Equilibrium Statistical Physics: a Review. The goal of a typical equilibrium statistical physics (ESP) calculation is to go from the Hamiltonin description of a physical system to the thermodynamic description, i.e., from $\mathcal{H}(\mathbf{x}_i, \mathbf{p}_i)$ of a collection of particles to a description in terms of T, P, V, N, $\cdots$. It is the thermodynamic description that usually interfaces experiment and personal experience.

I. The two essential ingredients in an ESP calculation are

1. Microscopic knowledge of the physical system of interest, that means $\mathcal{H}$. [It would be nice if you knew all of the energy states of the system, e.g., had complete solution to the problem $\mathcal{H}\Psi_\alpha = E_\alpha \Psi_\alpha$.]

2. Knowledge of the circumstance in which the system resides. This circumstance is described by thermodynamic variables and it is here that these variables enter ESP. Examples;

   (a) (T, V, N): A sample chamber of fixed volume, V, containing N particles, say Argon atoms, is in contact with a **temperature reservoir** characterized by T. [A temperature reservoir is a large physical system having an energy density that is characterized by a temperature. To say a system is in contact with a temperature reservoir means that the system, small in terms of the energy within it compared to the energy in the reservoir, can exchange energy with the reservoir. In thermodynamics one often says that the walls of the system are permeable to energy.]

   (b) (T, P, N): A sample chamber containing N particles, say Argon atoms, is in contact with a **temperature reservoir** characterized by T and with a **pressure reservoir** characterized by P. [A piston with the atmosphere on the outside will do. To say a system is in contact with a pressure reservoir means that the system, small in volume compared to the volume of the reservoir, can exchange volume with the reservoir. The piston can move to maintain constant pressure.]

   (c) (E, V, N): A sample chamber of fixed volume, V, containing N particles, say

Argon atoms, that have a total energy within very tight limits, e.g., $E \leq E_\alpha \leq E + \Delta$, $\Delta \ll E$. This system is completely isolated, no particles get in or out, the volume is fixed (no work can be done on the system) and there is no method of changing the energy.

(d) (T, V, μ): A sample chamber of fixed volume, V, with Argon atoms within, is in contact with a **temperature reservoir** characterized by T and a **chemical potential reservoir** characterized by μ. [A system in equilibrium with a chemical potential reservoir does not have a definite number of particles. It exchanges particles with the chemical potential reservoir and has an average number of particle set by the value of the chemical potential.]

(e) (T, P, μ): A sample chamber, with Argon atoms within, is in contact with a **temperature reservoir** characterized by T, a **pressure reservoir** characterized by P and a **chemical potential reservoir** characterized by μ.

TABLE I: The recipes of ESP; overview.

circumstance	ESP name	partition function	Thermodynamic potential	Thermodynamic name
(E, V, N)	microcanonical ensemble	$\Gamma(E, V, N)$	$S(E, V, N)$	entropy
(T, V, N)	canonical ensemble	$Z(T, V, N)$	$F(T, V, N)$	Helmholtz free energy
(T, V, μ)	grand canonicl ensemble	$\mathcal{Z}(T, V, \mu)$	$P(T, V, \mu)$	pressure
(T, P, N)			$H(T, P, N)$	enthalpy
(T, P, μ)			$G(T, P, \mu)$	Gibbs free energy

Of the 5 circumstance in which a system may reside, listed in the table above, those at constant pressure do not have a statistical description. They do have a thermodynamic description about which we will say more later. [A quick reason why these cases are different. In contrast to a system at constant volume, in which a particle is confined in space (think of the quantum particle in a box, pretty simple), a system at constant pressure has external forces near the system surface. It is hard to write a convenient Hamiltonian for this case; hard to make much progress with what you do write.] Note. Reservoirs are characterized by intensive variables. Things you can buy a gauge for, e.g., temperature, pressure, $\cdots$. (Exception, chemical potential; don't ask for a chemical potential gauge at the hardware store. But there are ways to measure the chemical potential. They are just unfamiliar and not of commercial value.)

II.A The most familiar ESP calculations are those appropriate to circumstance (T, V, N). When this circumstance occurs the systems is said to be described by the *canonical ensemble*. What this means is that you learn its thermodynamics from the recipe

1. Calculate the auxiliary function $Z(T, V, N)$, called the *canonical* partition function,

$$Z(T, V, N) = \sum_{\alpha} e^{-\beta E_\alpha}. \quad \beta^{-1} = k_B T, \tag{1}$$

   where the sum is over all states of the system, see I.1.

2. Form the Helmholtz free energy

$$F(T, V, N) = -k_B T \; ln \; Z(T, V, N). \tag{2}$$

3. Make use of the equation for $F(T, V, N)$ by using thermodynamics. Most importantly

$$dF = -SdT - PdV + \mu dN. \tag{3}$$

from which you get the equations of state:

$$S(T, V, N) = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \tag{4}$$

$$\vdots \quad . \tag{5}$$

As Eq. (1) only seems to contain the T you may ask how V and N become involved. The Hamiltonian is a function of the number of particles, N. The volume, V, shapes the permissible wavefunctions.

II.B Consider the circumstance (E, V, N). When this circumstance occurs the systems is said to be described by the *microcanonical ensemble*. You learn its thermodynamics from the recipe

1. Calculate the auxiliary function $\Gamma(E, V, N)$, called the *microcanonical* partition function,

$$\Gamma(E, V, N) = \sum_\alpha \int_0^\Delta dX \delta(E_\alpha - E + X), \tag{6}$$

where the sum is over all states of the system, see I.1. This formula is a device for simply counting up the number of states of the system with energy in the interval, $E \rightarrow E + \Delta$

2. Form the entropy

$$S(E, V, N) = k_B \; ln \; \Gamma(E, V, N). \tag{7}$$

3. Make use of the equation for $S(E, V, N)$ by using thermodynamics. Most importantly

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \tag{8}$$

from which you get the equations of state:

$$\frac{1}{T(E, V, N)} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \tag{9}$$

$$\vdots \quad . \tag{10}$$

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II.C Consider the circumstance (T, V, μ). When this circumstance occurs the systems is said to be described by the *grand canonical ensemble*. You learn its thermodynamics from the recipe

1. Calculate the auxiliary function $\mathcal{Z}(T, V, \mu)$, called the *grand canonical* partition function,

$$\mathcal{Z}(T, V, \mu) = \sum_N e^{\beta \mu N} \; Z(T, V, N) \tag{11}$$

   where the sum is over all numbers of particles in the system and $Z(T, V, N)$ is from Eq. (1).

2. Form the pressure as

$$P(T, V, \mu) = \frac{k_B T}{V} ln \; \mathcal{Z}(T, V, \mu). \tag{12}$$

3. Make use of the equation for $P(T, V, \mu)$ by using thermodynamics. The grand canonical circumstance is handled differently than A and B above because μ is not often a convenient variable. See your ESP text for examples of how you work with the grand canonical description.