation with the classical definition of the Helmholtz free energy leads to the statistical definition

\[ F(T,V,N) = \beta^{-1}\bar{\xi}(\beta,V,N) \]

\[ = -\frac{1}{\beta} \ln[Z(\beta)] \]  

With this definition the canonical distribution function can be written

\[ \rho(q,p) = e^{\beta[F-E(q,p)\big]}} \]  

for those states \((q,p)\) whose net momenta vanish and whose spatial coordinates lie within the volume, \(V\).

The function \(\tilde{F}(T,V,N)\) is the fundamental equation for a one-component fluid that is in contact with a thermal reservoir across a rigid, impermeable wall. This is precisely the situation in which the fluid is represented by a canonical ensemble. However, to complete the demonstration that the function that is given in equation is the Helmholtz free energy we need to show that it has the proper functional dependence and contains the information that is contained in the classical free energy function.

The functional dependence of \(\tilde{F}\) follows from equation 10.72 with the identification

\[ \beta = \frac{1}{T} \]  

which was established in the discussion of the microcanonical ensemble.

\[ F = \tilde{F}(\beta,V,N) = \tilde{F}(T,V,N) \]  

and the natural variables of the statistical function are the same as those of the classical one.

To show that \(\tilde{F}(T,V,N)\) contains the information appropriate to the Helmholtz free energy we need only show that its first derivatives are the statistical analogues of the thermodynamic variables conjugate to \(T\), \(V\) and \(N\). The thermal derivative of the Helmholtz free energy is

\[ \left[ \frac{\partial \tilde{F}}{\partial T} \right] = -S(T,V,N) \]
The statistical analog is, from equations 10.72 and 10.74,

\[
\left[ \frac{\partial \tilde{F}}{\partial T} \right] = \frac{\partial}{\partial T} \{ -T \ln[Z(\beta)] \} \\
= \beta F + \beta \frac{\partial}{\partial \beta} \ln[Z] \\
= \beta F - \beta \left[ \frac{1}{Z} \sum E e^{-\beta E(q,p)} dq dp \right] \\
= \beta (F - \langle E \rangle) = -S(T,V,N)
\]

which is identical to 10.76.

10.5.4 The pressure and the chemical potential

The thermodynamic pressure of a macroscopic system is defined as the volume derivative of the Helmholtz free energy function:

\[
P = -\left[ \frac{\partial \tilde{F}}{\partial V} \right]
\]

The statistical analog of this expression is

\[
P = \frac{\partial}{\partial V} \{ T \ln[Z(\beta)] \} = \left[ \frac{1}{\beta Z(\beta)} \right] \left[ \frac{\partial Z(\beta)}{\partial V} \right]
\]

To show that this is a consistent definition recognize that the volume fixes the phase space of the system. Changing the volume changes the phase space. If the canonical partition function is written

\[
Z(\beta) = \int_{E_0}^{\infty} \omega(E,V,N) e^{-\beta E} dE
\]

then a change in the volume alters the partition function by changing the degeneracy, \(\omega(E,V,N)\), of a state that has energy, \(E\). The factor \(e^{-\beta E}\) is simply a weighting factor that depends on the energy, \(E\), only. Differentiating equation 10.80,

\[
\left[ \frac{\partial Z(\beta)}{\partial V} \right] = \int_{E_0}^{\infty} \left[ \frac{\partial \omega}{\partial V} \right] e^{-\beta E} dE
\]
The function \( \omega(E,V,N) \) is the degeneracy of the microcanonical ensemble that represents an isolated system with the coordinates \((E,V,N)\), and \( \ln(\omega) \) is its entropy. The partial derivative

\[
\frac{\partial}{\partial V} \{ \ln[\omega(E,V,N)] \} = \frac{\partial}{\partial V} [ \tilde{S}(E,V,N) ] = \beta P(E,V,N)
\]

gives the pressure of the isolated system characterized by \((E,V,N)\). Hence equation 10.81 can be re-written

\[
\left[ \frac{\partial Z(\beta)}{\partial V} \right] = \int_{E_0}^{\infty} \left[ \frac{\partial}{\partial V} \tilde{S}(E,V,N) \right] \omega(E)e^{-\beta E} dE
\]

Returning to equation 10.79 we have

\[
P = \left[ \frac{1}{\beta Z(\beta)} \right] \left[ \frac{\partial Z(\beta)}{\partial V} \right]
\]

\[
= \left[ \frac{1}{\beta Z(\beta)} \right] \int_{E_0}^{\infty} \left[ \frac{\partial}{\partial V} \tilde{S}(E,V,N) \right] \omega(E)e^{-\beta E} dE
\]

\[
= \frac{1}{\beta} \left( \frac{\partial \tilde{S}}{\partial V} \right) = \langle P \rangle
\]

Hence the value of the thermodynamic pressure that is defined by equations 10.78 and 10.79 is the mean value of the pressure that would be measured by randomly selecting members of the ensemble, isolating them, and determining their pressures individually. The influence of the change of volume on the phase space of the ensemble is fully accounted for in the derivation of this expression.

There are two other methods of establishing equation 10.79 that are also useful, and are worth exploring because they help to establish the consistency between the classical and statistical meaning of the partial derivatives of the fundamental equation.

The first is based on a slightly different formulation of the partition function. If we were to randomly select a member of the canonical ensemble it would instantaneously have an energy, \( E \), and a temperature \( \beta^{-1} \) that is fixed by the reservoir. The systems that have energy \( E \) are represented by a microcanonical ensemble with degeneracy \( \omega(E) \), and hence have the Helmholtz free energy.
Notes on the Thermodynamics of Solids  

\[
F(E) = E - \beta^{-1}\ln(\omega) = E - \beta^{-1}S \quad 10.85
\]

Using this relation the partition function, \(Z(\beta)\), can be written

\[
Z(\beta) = \int_{E_0}^{\infty} \omega(E,V,N)e^{-\beta E}dE
\]

\[
= \int_{E_0}^{\infty} e^{-\beta F(E)}dE \quad 10.86
\]

Given the thermodynamic definition of the pressure, the mean value of the pressure over the ensemble is

\[
\langle P \rangle = \left[ \frac{1}{Z(\beta)} \right] \int_{E_0}^{\infty} P e^{-\beta F(E)}dE = -\left[ \frac{1}{Z(\beta)} \right] \int_{E_0}^{\infty} \left[ \frac{\partial F}{\partial V} \right] e^{-\beta F(E)}dE
\]

\[
= \left[ \frac{1}{\beta Z(\beta)} \right] \left[ \frac{\partial Z(\beta)}{\partial V} \right]
\]

\[
= -\left[ \frac{\partial \tilde{E}}{\partial V} \right] \quad 10.87
\]

The second alternate derivation is based directly on the method of measurement that was originally used to define the pressure in classical thermodynamics. Suppose that we randomly select a member of the ensemble, enclose it in an adiabatic wall, and determine its pressure by changing its volume quasi-statically. The pressure is defined by the partial derivative of the energy function

\[
P = -\frac{\partial}{\partial V} \tilde{E}(S,V,N) = -\left[ \frac{\partial \tilde{E}}{\partial V} \right] \quad 10.88
\]

The average value of this quantity over the ensemble is

\[
\langle P \rangle = -\left[ \frac{\partial \tilde{E}}{\partial V} \right] = -\int \Sigma \left[ \frac{\partial \tilde{E}}{\partial V} \right] \rho(q,p)dqdp
\]

\[
= -\left[ \frac{1}{Z(\beta)} \right] \int_{E_0}^{\infty} \omega(E)e^{-\beta E}dE
\]

\[
= \left[ \frac{1}{\beta Z(\beta)} \right] \left[ \frac{\partial Z(\beta)}{\partial V} \right] = T \frac{\partial}{\partial V} \{\ln[Z(\beta)]\} \quad 10.89
\]

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where we have used the fact that the partial derivative is taken at constant entropy, hence at constant \( \omega \), in making the transition from the third to the fourth form on the right-hand side. This is operationally consistent, since the act of selecting a member of the ensemble does not change the number of states in the ensemble.

Both these derivations show that the thermodynamic pressure, \( P \), is defined by the volume derivative of the Helmholtz free energy, \( F \), and is equal to the mean value of the pressures of the individual members of the ensemble.

A similar argument shows that the thermodynamic definition of the chemical potential

\[
\mu = \left[ \frac{\partial \tilde{F}}{\partial N} \right] = - T \left[ \frac{\partial}{\partial N} \{ \ln[Z(\beta)] \} \right]
\]

is equivalent to the definition

\[
\mu = \langle \mu \rangle
\]

where \( \langle \mu \rangle \) is the mean value of a series of measurements of the chemical potentials of members of the ensemble that have given values of the energy, \( E \).

Finally, the integrated form of the function, \( \tilde{F} \), is fixed by equations 10.35, 10.55-56, and 10.63, and is

\[
F = - PV + \mu N
\]

**10.5.5 The Helmholtz free energy of other classes of materials**

It is straightforward to extend these results to other classes of materials. Assuming the coordinates \((T, \{u\}, \{N\})\) the canonical distribution function can be written

\[
\ln[\rho(\beta, \{u\}, \{N\})] = \beta [F(T, \{u\}, \{N\}) - E]
\]

where

\[
\tilde{F}(T, \{q\}, \{N\}) = - T \ln[Z(\beta)]
\]

and the canonical partition function, \( Z(\beta) \), is given by equation 10.65. The arguments leading to equation 10.77 still hold, which shows that

\[
\left[ \frac{\partial \tilde{F}}{\partial T} \right] = - S
\]
The results of Section 10.5.4 then show that the thermodynamic force, $p_k$, is defined by the relation

$$ p_k = \left[ \frac{\partial F}{\partial u_k} \right] = -T \left[ \frac{\partial}{\partial u_k} \ln[Z(\beta)] \right] = \langle p_k \rangle $$

10.96

where $\langle p_k \rangle$ is the average over the members of the ensemble. The chemical potential is

$$ \mu_k = \left[ \frac{\partial F}{\partial N_k} \right] = -T \left[ \frac{\partial}{\partial N_k} \ln[Z(\beta)] \right] = \langle \mu_k \rangle $$

10.97

which is the statistical definition of the chemical potential of the $k$th component. The integrated form of the fundamental equation is

$$ F = \sum_k p_k q_k + \sum_k \mu_k N_k $$

10.98

These equations reproduce the classical results and show that $\tilde{F}(T,\{q\},\{N\})$ is the Helmholtz free energy.

### 10.6 The Grand Canonical Ensemble: Work Function

#### 10.6.1 The grand canonical ensemble

The third type of system that is commonly treated in statistical thermodynamics is the open system, which is constrained by fixed, imaginary boundary and interacts both chemically and thermally with its environment, which functions as a reservoir to fix the temperature and the chemical potentials. Both the energy and the molar content of the system are variable, and can have arbitrary values if the reservoir is sufficiently large. The representative ensemble therefore contains systems with all possible energies and molar contents in all states that are consistent with its volume. Such an ensemble is called the grand canonical ensemble.

The phase space for the grand canonical ensemble is complicated by the variation in the number of particles, $N$, since $N$ determines the dimension of the phase space. To avoid confusion the members of the grand canonical ensemble are divided into sets, each of which has a given value of the molar content. The image points of the systems in a set of given $N$ (or given $(N,\{x\})$ if more than one chemical component is present) are distributed over its $6N$-dimensional phase space. The distribution function for the ensemble reflects both the distribution of the image points of the ensemble over the sets of different $N$ and over the phase space for each possible value of $N$.

The grand canonical distribution function for a one-component fluid can be written directly from equation 10.33, and is
\[ \ln[p(\beta, \gamma, V)] = \xi(\beta, \gamma, V) - \beta E + \gamma N \]  

where \( \xi(\beta, \gamma, V) \) is a constant for given values of its arguments, which are fixed by the boundary of the system and the state of the reservoir. The grand canonical distribution function is normalized by integrating it for fixed N and then summing over all possible values of N:

\[
\sum_{N=0}^{\infty} \left[ \int [\rho_N(\beta, \gamma, V)] dq dp \right] = 1
\]

where the symbol, \( \rho_N \), indicates the value of the density function for a given value of N and the integral is taken over the phase space, \( \Sigma_N \), of a system that has that value of N.

### 10.6.2 The grand canonical partition function

If equation 10.99 is substituted into 10.100 the result is

\[ \xi(\beta, \gamma, V) = - \ln[Z(\beta, \gamma)] \]

where \( Z(\beta, \gamma) \) is the grand canonical partition function,

\[
Z(\beta, \gamma) = \sum_{N=0}^{\infty} \left[ e^{\gamma N} \left\{ \int_{\Sigma_N} e^{-\beta E(q, p)} dq dp \right\} \right]
\]

Proceeding as we did in the case of the canonical partition function, the grand canonical partition function can be written in the alternate form

\[
Z(\beta, \gamma) = \sum_{N=0}^{\infty} \left[ e^{\gamma N} \left\{ \int_{E(0)}^{\infty} \omega(E, N) e^{-\beta E} dE \right\} \right]
\]

where \( E_0(N) \) is the minimum energy of a system with reciprocal temperature, \( \beta \), and particle number, \( N \), and \( \omega(E, N) \) is the degeneracy of a system with given \( E \) and \( N \). Alternately defining the work function of the microcanonical ensemble of given energy, \( E \), and particle number, \( N \), as

\[ \Omega(E, V, N) = E - TS - \mu N \]

where

\[
S(E, N) = \ln[\omega(E, N)]
\]

and

\[ \ln[p(\beta, \gamma, V)] = \xi(\beta, \gamma, V) - \beta E + \gamma N \]

10.99

where \( \xi(\beta, \gamma, V) \) is a constant for given values of its arguments, which are fixed by the boundary of the system and the state of the reservoir. The grand canonical distribution function is normalized by integrating it for fixed N and then summing over all possible values of N:

\[
\sum_{N=0}^{\infty} \left[ \int [\rho_N(\beta, \gamma, V)] dq dp \right] = 1
\]

where the symbol, \( \rho_N \), indicates the value of the density function for a given value of N and the integral is taken over the phase space, \( \Sigma_N \), of a system that has that value of N.

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where \( Z(\beta, \gamma) \) is the grand canonical partition function,

\[
Z(\beta, \gamma) = \sum_{N=0}^{\infty} \left[ e^{\gamma N} \left\{ \int_{\Sigma_N} e^{-\beta E(q, p)} dq dp \right\} \right]
\]

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\[
Z(\beta, \gamma) = \sum_{N=0}^{\infty} \left[ e^{\gamma N} \left\{ \int_{E(0)}^{\infty} \omega(E, N) e^{-\beta E} dE \right\} \right]
\]

where \( E_0(N) \) is the minimum energy of a system with reciprocal temperature, \( \beta \), and particle number, \( N \), and \( \omega(E, N) \) is the degeneracy of a system with given \( E \) and \( N \). Alternately defining the work function of the microcanonical ensemble of given energy, \( E \), and particle number, \( N \), as

\[ \Omega(E, V, N) = E - TS - \mu N \]

where

\[
S(E, N) = \ln[\omega(E, N)]
\]

and
\[ \mu = \beta^{-1} \gamma \]  

the grand canonical partition function can be written in the simple form

\[ Z(\beta, \gamma) = \sum_{N=0}^{\infty} \left\{ \int_{E_0(N)}^{\infty} e^{-\beta \Omega(E,V,N)} dE \right\} \]  

The expected value of a dynamical variable, \( R \), in the grand canonical ensemble is

\[ \langle R \rangle = \frac{1}{Z(\beta, \gamma)} \sum_{N=0}^{\infty} \left[ e^{\gamma N} \left\{ \int_{\Sigma_N} R(q, p) e^{-\beta \Omega(q, p)} dq dp \right\} \right] \]  

if \( R \) is a function of the energy, volume and mole number,

\[ R = R(E, V, N) \]  

as it is for any macroscopic thermodynamic variable, then its mean value can be written in the simpler form

\[ \langle R \rangle = \sum_{N=0}^{\infty} \left\{ \int_{E_0(N)}^{\infty} R(E, V, N) e^{-\beta \Omega(E,V,N)} dE \right\} \]  

### 10.6.3 The work function of a one-component fluid

The thermodynamic potential that governs the behavior of an open system that contains a one-component fluid is the work function, \( \Omega(T, V, \mu) \). To phrase a statistical definition for this quantity we again consider a sequence of experiments in which the open system is isolated and its entropy measured. As in the case of the canonical ensemble the result is

\[ S = -\langle \ln[p(\beta, \gamma, V)] \rangle \]  

Introducing equation 10.99 leads to the result
\[ S = - \sum_{N=0}^{\infty} \left[ \int \rho_N \ln(\rho_N) d\eta d\rho \right] \]

\[ = - \sum_{N=0}^{\infty} \left[ \int [\xi(\beta, \gamma, V) - \beta E + \gamma N] \rho_N d\eta d\rho \right] \]

\[ = - \xi(\beta, \gamma, N) + \beta \langle E \rangle - \gamma \langle N \rangle \]

Equation 10.112 is consistent with the classical thermodynamics of the open system if

\[ \beta = \frac{1}{T} \]

\[ \gamma = \frac{\mu}{T} \]

and the work function, \( \tilde{\Omega}(T, V, \mu) \), is defined by the relation

\[ \tilde{\Omega}(T, V, \mu) = \xi(\beta, \gamma, V) \beta = - T \ln[Z(\beta, \gamma)] \]

which determines the work function from the grand canonical partition function.

Given the definition 10.115 the distribution function for the grand canonical ensemble can be written

\[ \rho(\beta, \mu, N) = e^{\frac{\beta [\Omega(\mu) + \mu N]}{\beta}} \]

To complete the demonstration that the work function defined in equation 10.101 is equivalent to the fundamental equation of an open system, \( \tilde{\Omega}(T, V, \mu) \), we must show that its differentials produce the statistical analogues of the conjugate variables, S, N and P. Differentiating equation 10.116 and using equation 10.110 gives the relations

\[ \frac{\partial \tilde{\Omega}}{\partial T} = \langle \ln[\rho(\beta, \gamma, V)] \rangle = - S \]

\[ \frac{\partial \tilde{\Omega}}{\partial \mu} = - \langle N \rangle \]

To obtain the partial derivative with respect to the volume we proceed as in Section 10.5.4. Since changing the volume changes the phase space,
\[
\frac{\partial \Omega}{\partial V} = - T \left[ \frac{\partial}{\partial V} \{\ln Z(\beta, \gamma)\} \right]
\]

\[
= - \left[ \frac{1}{\beta Z(\beta)} \right] \sum_{N=0}^{\infty} \left[ e^{\gamma N} \int_{E_0(N)}^{\infty} \wedge \left[ \frac{\partial}{\partial V} \ln(\omega) \right] \omega(E, V, N) e^{-\beta E} dE \right]
\]

\[
= - \left[ \frac{1}{\beta Z(\beta)} \right] \sum_{N=0}^{\infty} \left[ e^{\gamma N} \int_{E_0(N)}^{\infty} \wedge \left[ \frac{\partial S(E, V, N)}{\partial V} \right] \omega(E, V, N) e^{-\beta E} dE \right]
\]

\[
= - \left( \frac{\partial S}{\partial V} \right) = - \langle P \rangle \quad 10.119
\]

from which it follows that the thermodynamic pressure is defined by the relation

\[
P = \langle P \rangle = - \left[ \frac{\partial \Omega}{\partial V} \right] = T \left[ \frac{\partial}{\partial V} \{\ln Z(\beta, \gamma)\} \right] \quad 10.120
\]

The values of the partial derivatives are identical to those for the macroscopic work function.

The integrated form of the work function follows from equations 10.33 and 10.116 and is

\[
\Omega = - PV \quad 10.121
\]

in agreement with the macroscopic result.

### 10.6.4 The work function for general classes of materials

It is reasonably straightforward to generalize the grand canonical ensemble to systems with several mechanical and chemical coordinates. The open system it represents is one whose temperature and chemical potentials are fixed by a macroscopic reservoir while its mechanical coordinates are set by a rigid boundary that is usually imaginary. The appropriate ensemble of states includes systems with all possible numbers of the components present, and, for each chemical content, systems with all possible states that are consistent with the fixed values of the mechanical coordinates. The fundamental equation is, by analogy with the classical case, the work function, \( \Omega(T, \{u\}, \{\mu\}) \), which can be written in terms of the partition function, \( Z(\beta, \{\mu\}) \).
The relations are

\[ \tilde{\Omega}(T,\{u\},\{\mu\}) = - T \ln[Z(\beta,\{\mu\})] \] 10.122

where

\[ Z(\beta,\{\mu\}) = \sum_{\{N\}} \left\{ \exp \left[ \beta \sum_{k=1}^{n} \mu_k N_k \right] \int_{E_0(\{N\})}^{\infty} \omega(E) e^{\cdot \beta E} dE \right\} \] 10.123

where the first summation is taken over all possible sets of numbers \((N_1,\ldots,N_n)\) of the \(n\) components, and the integral inside the bracket is taken over all possible values of the energy of a system that has the given values \((N_1,\ldots,N_n)\) for the particular term in the summation. With some algebra it is possible to show that the expected value of the content of the \(k^{th}\) component is

\[ \langle N_k \rangle = - \frac{\partial \tilde{\Omega}}{\partial \mu_k} \] 10.124

as in equation 10.113. The thermodynamic force conjugate to the \(k^{th}\) mechanical coordinate is

\[ p_k = \langle p_k \rangle = \frac{\partial \tilde{\Omega}}{\partial u_k} \] 10.125

The integrated form of the work function is

\[ \Omega = \sum_k p_k u_k \] 10.126

10.7 OTHER USEFUL ENSEMBLES

The microcanonical, canonical, and grand canonical ensembles are the ones that are most frequently used in statistical thermodynamics. However, other ensembles are applicable to particular experimental situations and are occasionally useful, just as other forms of the fundamental equation are useful in classical thermodynamics. We shall first illustrate the construction of a particular ensemble by considering the Gibbs function for a one-component fluid, and then give a general prescription for constructing statistical ensembles to treat particular cases.

10.7.1 The Gibbs free energy
Consider a one-component fluid that is in thermal and mechanical equilibrium with its environment across an impermeable wall. In classical thermodynamics such a system is governed by the Gibbs free energy. The representative ensemble in statistical thermodynamics contains systems with all possible volumes and systems in all possible states of all possible energies for each value of the volume. The appropriate distribution function is, from equation 10.33,

\[ \ln[(\rho(\beta,\pi,N)) = \xi(\beta,\pi,N) - \beta E + \pi V \tag{10.127} \]

The statistical definition of the entropy gives the identity

\[ S = - \ln[\rho(\beta,\pi,N)] = - \xi(\beta,\pi,N) + \beta \langle E \rangle - \pi \langle V \rangle \tag{10.128} \]

which is consistent with classical thermodynamics if

\[ \beta = \frac{1}{T} \tag{10.129} \]

\[ \pi = - \frac{P}{T} \tag{10.130} \]

\[ \beta G(T,P,N) = \xi(\beta,\pi,N) \tag{10.131} \]

where \( G(T,P,N) \) is the Gibbs free energy.

The density function can then be written

\[ \rho(\beta,P,N) = e^{\beta G(T,P,N) - E - PV} \tag{10.132} \]

The requirement that the density function be normalized yields the relation

\[ G(T,P,N) = - T \ln[Z(\beta,P)] \tag{10.133} \]

where the partition function for the Gibbs ensemble is

\[ Z(\beta,P) = \int_{0}^{\infty} e^{-\beta PV} \left[ \int_{\Sigma V} e^{-\beta E(q,p)} dqdp \right] dV \]

\[ = \int_{0}^{\infty} e^{-\beta PV} \left[ \int_{E_0}^{\infty} \omega(E,V,N) e^{-\beta E} dE \right] dV \tag{10.134} \]
where the first integral is taken over all values of the volume and the second is taken over
the portion of phase space that is contained in the volume, \( V \). The expected value of the
dynamical variable, \( R(q,p) \), is

\[
\langle R \rangle = \frac{1}{Z(\beta,P)} \int_0^\infty e^{-\beta PV} \left[ \int \Sigma_V R(q,p)e^{-\beta E(q,p)} dqdp \right] dV
\]

10.135

The differentials of the statistical Gibbs free energy can be found after some
algebra and are

\[
\frac{\partial G}{\partial T} = \langle \ln(\rho) \rangle = -S
\]

10.136

\[
\frac{\partial G}{\partial P} = \langle V \rangle
\]

10.137

\[
\frac{\partial G}{\partial N} = \langle \mu \rangle
\]

10.138

in agreement with the results of classical thermodynamics.

**10.7.2 Arbitrary experimental conditions**

The results for the general case parallel these. Let a system be constrained so that
a subset of its geometric coordinates is fixed while the complementary set is varied. The
appropriate ensemble contains states that contain all possible values of the variable
quantities.

The logarithm of the density function can be written down immediately; the
defformation coordinates that are variable appear as linear terms with fixed coefficients.
This fact, which we have seen repeatedly in the previous sections, can be derived from
the properties of the Legendre transform of the entropy function. Recall the Massieu
functions, which were introduced and discussed in Section 8.12.7. These are the
thermodynamic potentials based on the entropy function, and have maximal values when
the system is in equilibrium. For the isolated system, the fundamental equation is

\[
S = \tilde{S}(E,\{u\},\{N\})
\]

10.139

which has a maximum at equilibrium. For the isothermal system the governing potential
is

\[
\Psi_1 = S - \beta E = \tilde{\Psi}_1(\beta,\{u\},\{N\}) = -\beta F
\]

10.140
which is maximum at equilibrium when these variables are controlled. Since it is impossible to vary any of the other external coordinates without permitting the energy to vary, if we represent the variables $(E,(q),N)$ by the set $\{x\}$, whose first member is always the energy, then, given that
\[
\begin{bmatrix}
\frac{\partial \tilde{S}}{\partial x_k}
\end{bmatrix} = -\beta \begin{bmatrix}
\frac{\partial \tilde{E}}{\partial x_k}
\end{bmatrix} = -\beta p_k \quad (k = 2,\ldots,n)
\]
the $r$th Massieu function can be written
\[
\Psi_r = S - \beta E + \beta \sum_{k=2}^{r} p_k x_k = \tilde{\Psi}_r(\beta,p_2,\ldots,p_r,x_{r+1},\ldots,x_n)
\]
\[
= -\beta \Phi_r(T,p_2,\ldots,p_r,x_{r+1},\ldots,x_n)
\]
where $\Phi_r(T,p_2,\ldots,p_r,x_{r+1},\ldots,x_n)$ is the $r$th Legendre transform of the energy function. When the variables $T,p_2,\ldots,p_r,x_{r+1},\ldots,x_n$ are the controlled variables the potential $\Psi_r$ has a maximal value while $\Phi_r$ is minimal.

When the variables $T,p_2,\ldots,p_r,x_{r+1},\ldots,x_n$ are controlled the entropy is, from equation 10.142,
\[
S = \Psi_r + \beta E - \beta \sum_{k=2}^{r} p_k x_k
\]
\[
= -\beta \left[ \Phi_r - E + \sum_{k=2}^{r} p_k x_k \right]
\]
10.143
The statistical analog of equation 10.142 can be found by replacing $S$ by $\langle \ln(\rho) \rangle$, and $E$ and the $x_k$ that are variable by their expectation values. The potentials $\Phi_r$ and $\Psi_r$ are properties of the representative ensemble, so their values are not expectation values. The result is
\[
\langle \ln(\rho) \rangle = \beta \left[ \Phi_r - \langle E \rangle - \sum_{k=2}^{r} p_k \langle x_k \rangle \right]
\]
10.144
The density function that leads to this relation among the expectation values can be written by inspection, and is
\[
\ln(\rho) = \beta \left[ \Phi_T - E - \sum_{k=2}^{r} p_k x_k \right]
\]

which must be the density function for the representative ensemble that governs a system with given values of the set of variables \(T, p_2, \ldots, p_r, x_{r+1}, \ldots, x_n\).

The partition function, \(Z(\beta, p_2, \ldots, p_r)\), is defined by the relation

\[
\int \rho dq dp = e^{\beta \Phi_T} \ Z(\beta, p_2, \ldots, p_r) = 1
\]

where the integral is taken over the whole phase space of the ensemble. Its general form is

\[
Z(\beta, p_2, \ldots, p_r) = \int_{x_2} \ldots \int_{x_r} e^{\beta \sum_{k=2}^{r} p_k x_k} \left\{ \int_{E_0[x]}^{\infty} \omega(E) e^{-\beta E} dE \right\} dx_2 \ldots dx_r
\]

where the integrals outside the braces are taken over the range of permissible values of their arguments (usually zero to infinity). If the variable, \(x_k\), is discrete rather than continuous, for example, if \(x_k\) is a mole number, \(N_k\), the integral is replaced by a summation over the permissible values. The integral inside the braces is taken over all possible values of the energy of a system with fixed values of \(x_2, \ldots, x_r\). The partition function can be calculated from a knowledge of the nature and dynamics of the system, and therefore usually becomes the fundamental quantity. The thermodynamic potential is given in terms of it by the simple relation,

\[
\tilde{\Phi}_T(T, p_2, \ldots, p_r, x_{r+1}, \ldots, x_n) = -T \ln[Z(\beta, p_2, \ldots, p_r)]
\]

The forces and quantities that are conjugate to the set \((T, p_2, \ldots, p_r, x_{r+1}, \ldots, x_n)\) are given by the usual thermodynamic relations. However, the explicit equations for these depend on whether the desired quantity is a force or a geometric coordinate. The entropy is

\[
S = -\left[ \frac{\partial \tilde{\Phi}_T}{\partial T} \right] = \ln[Z(\beta, p_2, \ldots, p_r)] - \beta \frac{\partial}{\partial \beta} \ln[Z(\beta, p_2, \ldots, p_r)]
\]

The expected values of the undetermined quantities are

\[
\left\langle x_k \right\rangle = -\left[ \frac{\partial \tilde{\Phi}_T}{\partial p_k} \right] = T \frac{\partial}{\partial p_k} \ln[Z(\beta, p_2, \ldots, p_r)]
\]
\[
\frac{1}{Z} \int_{x_2}^{x_1} \cdots \int_{x_r}^{x_1} \exp \left\{ \beta \sum_{k=2}^{r} p_k x_k \right\} \left\{ \int_{E_0\{\{x\}\}}^{\infty} \exp \left\{ -\beta E \right\} dE \right\} dx_2 \cdots dx_r \quad 10.150
\]

The values of the undetermined forces are
\[
p_k = \frac{\partial \Phi}{\partial x_k} = -T \frac{\partial}{\partial x_k} \ln[Z(\beta, p_2, \ldots, p_r)]
\]

\[
\frac{1}{\beta Z} \int_{x_2}^{x_1} \cdots \int_{x_r}^{x_1} \exp \left\{ \beta \sum_{k=2}^{r} p_k x_k \right\} \left\{ \int_{E_0\{\{x\}\}}^{\infty} \frac{\partial S}{\partial x_k} \exp \left\{ -\beta E \right\} dE \right\} dx_2 \cdots dx_r
\]

\[
= \langle p_k \rangle \quad 10.151
\]

The value of any other dynamical variable is
\[
\langle R \rangle = \frac{1}{Z} \int_{x_2}^{x_1} \cdots \int_{x_r}^{x_1} \exp \left\{ \beta \sum_{k=2}^{r} p_k x_k \right\} \left\{ \int_{\Sigma\{\{x\}\}} \exp \left\{ -\beta E \right\} dqdp \right\} dx_2 \cdots dx_r \quad 10.152
\]

These formulae contain all the results of classical statistical mechanics in a compact, if somewhat complex, set of equations.

### 10.8 DISTINCTABLE STATES; THE GIBBS FACTOR

Throughout this section we have used the symbol for integration over the phase space, \( \Sigma^N \), to mean an integration over the distinguishable classical states. Before using the formulae for calculations it is important to be more specific about what this means.

The formal problem arises from the indistinguishability of identical particles. Suppose that a system consists of \( N \) identical particles, and imagine an experiment in which the coordinates and momenta of two of these are interchanged. This interchange apparently alters the state \((q, p)\) of the system, since the image point is displaced to a different subvolume. But because the particles are indistinguishable there is no experiment that could possibly distinguish the state of the system before the interchange from that afterwards.

In fact, the act of interchanging identical particles must not only lead to identical states of the system, but to the same state. If this were not true the distribution function could not be multiplicative since the act of joining two identical systems would lead to a host of new states that differ only through the interchange of like particles.
We can easily account for this effect algebraically. A state of the system occupies a unit volume in $\Sigma^N$ that is specified by the values of the vectors $p_1, \ldots, p_N, q_1, \ldots, q_N$. There are $N!$ indistinguishable examples of this state that are obtained by permuting the coordinates and momenta of the $N$ particles. Hence an integral over the distinguishable states of a system of $N$ particles is obtained by dividing the integral over $\Sigma^N$ by the Gibbs factor, $N!$. We account for this by defining the symbol

$$
\int_{\Sigma} dqdp = \frac{1}{N!} \int_{\Sigma} dqdp 
$$

where the integral on the right-hand side is an unrestricted integral over the $6N$-dimensional phase space that does not take the indistinguishability of the particles into account.