4. ELEMENTS OF EQUILIBRIUM STATISTICAL MECHANICS: THE EQUILIBRIUM ENSEMBLES

4.1 Introduction

Within the framework of equilibrium statistical mechanics one can derive the laws of macroscopic thermodynamics, starting from basic postulates about the microscopic states of material systems. Perhaps more important for applications is the fact that equilibrium statistical mechanics provides expressions for thermodynamic properties (*e.g.*, heat capacity, equation of state behavior of solids, liquids, and gases in pure form and in mixtures, phase coexistence properties, elastic constants, surface and interfacial tension) in terms of interactions at the molecular level. In addition, as we have already mentioned, studies based on equilibrium statistical mechanics reveal a wealth of detailed information about how molecules organize themselves in space, how thermal fluctuations affect this organization, and how molecular structure and motion shape macroscopically manifested behavior; such information is potentially very useful for the engineering design of materials systems.

Central to equilibrium statistical mechanics is the theory of equilibrium ensembles. In section 3.2.2 we introduced the concept of an ensemble and dealt in some detail with ensembles of isolated systems with fixed number of molecules, spatial extent, and total energy. We argued that the nonlinearity of the potential energy functions characterizing

such systems leads to mixing flow in phase space, wherein state points diverge from each other and spread out evenly over the entire constant energy hypersurface. The equilibrium probability distribution of such a constant NVE *microcanonical* ensemble is therefore expected to be uniform over the E-hypersurface; this will be introduced axiomatically in the theory of equilibrium ensembles. In general, we will use the term *equilibrium ensemble* to describe the equilibrium probability density distribution in phase space of a system subject to given external constraints. Different ensembles correspond to different sets of external constraints. Working with different ensembles is equivalent to working with different representations of the fundamental equation in thermodynamics. In the "thermodynamic limit" ($N \to \infty$, all intensive properties being kept constant) all ensembles yield the same thermodynamic behavior. Thus, choosing which ensemble to work with is largely a matter of convenience, dictated by what we know about the system under investigation and which aspects of its microscopic and macroscopic behavior we wish to elucidate.

4.2 The Microcanonical Ensemble

The microcanonical ensemble describes the equilibrium phase-space distribution of a system subject to the constraints of given number(s) of particles, volume, and total energy. (In thermodynamic language, this is an isolated system.) In view of our discussion in section 1.2 we introduce the following postulates, which form the foundation of all equilibrium statistical mechanics:

Postulate of equal a priori probabilities For an isolated system of fixed total energy E and fixed size (V, N) [or $(V, N_1, N_2, \ldots, N_n)$ in the case of a multicomponent system], all possible microstates are equally likely at thermodynamic equilibrium.

Ergodic hypothesis Given enough time, an isolated system will sample all microstates consistent with the macroscopic constraints imposed on it. As a consequence, the time average of any phase function can be substituted by the corresponding equilibrium ensemble average [compare Eqs. (3.20), (3.21), (3.23), (3.24)]. Measured values of thermodynamic properties (*e.g.*, pressure) can be thought of as time averages of microscopic dynamical quantities (*e.g.*, force on a container wall due to molecules colliding with the wall per unit area of wall). By this hypothesis, therefore, properties can be estimated as equilibrium ensemble averages.

In a *quantum mechanical description*, microstates (quantum states) are discrete. The probability distribution of microstates is also discrete (*i.e.*, we speak of microstate *probabilities*, rather than of a probability density in phase space).

Let $\Omega(N, V, E)$ be the number of microstates with energy between E and $E - \delta E$, where δE is very small relative to the total energy E, yet sufficiently large, so that at least one energy level (eigenvalue of the Hamiltonian operator) lies within the considered energy interval. By virtue of the postulate of equal *a priori* probabilities, the probability of a given microstate ν is

$$P_\nu^{NVE} = \begin{cases} \dfrac{1}{\Omega(N,V,E)}, & \text{if } E - \delta E < E_\nu < E; \\ 0, & \text{otherwise.} \end{cases} \tag{4.1}$$

Note that P_ν^{NVE} is the probability of a *microstate*, not of an energy level. To determine the probability of an energy level E_ν, P_ν^{NVE} must be multiplied by the degeneracy of that level.

In a *classical description*, microstates form a continuum in phase space. We speak of an equilibrium *probability density* $\rho^{NVE}(\mathbf{p},\mathbf{q})$. The analogue of definition (4.1) is

$$\rho^{NVE}(\mathbf{p},\mathbf{q}) = \begin{cases} \dfrac{1}{\Sigma(E)}, & \text{if } E-\delta E < \mathcal{H}(\mathbf{p},\mathbf{q}) < E\ ; \\ 0, & \text{otherwise.} \end{cases} \tag{4.2}$$

with

$$\Sigma(N,V,E) = \int_{\substack{\text{region in}\\ \text{phase space}\\ \text{where}\\ E-\delta E<\mathcal{H}(\mathbf{p},\mathbf{q})<E}} d^{3N}p\, d^{3N}q$$

Eq. (4.2) is essentially the same as Eq. (3.25). Note that we have dropped the designation "*eq*", since all discussion in this section will refer to equilibrium ensembles. The density ρ^{NVE} has dimensions of $(pq)^{-3N}$, as it should.

In the classical formulation, one can define a dimensionless quantity corresponding to the "number of microstates" $\Omega(N,V,E)$ as

$$\Omega(N,V,E) = \frac{1}{h^{3N}\,N!}\Sigma(N,V,E) = \frac{1}{h^{3N}\,N!} \int_{\substack{\text{region in}\\ \text{phase space}\\ \text{where}\\ E-\delta E<\mathcal{H}(\mathbf{p},\mathbf{q})<E}} d^{3N}p\, d^{3N}q \tag{4.3}$$

The prefactor $1/(h^{3N}N!)$ ensures consistency between the classical and quantum mechanical pictures. The factor h^{3N} essentially tells us that there is a lower limit to the resolution with which we can define state points in the phase space continuum, imposed

by the uncertainty principle along each molecular coordinate. The factor $N!$ has to do with the fact that in the correct (quantum mechanical) picture molecules are inherently indistinguishable: A microstate of the system would be described by an N-particle wavefunction; permutations of the particles can at most change the sign of the wavefunction, but do not produce a new system microstate (compare chapter 2.) Use of the factor $1/N!$ in classical statistical mechanics is referred to as "*correct Boltzmann counting*". It was introduced empirically by J.W.Gibbs to resolve the so-called Gibbs paradox (entropy increase upon mixing two quantities of the same gas without change in the temperature or density) [Huang 1963].

A connection with thermodynamics is established through the *definition of the entropy* (Boltzmann equation):

$$S(N,V,E) \equiv k_B \ln \Omega(N,V,E) \tag{4.4}$$

where $k_B = R/N_A = 1.380 \times 10^{-23}$ J/(molecule K) is the Boltzmann constant.

One can readily see that, in the thermodynamic limit ($N \to \infty$, $V \to \infty$, N/V remaining constant), the entropy, as defined by Eq. (4.4), is an extensive property. If the total system is composed of two subsystems A and B with numbers of microstates Ω_A and Ω_B, respectively, then the number of microstates for the total system will be $\Omega_A \Omega_B$, and $S_{A+B} = k_B \ln(\Omega_A \Omega_B)$. [For a rigorous proof see Reichl 1980, p 242.]

Eq. (4.4) establishes a **fundamental thermodynamic equation in the entropy representation**, in the form $S = S(n,V,U)$ (where n is the number of moles and U the

internal energy). From this equation, all thermodynamic properties of the system can be derived [Modell and Reid 1983].

In particular, the *temperature* T is defined by

$$\beta \equiv \frac{1}{k_B T} = \frac{\partial \ln \Omega}{\partial E} = \frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)_{N,V} \tag{4.5}$$

Quantum mechanics teaches us that the number of microstates $\Omega(N, V, E)$ is a rapidly increasing function of the energy E. This ensures that the temperature is positive.

In practice, the value of S does not change if, in place of Ω (volume of shell in phase space between energies $E - \delta E$ and E) one uses the quantity $\sum_{i=1}^{E/\delta E} \Omega(N, V, E_i)$ (total volume of phase space corresponding to energies up to E). The reason is that, because of the high dimensionality of phase space, the outermost shell of the region corresponding to energies up to E contains an overwhelmingly large fraction of the volume of that region. For a formal proof see Reichl 1980, p 243. Use of the total volume, rather than the shell volume, in Eq. (4.4) may be advantageous in some calculations.

4.3 Second Law of Thermodynamics

We briefly sketch here how one can derive the second law of thermodynamics from the Boltzmann equation for the entropy, hence from the fundamental postulates of section 4.1.

There are several equivalent statements of the second law. According to the variational statement [Chandler 1987], the entropy of an isolated system at equilibrium is at a maximum with respect to the imposition of any internal constraint on the system. By

internal constraint is meant a constraint that does not change the total number of moles of each species present, the total volume, and the total energy.

Consider a system at equilibrium at fixed total N, V, and E. Imagine that an internal constraint is imposed on it, *e.g.*, by dividing it into two subsystems A and B, such that $N_A + N_B = N$, $V_A + V_B = V$, $E_A + E_B = E$. The set of microstates accessible to the partitioned system is necessarily a subset of the set of microstates that the system could assume in its initial state (*i.e.*, before imposing the internal constraint). Consequently,

$$\Omega(N, V, E) > \Omega(N, V, E; \text{ internal constraint})$$

and, by Eq. (4.4),

$$S(N, V, E) > S(N, V, E; \text{ internal constraint}) \tag{4.6}$$

Eq. (4.6) constitutes the variational statement of the second law.

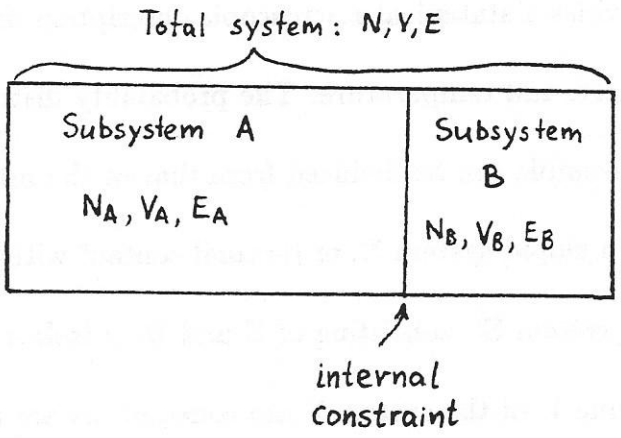

Figure 4.1 For the derivation of the variational statement of the second law

4.4 Third Law of Thermodynamics

The Boltzmann equation, Eq. (4.4), establishes an absolute value for entropy. At absolute zero, a perfect crystalline substance of given density localizes itself in its lowest-energy quantum microstate (ground state). Thus, $\Omega(N, V, E) = 1$, hence

$$S = k_B \ln \Omega(N, V, E) = 0 \tag{4.7}$$

Eq. (4.7) is a statement of the third law.

4.5 The Canonical (NVT) Ensemble

4.5.1 Boltzmann Distribution and the Canonical Partition Function

The canonical ensemble provides a statistical microscopic description of a system at constant number of moles, volume, and temperature. The probability distribution of microstates in the canonical ensemble can be deduced from that of the microcanonical ensemble as follows. Consider a closed system Σ, in thermal contact with a much larger system (bath) B. The total system Σ', consisting of Σ and B, is isolated. The number of molecules N and the volume V of the system Σ are constant, as are the total quantities $N_{\Sigma'} = N + N_B$ and $V_{\Sigma'} = V + V_B$. As a result of interaction with the bath, the energy E of system Σ fluctuates. We will use the label ν for the various microstates that

the system Σ can assume, each characterized by an energy level E_ν. The total energy $E_{\Sigma'} = E + E_B$, however, remains constant.

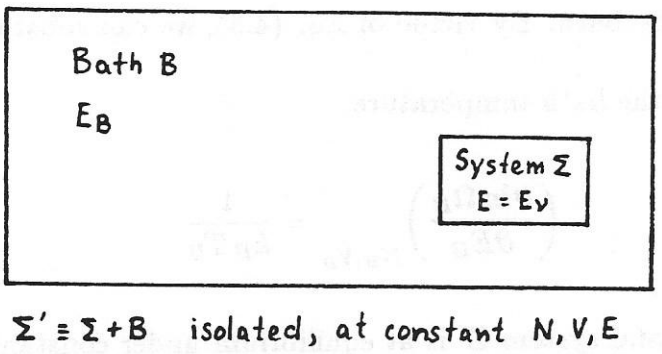

Figure 4.2 For the derivation of the probability distribution of microstates in the canonical ensemble.

If the system Σ is in a *definite* microstate ν, the number of microstates accessible to the *total* system is equal to the number of microstates accessible to the bath. Let us call that number $\Omega_B(N_B, V_B, E_{\Sigma'} - E_\nu)$, or, for the sake of brevity, $\Omega_B(E_{\Sigma'} - E_\nu)$. Since the total system $\Sigma' = \Sigma + B$ is isolated, therefore described by the microcanonical ensemble, all its microstates are equiprobable. The probability of observing the system Σ in state ν will then be

$$P_\nu^{NVT} = \frac{\Omega_B(E_{\Sigma'} - E_\nu)}{\Omega_{\Sigma'}(E_{\Sigma'})} \propto \Omega_B(E_{\Sigma'} - E_\nu) = \exp\left[\ln \Omega_B(E_{\Sigma'} - E_\nu)\right] \qquad (4.8)$$

since $\Omega_{\Sigma'}(E_{\Sigma'})$ is a constant. Now, since $E_\nu << E_{\Sigma'}$, the quantity within the brackets in Eq. (4.8) is given, to an excellent approximation, by the following Taylor expansion,

truncated after the first order term:

$$\ln \Omega_B(E_{\Sigma'} - E_\nu) = \ln \Omega_B(E_{\Sigma'}) - E_\nu \left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)_{N_B, V_B} \tag{4.9}$$

The quantity $\ln \Omega(E_{\Sigma'})$ is a constant. The quantity $(\partial \ln \Omega_B / \partial E_B)_{N_B, V_B}$ is also a constant, characteristic of the bath. By virtue of Eq. (4.5), we can substitute the derivative in Eq. (4.9) in terms of the bath temperature.

$$\left(\frac{\partial \ln \Omega_B}{\partial E_B} \right)_{N_B, V_B} = \frac{1}{k_B T_B} \tag{4.10}$$

Furthermore, since the total system Σ' is at equilibrium under constant total energy,

$$\frac{S_{\Sigma'}}{k_B} = \ln \Omega_{\Sigma'}(N_{\Sigma'}, V_{\Sigma'}, E_{\Sigma'}) = \ln \left[\Omega(N, V, E) \Omega_B(N_B, V_B, E_B) \right] =$$

$$\ln \Omega(N, V, E) + \ln \Omega_B(N_B, V_B, E_B) = max$$

with respect to the value of E, with $E + E_B = E_{\Sigma'} = \text{const}$. Then,

$$\left(\frac{\partial \ln \Omega(N, V, E)}{\partial E} \right)_{N,V} = -\left(\frac{\partial \ln \Omega_B(N_B, V_B, E_B)}{\partial E} \right)_{N_B, V_B} = \left(\frac{\partial \ln \Omega_B(N_B, V_B, E_B)}{\partial E_B} \right)_{N_B, V_B}$$

or (*Zeroth Law of Thermodynamics*)

$$T = T_B \text{ for the systems } \Sigma \text{ and } B \text{ at equilibrium} \tag{4.11}$$

Combining (4.8) to (4.11), we obtain

$$P_\nu^{NVT} \propto \exp(-\beta E_\nu), \text{ where } \beta = \frac{1}{k_B T} \tag{4.12}$$

Eq. (4.12) is the *Boltzmann* (canonical) distribution law for the system under consideration. The constant of proportionality is determined by imposing the normalization condition, Eq (3.7). One obtains

$$P_\nu^{NVT} = \frac{1}{Q}\exp(-\beta E_\nu) \tag{4.13}$$

where

$$Q(N,V,T) \equiv Q(N,V,\beta) \equiv \sum_\nu e^{-\beta E_\nu} \tag{4.14}$$

is the *canonical partition function.* Note that the sum is taken over all *microstates*, and not over all energy levels. In other words, for a given energy level there will be as many terms in the sum of Eq. (4.14) as is the degeneracy of that level.

The classical analogues of Eq. (4.13) and (4.14) are

$$\rho^{NVT}(\mathbf{q},\mathbf{p}) = \frac{1}{Q(N,V,T)}\frac{1}{h^{3N}N!}e^{-\beta\mathcal{H}(\mathbf{q},\mathbf{p})} \tag{4.15}$$

and

$$Q(N,V,T) = \int_\Gamma \frac{e^{-\beta\mathcal{H}(\mathbf{q},\mathbf{p})}}{N!\,h^{3N}}\, d^{3N}q\, d^{3N}p \tag{4.16}$$

4.5.2 Connection with Thermodynamics

In establishing a correspondence between the formalism of the canonical ensemble and macroscopic thermodynamics, it would be reasonable to identify the ensemble average of the energy of microstates with the thermodynamic function U (internal energy):

$$U(N,V,T) = \langle E\rangle_{NVT} = \sum_\nu P_\nu^{NVT}E_\nu = \frac{1}{Q}\sum_\nu E_\nu e^{-\beta E_\nu} =$$

$$-\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V} = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = \left(\frac{\partial(-k_B \ln Q)}{\partial(1/T)}\right)_{N,V} \tag{4.17}$$

In view of the thermodynamic identity $U = \left(\frac{\partial(A/T)}{\partial(1/T)}\right)_{N,V}$ we *define* the Helmholtz energy as

$$A(N,V,T) = -k_B T \ln Q(N,V,T) = -\frac{1}{\beta} \ln Q(N,V,T) \tag{4.18}$$

Eq. (4.18) establishes a connection between the formalism of the canonical ensemble and macroscopic thermodynamics. It is again **a fundamental equation, in the Helmholtz energy representation.**

In the above development, we have implicitly considered a one-component system. In a multicomponent system the formulation of the canonical ensemble through Eqs. (4.15) to (4.18) proceeds identically, using the sum of particle numbers $N_1 + N_2 + \cdots$ in place of N, and the product $N_1! N_2! N_3! \ldots$ in place of $N!$.

Many physical systems have Hamiltonians of the form

$$\mathcal{H} = \sum_j a_j q_j^2 + \sum_j b_j p_j^2$$

where q_j and p_j are generalized coordinates and momenta. In an ideal monatomic gas, for example, $b_j = \frac{1}{2m}$, with p_j the components of the particle momenta in each of the three coordinate directions, and $a_j = 0$. Suppose that f of the constants a_j and b_j are nonvanishing. Then, one can readily prove within the classical formalism of the canonical ensemble, that

$$U = \langle \mathcal{H} \rangle = \frac{1}{2} f k_B T \tag{4.19}$$

Each independent harmonic term in the Hamiltonian contributes $\frac{1}{2} k_B T$ to the total energy of the system. This statement constitutes the *theorem of equipartition of energy.* The theorem holds only for degrees of freedom that can be treated classically; it breaks down when quantum effects are important. In the monatomic ideal gas example, $f = 3N$ and $U = \frac{3}{2} N k_B T$.

It is instructive to calculate the magnitude of *energy fluctuations* in the canonical ensemble. The variance (mean squared fluctuation) of the energy is

$$\langle (\delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Q} \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{N,V} - \frac{1}{Q^2} \left[\left(\frac{\partial Q}{\partial \beta} \right)_{N,V} \right]^2 =$$

$$\left(\frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{N,V} = -\frac{\partial}{\partial \beta} \left(-\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} = -\left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{N,V} = k_B T^2 \left(\frac{\partial U}{\partial T} \right)_{N,V}$$

All brackets denote averages at constant N, V, T. With our usual thermodynamic definition of heat capacity $C_v = \left(\frac{\partial U}{\partial T} \right)_{N,V}$,

$$\langle (\delta E)^2 \rangle = k_B T^2 C_v \tag{4.20}$$

Interestingly, Eq. (4.20) relates the size of spontaneous fluctuations in energy at equilibrium to the rate at which the energy of the system will change with changes in temperature. It can serve as a basis for estimating the heat capacity through simulations carried out at a single temperature in the canonical ensemble.

To appreciate the magnitude of energy fluctuations in a macroscopic system, we can compare the root mean squared fluctuation (standard deviation) of the energy to its average value:

$$\frac{\langle (\delta E)^2 \rangle^{1/2}}{\langle E \rangle} = \frac{(k_B T^2 C_v)^{1/2}}{\langle E \rangle} = \frac{\left[\frac{R}{N_A} T^2 C_v \right]^{1/2}}{n u} = \left(\frac{R T^2 c_v}{u^2} \right)^{1/2} \frac{1}{N^{1/2}} \tag{4.21}$$

where u and c_v, stand for the molar internal energy and the molar heat capacity, respectively. The prefactor in front of $N^{-1/2}$ in Eq. (4.21) is an intensive thermodynamic quantity. Thus, one sees that the ratio $\langle (\delta E)^2 \rangle^{\frac{1}{2}} / \langle E \rangle$ is on the order of $N^{-\frac{1}{2}}$, where N the number of particles in the system. For a macroscopic system ($N = \mathcal{O}(10^{23})$, "thermodynamic limit"), ~~far from thermodynamic states where c_v diverges (e.g., critical points)~~, the right-hand side of Eq. (4.21) is a *very* small number, *i.e.*, energy fluctuations are minute relative to the average value of the energy. This is why the formalisms of the microcanonical ensemble and of the canonical ensemble yield equivalent results (*i.e.*, macroscopic thermodynamics).

Another observation that can be made on the basis of Eq. (4.21) is that $c_v \geq 0$ always; this result, which falls naturally out of the statistical mechanical formulation, constitutes a criterion of thermodynamic stability.

All thermodynamic properties can be derived from the fundamental equation (4.18). For example, the pressure P is found as

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{\beta,N} \tag{4.22}$$

Eq (4.22) is a pressure-explicit equation of state.

4.5.3 Work, Heat, and Entropy in the Canonical Ensemble

Consider a reversible thermodynamic process that results in a change of the volume V of a system. The work done by the system, which is assumed to be in thermodynamic

equilibrium during the entire (reversible) process, is

$$\delta W_{rev} = PdV$$

By Eq. (4.13), (4.14), and (4.22),

$$P = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{\beta,N} = \frac{1}{\beta Q}\sum_{\nu}\left[\left(-\beta e^{-\beta E_\nu}\right)\left(\frac{\partial E_\nu}{\partial V}\right)_N\right] = -\sum_{\nu} P_\nu^{NVT}\frac{dE_\nu}{dV}$$

Therefore,

$$\delta W_{rev} = -\sum_{\nu} P_\nu^{NVT}\, dE_\nu \tag{4.23}$$

Thus, doing reversible work on the system amounts to changing the energy levels of microstates, while keeping the population (probability distribution) of the microstates constant.

On the other hand, the change in internal energy of the system during this process is, from Eq. (4.17),

$$dU = d\left[\sum_{\nu} P_\nu^{NVT}\, E_\nu\right] = \sum_{\nu} P_\nu^{NVT}\, dE_\nu + \sum_{\nu} E_\nu\, dP_\nu^{NVT} \tag{4.24}$$

By the first law (energy conservation), applied to the reversible process considered,

$$dU = \delta Q_{rev} - \delta W_{rev}$$

or, using Eq. (4.23) and (4.24),

$$\delta Q_{rev} = dU + \delta W_{rev} = \sum_{\nu} E_\nu\, dP_\nu^{NVT} \tag{4.25}$$

Thus, exchanging heat with the system in a reversible manner amounts to changing the population of microstates, while keeping the energy levels constant.

Given the form of the probability distribution of microstates in the canonical ensemble, Eq. (4.13), Eq. (4.25) can be written as:

$$\delta Q_{rev} = \sum_{\nu} \left[-\frac{1}{\beta} \left(\ln P_{\nu}^{NVT} + \ln Q \right) \right] dP_{\nu}^{NVT} =$$

$$-\frac{1}{\beta} \sum_{\nu} \ln P_{\nu}^{NVT} \, dP_{\nu}^{NVT} - \frac{1}{\beta} \ln Q \; d\left(\sum_{\nu} P_{\nu}^{NVT} \right)$$

and, since $\sum_{\nu} P_{\nu}^{NVT} = 1$,

$$\delta Q_{rev} = -k_B \, T \sum_{\nu} \ln P_{\nu}^{NVT} \, dP_{\nu}^{NVT} \tag{4.26}$$

On the other hand, the *entropy* S is obtained from Eq. (4.17) and Eq. (4.18) as

$$S = \frac{U - A}{T} = k_B \, \beta \sum_{\nu} P_{\nu}^{NVT} \, E_{\nu} + k_B \ln Q$$

$$k_B \, \beta \sum_{\nu} P_{\nu}^{NVT} \left[-\frac{1}{\beta} \left(\ln P_{\nu}^{NVT} + \ln Q \right) \right] + k_B \ln Q$$

or

$$S = -k_B \sum_{\nu} P_{\nu}^{NVT} \ln P_{\nu}^{NVT} \equiv -k_B \left\langle \ln P_{\nu}^{NVT} \right\rangle_{NVT} \tag{4.27}$$

(*Gibbs entropy formula in the canonical ensemble*)

Differentiating Eq. (4.27), and using the fact that the probabilities P_{ν}^{NVT} are normalized,

$$dS = -k_B \sum_{\nu} d\left(P_{\nu}^{NVT} \ln P_{\nu}^{NVT} \right) = -k_B \sum_{\nu} \ln P_{\nu}^{NVT} \, dP_{\nu}^{NVT} - k_B \sum_{\nu} dP_{\nu}^{NVT} =$$

$$-k_B \sum_{\nu} \ln P_{\nu}^{NVT} \, dP_{\nu}^{NVT} \tag{4.28}$$

Comparing Eq. (4.26) and (4.28), one sees immediately that

$$\delta Q_{rev} = T\, dS \tag{4.29}$$

Eq. (4.29) forms the basis for the definition of entropy in macroscopic thermodynamics. It was derived here from the formalism of the canonical ensemble. We presented its derivation as an indication of the internal consistency between macroscopic and statistical thermodynamics.

4.6 Elementary Statistical Mechanics of Fluids. Separation of Kinetic and Potential Energy Contributions to the Partition Function. Configurational Integral

The canonical ensemble provides a powerful framework for deriving the thermodynamic properties of liquids and gases from molecular-level information.

Consider a pure fluid, consisting of N molecules in volume V at temperature T. To specify the microstate in configuration space, one must specify the position, orientation, and shape of all constituent molecules. For a molecule consisting of s atoms, this entails fixing $3s$ configurational degrees of freedom. These can be chosen as the Cartesian coordinates of all atoms. Alternatively, generalized coordinates can be used. For an example of how these can be defined, consider a linear molecule, such as the chlorine molecule depicted in Figure 4.3 (a). This molecule can be fully specified in space by the three Cartesian coordinates of its center of mass, $\mathbf{r}$; two orientation angles (ψ_1, ψ_2), fixing the orientation of its axis with respect to the laboratory frame of reference (here these are

chosen as the polar and azimuthal angle of the bond vector); and the bond length ℓ. In general, for a linear molecule of s atoms we have 3 translational, 2 orientational, and $3s - 5$ vibrational degrees of freedom. Figure 4.3(b), on the other hand, displays a flexible nonlinear molecule (1,2-dichloroethane). One can fully specify this molecule in space using three translational degrees of freedom (*e.g.*, the position vector $\mathbf{r}_1$ of one of the chlorine atoms); three rotational degrees of freedom (*e.g.*, the polar angles ψ_1 and ψ_2 fixing the orientation of bond 12, and the dihedral angle ψ_3 between the plane of bonds 12 and 23 and the plane parallel to the z- axis through bond 12); an internal torsional degree of freedom, defined here as the dihedral angle ϕ between the plane of bonds 12 and 23 and the plane of bonds 23 and 34 (ϕ fixes the *conformation* of the molecule); and 17 vibrational degrees of freedom, fixing the 7 bond lengths and 10 independent bond angles of the molecule for the given ϕ. In general, a nonlinear molecule with s atoms and b internal torsion angles has 3 translational, 3 rotational, b torsional, and $3s - b - 6$ vibrational degrees of freedom. The vibrational degrees of freedom are conveniently chosen as the normal coordinates, *i.e.*, the eigenvectors of the Hessian matrix of second derivatives of the potential energy with respect to displacements of the atoms away from the minimum energy configuration of the molecule at given values of the translational, orientational and conformational degrees of freedom [Wilson, Decius, and Cross, 1955]. The vibrational degrees of freedom are sometimes called "hard", as their distortion is typically associated with high energetic cost; the rest of the degrees of freedom are called "soft".

The total energy of the fluid is a function of the configurational degrees of freedom (generalized coordinates) of all molecules, and of the generalized momenta conjugate to them. In addition, nuclear and electronic degrees of freedom can be excited in some systems at ordinary temperatures, and thus have to be included in a statistical mechanical formulation for the calculation of physical properties. The energy is often distinguished into *intramolecular* and *intermolecular* contributions. Intramolecular contributions are associated with nuclear, electronic, vibrational, and torsional degrees of freedom. Intermolecular contributions arise from the potential energy of interaction between molecules. The intermolecular energy is a function of the relative position and orientation of the constituent parts ("interaction sites") on different molecules.

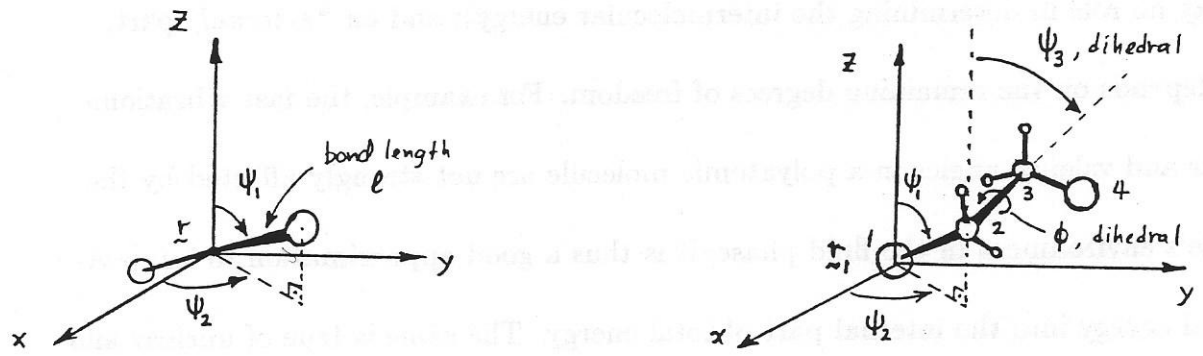

Figure 4.3 Specification of the configurational degrees of freedom of molecules. (*a*) Chlorine, a linear diatomic. (*b*) 1,2-dichloroethane, a nonlinear, flexible polyatomic.

The contribution from a given degree of freedom to the system energy must be treated with *quantum statistical mechanics* if the separation of successive energy levels

associated with this degree of freedom is large compared to the thermal energy $k_B T$. ($k_B T = 4.1 \times 10^{-21}$ J/degree of freedom = 2.5 kJ/mol = 0.6 kcal/mol at room temperature). Thus, nuclear spin contributions [separation of energy levels $\mathcal{O}(10^{-11}$ J/d.o.f.)], electronic contributions [separation of energy levels $\mathcal{O}(10^{-17}$ J/d.o.f.)], and vibrational contributions [separation of energy levels $\mathcal{O}(10^{-20}$ J/d.o.f.)] must be treated quantum mechanically. A classical treatment is usually satisfactory for overall rotational, internal torsional, and translational contributions in fluids.

It is usually a good approximation to separate the total energy into two *independent* parts: an "*internal*" part, consisting of contributions from those nuclear, electronic, vibrational, and rotational degrees of freedom of individual molecules which are not affected by the presence of other molecules (*i.e.*, contributions from degrees of freedom that play no role in determining the intermolecular energy); and an "*external*" part, which depends on the remaining degrees of freedom. For example, the fast vibrations of bonds and valence angles in a polyatomic molecule are not strongly affected by the molecule's environment in the fluid phase; it is thus a good approximation to lump vibrational energy into the internal part of total energy. The same is true of nuclear and electronic contributions in most fluids, when these play a role. The kinetic energy of overall rotational motion (tumbling) of molecules in a fluid is independent of the fluid configuration, and therefore part of the "internal" contribution to the total energy if the molecules have no internal torsional degrees of freedom that would cause changes in their shape ($b = 0$). The kinetic energy associated with translational motion is always included as a component of the "external" part of the energy.

With this separation into internal and external contributions to the potential energy, the partition function can be factored as follows:

$$Q(N,V,T) = \sum_{all\ microstates} e^{-\beta E} = \sum_{all\ microstates} exp\left[-\beta \sum_{i=1}^{N} E_i^{int} - \beta E^{ext}\right] =$$

$$\left[\sum_{\substack{all\ combinations\\ of\ internal\ degrees\\ of\ freedom\ of\\ N\ molecules}} exp\left(-\beta \sum_{i=1}^{N} E_i^{int}\right)\right]\left[\sum_{\substack{all\ combinations\\ of\ external\\ degrees\ of\ freedom}} exp\left(-\beta E^{ext}\right)\right] =$$

$$\prod_{i=1}^{N}\left[\sum_{\substack{all\ combinations\\ of\ internal\ degrees\\ of\ freedom\ of\\ molecule\ i}} exp\left(-\beta E_i^{int}\right)\right]\left[\sum_{\substack{all\ combinations\\ of\ external\\ degrees\ of\ freedom}} exp\left(-\beta E^{ext}\right)\right] \equiv$$

$$\left[q^{int}(T)\right]^N Q_{ext}(N,V,T) \tag{4.30}$$

The utility of this factorization lies in that only the factor $Q_{ext}(N,V,T)$ depends on the volume (or density) of the system. Q_{ext} contains contributions from the following components of the Hamiltonian: (a) kinetic energy for all modes of motion that are not included in q^{int} (*e.g.*, translation); (b) potential energy $\mathcal{V}$, which is a function of the system configuration (*e.g.*, center of mass positions $\mathbf{r}$, orientation angles $\underset{\sim}{\psi}$, and torsion angles $\underset{\sim}{\phi}$ of all molecules). In general, then,

$$\mathcal{V} = \mathcal{V}(\mathbf{r}_1, \psi_1, \phi_1, , \mathbf{r}_2, \psi_2, \phi_2, \ldots, \mathbf{r}_N, \psi_N, \phi_N)$$

For the sake of simplicity, the following discussion will focus on a system of inflexible molecules ($b = 0$) in which the total potential energy of intermolecular interactions can be expressed reasonably well as a function of the molecular center of mass positions

$\mathbf{r}_i$ only. This would be a satisfactory representation for nonpolar fluids of roughly spherical molecules, such as methane. It would be a poor approximation in a dense fluid of long, flexible molecules, such as hexadecane; it would also be a poor approximation if strongly orientation-dependent dipolar forces are present, *e.g.*, in liquid water. Such cases can be handled in a manner analogous to what we will discuss below; the main difference is that a whole set of generalized coordinates $\mathbf{q}_i = (\mathbf{r}_i, \psi_i, \phi_i)$ must be used in place of the center of mass position $\mathbf{r}_i$ for each molecule.

Under the conditions stated in the beginning of the last paragraph, the factor Q_{ext} of the partition function can be derived from the Hamiltonian

$$\mathcal{H}(\mathbf{r}, \mathbf{p}) = \mathcal{K}(\mathbf{p}) + \mathcal{V}(\mathbf{r}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \mathcal{V}(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{4.31}$$

where $\mathcal{V}$ is the *intermolecular potential energy* and m the molecular mass (compare Eq. (3.3)). The kinetic energy term in Eq. (4.31) depends exclusively on center-of-mass momenta. The potential energy term depends exclusively on center-of-mass positions (configurational degrees of freedom). In forming the partition function, the two contributions are *separable*:

$$Q_{ext}(N, V, T) = \frac{1}{h^{3N} N!} \int exp\left[-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}\right] d^{3N}p \int exp\left[-\beta \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\right] d^{3N}r \tag{4.32}$$

Both integrals appearing in Eq. (4.32) are definite. The first integral is taken over all momentum space (each component of the momenta $\mathbf{p}_i$ ranging from $-\infty$ to $+\infty$). The second integral is taken over all configuration space (each position vector $\mathbf{r}_i$ ranging over

all points in the container, of volume V, in which the fluid is confined). Such a separation into momentum and configuration parts is possible in more complex cases, where configurational degrees of freedom other than the center of mass coordinates affect the potential energy, provided these degrees of freedom can be treated classically.

The integral over momentum space is really a product of $3N$ independent Gaussian integrals of the form

$$\int_{-\infty}^{+\infty} exp\left(-\beta\frac{p_\alpha^2}{2m}\right) dp_\alpha = (2\pi\, m\, k_B\, T)^{\frac{1}{2}} \tag{4.33}$$

This indicates that the center-of-mass momentum vectors of molecules obey the *Maxwell-Boltzmann* distribution

$$\rho^{M-B}(\mathbf{p}) = \frac{1}{(2\pi\, m\, k_B\, T)^{3/2}}\ exp\left(-\frac{\mathbf{p}^2}{2m\, k_B\, T}\right) \tag{4.34}$$

Combining Eqs. (4.30), (4.32) and (4.33) we obtain the "semiclassical" partition function

$$Q(N,V,T) = \left[q^{int}(T)\right]^N\ \frac{1}{N!}\left(\frac{2\pi\, m\, k_B\, T}{h^2}\right)^{3N/2} \int exp\left[-\beta\mathcal{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\right] d^3r_1\ \ldots d^3r_N$$

or

$$Q(N,V,T) = \frac{\left[q^{int}(T)\right]^N}{N!\,\Lambda^{3N}} \int exp\left[-\beta\mathcal{V}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\right] d^3r_1\, d^3r_2\, \ldots d^3r_N \tag{4.35}$$

where the quantity

$$\Lambda = \Lambda(T) \equiv \left(\frac{h^2}{2\pi\, m\, k_B\, T}\right)^{1/2} \tag{4.36}$$

is the *thermal wavelength* of molecules. Λ has dimensions of length. It is on the order of the de Broglie wavelength of a molecule with mass m and energy $k_B T$. When intermolecular separations become commensurate with Λ, a classical treatment of translational motion is no longer satisfactory. In the gas phase, this criterion reveals that quantum effects are important for He, H_2, and Ne.

Eq. (4.35) is also written as

$$Q(N,V,T) = \frac{\left[q^{int}(T)\right]^N}{N!\,\Lambda^{3N}}\, Z(N,V,T) \tag{4.37}$$

where

$$Z(N,V,T) \equiv \int exp[-\beta \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)]\, d^3r_1\, d^3r_2\, \ldots d^3r_N \tag{4.38}$$

is the **configurational integral.**

All dependence of the partition function, hence of the thermodynamics of the fluid, on the spatial extent (density) of the system is incorporated in the configurational integral. In particular, a pressure-explicit equation of state is derived from Eq. (4.22) as

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} = k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} \tag{4.39}$$

As a result of the separation of system degrees of freedom into internal and external and of the classical treatment of external degrees of freedom, the equation of state is obtainable from the *configurational* part of the partition function only.

4.7 Thermodynamic Properties of an Ideal Gas

As a simple application of the analysis introduced in section 4.6, consider the case of an ideal gas of molecules. The ideal gas plays a central role as a reference substance in statistical thermodynamic formulations.

In an ideal gas there are no interactions between constituent molecules:

$$\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = 0 \tag{4.40}$$

The configurational integral, Eq. (4.38), degenerates into:

$$Z^{ig}(N, V, T) = \int d^{3N}r = V^N \tag{4.41}$$

and the canonical partition function becomes

$$Q^{ig}(N, V, T) = \frac{[q^{int}]^N}{N!} \left(\frac{V}{\Lambda^3}\right)^N \tag{4.42}$$

The equation of state, derived from Eq. (4.39), is

$$P^{ig} = k_B T \left(\frac{\partial \ln(V^N)}{\partial V}\right)_{T,N} = \frac{N k_B T}{V}, \text{ or } P^{ig} V = N k_B T = n R T \tag{4.43}$$

The Helmholtz energy is obtained from Eq. (4.42) using Stirling's approximation $\ln N! \simeq N \ln N - N$:

$$A^{ig}(N, V, T) = -\frac{1}{\beta} \ln \left[\frac{1}{N!} \left(\frac{q^{int} V}{\Lambda^3}\right)^N\right] = -\frac{1}{\beta} \left[-(N \ln N - N) + N \ln \left(\frac{q^{int} V}{\Lambda^3}\right)\right] =$$

$$N k_B T \left[-1 + \ln \left(\frac{N \Lambda^3}{V q^{int}}\right)\right] = N k_B T \left[-1 + \ln \left(\frac{1}{q^{int}} \rho \Lambda^3\right)\right] \tag{4.44}$$

where $\rho = N/V$, the *molecular density*. The chemical potential can be obtained directly from Eq (4.43) and (4.44) as the Gibbs energy per molecule:

$$\mu^{ig} = \frac{G^{ig}}{N} = \frac{A^{ig} + P^{ig}V}{N} = k_B T \left[-1 + \ln\left(\frac{1}{q^{int}}\rho\Lambda^3\right) + 1 \right], \text{ or}$$

$$\mu^{ig}(\rho, T) = k_B T \ln\left(\frac{\rho\Lambda^3}{q^{int}}\right) \tag{4.45}$$

For a monatomic ideal gas, this equation simplifies to $\mu^{ig}(\rho, T) = k_B T \ln(\rho\Lambda^3)$. Eq. (4.45) defines an absolute chemical potential for the gas. This is possible because of the absolute scales of entropy and energy used in statistical mechanics.

The internal energy of the gas is

$$U^{ig} = \left(\frac{\partial(\beta A)}{\partial\beta}\right)_{N,V} = N k_B T \left[\frac{3}{2} + T\frac{d\ln q^{int}}{dT}\right] \tag{4.46}$$

and the molar heat capacity is

$$c_v^{ig} = \left(\frac{\partial u^{ig}}{\partial T}\right)_v = \frac{3}{2}R + R\left[2T\frac{d\ln q^{int}}{dT} + T^2\frac{d^2\ln q^{int}}{dT^2}\right] \tag{4.47}$$

For a monatomic gas (*e.g.*, Ar) Eq. (4.47) reduces to the more familiar equipartition result $c_v^{ig} = \frac{3}{2}R$. If the molecules have internal structure, there are additional contributions from vibrational, rotational, and possibly even electronic and nuclear degrees of freedom incorporated in $q^{int}(T)$, so c_v and, consequently, $c_P = c_v + R$, will be temperature-dependent, their values reflecting the structure of the molecules. Eq. (4.47) is the origin of the $c_P^{ig}(T)$ expressions we use in thermodynamic calculations. The internal partition function q^{int} can be obtained through straightforward quantum statistical mechanical analysis of vibrational and rotational motion in a single molecule [McQuarrie

1976, Chap 6]. As the characteristic frequencies of vibrational and rotational motion can be obtained from infrared spectra, Eq. (4.47) provides a pathway for estimating the heat capacity from spectroscopic measurements.

The absolute entropy is readily obtained from Eqs. (4.44) and (4.46):

$$S^{ig} = \frac{U^{ig} - A^{ig}}{T} = N\,k_B \left[\frac{5}{2} - \ln(\rho\Lambda^3) + \left(\ln q^{int} + T\frac{d\ln q^{int}}{dT}\right)\right]$$

or, for the molar entropy,

$$s^{ig} = R \left[\frac{5}{2} - \ln(\rho\Lambda^3) + \left(\ln q^{int} + T\frac{d\ln q^{int}}{dT}\right)\right] \tag{4.48}$$

For a monatomic gas, Eq. (4.48) becomes

$$s^{ig} = R \left[\frac{5}{2} - \ln(\rho\Lambda^3)\right], \text{ or, in dimensional form,}$$

$$s^{ig} = R \left[\frac{3}{2}\ln M + \frac{5}{2}\ln T - \ln P - 1.1645\right] \tag{4.49}$$

where M = molecular weight in g/mol, T the temperature in K, and P the pressure in atmospheres. Eq. (4.49) is known as the Sackur-Tetrode equation.

4.8 Pressure as an Equilibrium Ensemble Average: The Virial Theorem of Clausius

Eq. (4.39) provides a route for the calculation of the pressure of a fluid from the volume-dependence of the configurational integral. In practice, one often faces the need to calculate pressure from molecular simulations. Common simulation techniques do not provide

partition functions or configurational integrals directly. Instead, they are designed to compute ensemble averages or time averages of dynamical quantities, *i.e.*, of functions of the positions and momenta of particles. Thus, expressions of thermodynamic properties as *ensemble averages* are very useful in simulation work.

The *virial theorem* expresses pressure in an isotropic medium as an ensemble average involving the positions of molecular interaction sites and the forces exerted between them. There are many ways to write the virial theorem and many ways to prove it. Our derivation here, resting directly on Newtonian mehanics, is close in spirit to the one followed by Clausius in his original statement of the theorem.

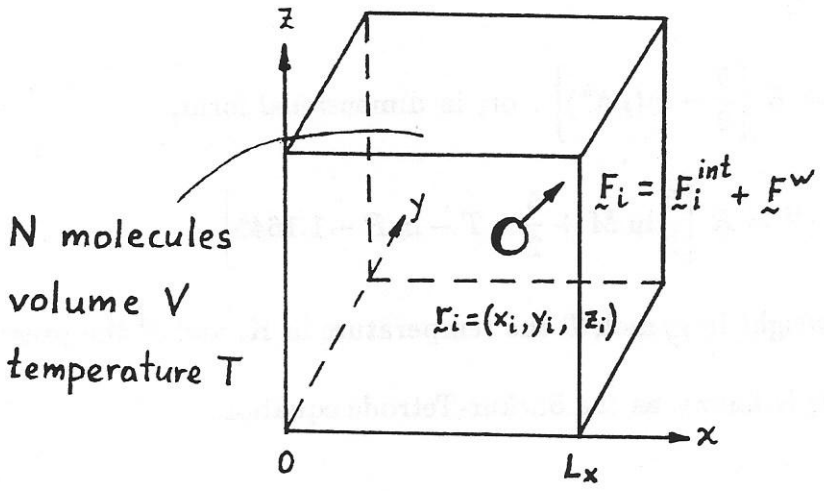

Figure 4.4 For the derivation of the virial theorem

Consider an isotropic material, consisting of N molecules contained in a box of volume V at temperature T. (For simplicity, we will consider structureless molecules subject to central forces. The derivation can be straightforwardly extended to molecules with internal structure by considering each molecule as a collection of sites, some of

which interact through bonded forces.) Newton's law of motion, applied to a given molecule i, gives

$$m_i \frac{d^2 x_i}{dt^2} = F_{i,x} \tag{4.50}$$

and analogous equations along the y and z directions. $\mathbf{F}_{i,x}$ here is the total force experienced by molecule i at a given time. Multiplying Eq. (4.50) by x_i, one obtains

$$x_i F_{i,x} = m_i x_i \frac{d^2 x_i}{dt^2} = \frac{d}{dt}\left(m_i x_i \frac{dx_i}{dt} \right) - m_i \left(\frac{dx_i}{dt} \right)^2$$

Summing over all molecules and taking the time average of both sides under equilibrium conditions (compare Eq. (3.21)), one obtains

$$\left\langle \sum_i x_i F_{i,x} \right\rangle_t = \left\langle \sum_i \frac{d}{dt}(x_i p_{i,x}) \right\rangle_t - \left\langle \sum_i \frac{p_{i,x}^2}{m_i} \right\rangle_t \tag{4.51}$$

In Eq. (4.51) we have recognized that $\mathbf{p}_i = m_i \frac{d\mathbf{r}_i}{dt}$. By definition, the first term in Eq. (4.51) can be written

$$\left\langle \sum_i \frac{d}{dt}(x_i p_{i,x}) \right\rangle_t = \lim_{t' \to \infty} \frac{1}{t'} \int_0^{t'} \left[\sum_i \frac{d}{dt}(x_i p_{i,x}) \right] dt =$$

$$\lim_{t' \to \infty} \frac{1}{t'} \int_0^{t'} \frac{d}{dt} \left[\sum_i (x_i p_{i,x}) \right] dt =$$

$$\lim_{t' \to \infty} \frac{1}{t'} \left\{ \left[\sum_i x_i p_{i,x} \right]_{t'} - \left[\sum_i x_i p_{i,x} \right]_0 \right\} \tag{4.52}$$

The momentum $p_{i,x}$ is bounded (its absolute value cannot be infinity). The position x_i is also bounded, as molecule i cannot get out of the finite space defined by the box. As a consequence, the limit on the right-hand side of Eq. (4.52) is zero, and

$$\left\langle \sum_i \frac{d}{dt}(x_i p_{i,x}) \right\rangle_t = 0 \tag{4.53}$$

On the other hand, since motion in the system is isotropic,

$$\left\langle \sum_i \frac{p_{i,x}^2}{m_i} \right\rangle_t = \frac{1}{3} \left\langle \sum_i \frac{\mathbf{p}_i^2}{m_i} \right\rangle_t = \frac{2}{3} \langle \mathcal{K} \rangle_t$$

where $\mathcal{K}$ is the kinetic energy. Invoking the ergodic hypothesis, and realizing that the average kinetic energy is related to temperature and to the number of degrees of freedom (equipartition theorem), we have

$$\left\langle \sum_i \frac{p_{i,x}^2}{m_i} \right\rangle_t = \frac{2}{3} \frac{3N}{2} k_B T = N k_B T \tag{4.54}$$

Combining Eqs. (4.51), (4.53), and (4.54) we obtain

$$\left\langle \sum_i x_i F_{i,x} \right\rangle = -N k_B T \tag{4.55}$$

Adding Eq. (4.55) with the corresponding equations along the y- and z-directions and dividing by 3, one obtains

$$\frac{1}{3} \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = -N k_B T \tag{4.56}$$

In Eqs (4.55) and (4.56) we have dropped the subscript t, indicating that we are replacing the time average by an equilibrium ensemble average. The equations are valid in any ensemble with constant number of particles N. The quantity $\frac{1}{3} \sum_i \mathbf{r}_i \cdot \mathbf{F}_i$ is called *(total) virial.*

The force $\mathbf{F}_i$ on atom i is due to two sources: Forces arising due to interactions of i with the box walls, which result in a component $\mathbf{F}_i^w$; and forces due to interactions with other molecules, which result in a component $\mathbf{F}_i^{int}$:

$$\mathbf{F}_i = \mathbf{F}_i^{int} + \mathbf{F}_i^w \tag{4.57}$$

Eq. (4.55) can thus be written as

$$\left\langle \sum_i x_i \, F_{i,x}^w \right\rangle + \left\langle \sum_i x_i \, F_{i,x}^{int} \right\rangle = -N \, k_B \, T \tag{4.58}$$

and Eq. (4.56) can be written as

$$\frac{1}{3} \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i^w \right\rangle + \frac{1}{3} \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i^{int} \right\rangle = -N \, k_B \, T$$

The quantities $\frac{1}{3} \sum_i \mathbf{r}_i \cdot \mathbf{F}_i^w$ and $\frac{1}{3} \sum_i \mathbf{r}_i \cdot \mathbf{F}_i^{int}$ are referred to as *wall virial* $\mathcal{W}^w$ and *internal virial* $\mathcal{W}^{int}$, respectively.

For most physical systems, "wall forces" are short-ranged. They will act on a molecule only as long as it is within a few molecular diameters from the "wall". Consequently, for all molecule-wall collisions that contribute to the wall virial term in Eq. (4.58), we can set $x_i = L_x$ or $x_i = 0$, and

$$\left\langle \sum_i x_i \, F_{i,x}^w \right\rangle = L_x \left\langle \sum_i F_{i,x}^w \right\rangle_{x=L_x} \tag{4.59}$$

Furthermore, $\left\langle \sum_i F_{i,x}^w \right\rangle_{x=L_x}$ is the average force exerted from the wall at L_x on the system. It is opposite to the average force exterted by the system on the wall, therefore immediately realted to the macroscopic pressure as

$$\left\langle \sum_i F_{i,x}^w \right\rangle_{x=L_x} = -P \, L_x \, L_z \tag{4.60}$$

Combining Eqs. (4.59) and (4.60),

$$\left\langle \sum_i x_i \, F_{i,x}^w \right\rangle = -P \, V \tag{4.61}$$

Combining Eqs. (4.58) and (4.61),

$$PV = N k_B T + \left\langle \sum_i x_i F_i^{int} \right\rangle \tag{4.62}$$

and, averaging Eq. (4.62) over all three directions,

$$P = \rho k_B T + \frac{1}{3} \left\langle \frac{1}{V} \sum_i \mathbf{r}_i \cdot \mathbf{F}_i^{int} \right\rangle = \rho k_B T + \left\langle \frac{1}{V} \mathcal{W}^{int} \right\rangle \tag{4.63}$$

where $\rho = \frac{N}{V}$ the molecular density. Eq. (4.63) is the *virial theorem*. It expresses the pressure directly in terms of density, temperature, and intermolecular forces and distances. It is valid for any force law and in any ensemble where the number of molecules N is kept constant (microcanonical, canonical, isothermal-isobaric). Note that Eq. (4.63) gives correct results in the special case of an ideal gas.

In molecular modelling work it is often adequate to consider intermolecular forces as *pairwise additive*:

$$\mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij}$$

$$\mathbf{F}_{ij} = -\mathbf{F}_{ji}$$

where $\mathbf{F}_{ij}$ symbolizes the force on i due to j.

With the assumption of pairwise additivity, Eq. (4.63) leads to

$$P = \rho k_B T + \frac{1}{3} \left\langle \frac{1}{V} \sum_{i=1}^{N} \sum_{j=i+1}^{N} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} \right\rangle \tag{4.64}$$

In the double sum of Eq. (4.64) each pair of molecules is counted once. The shorthand symbolism $\sum_{i} \sum_{j}$ is sometimes used for such double sums.

The Clausius derivation can readily be extended to express the entire stress tensor in a fluid or solid in terms of intermolecular forces and distances [Swenson 1983]. The stress analogue of Eq. (4.63) is

$$\tau^{\alpha\beta} = -\rho\, k_B\, T\, \delta_{\alpha\beta} - \left\langle \frac{1}{V} \sum_i r_i^\alpha\, F_i^\beta \right\rangle \tag{4.65}$$

where $\tau^{\alpha\beta}$ stands for the $\alpha\beta$-component of the stress tensor and the Kronecker $\delta_{\alpha\beta}$ equals 1 if $\alpha = \beta$ and 0 otherwise.

4.9 Chemical Potential as a Canonical Ensemble Average: Widom's Test Particle Insertion Method

The calculation of "statistical" thermodynamic properties (entropy, chemical potential, Gibbs and Helmholtz energies) from a simulation in the microcanonical, canonical, or isothermal-isobaric ensembles is in general more difficult than the calculation of "mechanical" thermodynamic properties (pressure, internal energy, enthalpy). An important pathway to "statistical" properties is established by Widom's *test particle insertion method* for calculating the chemical potential μ as a canonical ensemble average [Widom 1963, 1982]. We outline a derivation of this method below.

Consider a fluid containing N molecules in volume V at temperature T. By Eq. (4.18), we can obtain the fluid's thermodynamic properties from the canonical partition function, which is directly related to the Helmholtz energy:

$$A(N,V,T) = -\frac{1}{\beta} \ln Q(N,V,T) \tag{4.18}$$

Consider now the same fluid, but at slightly higher density, such that $N+1$ molecules are contained in the same volume V and temperature T:

$$A(N+1,V,T) = -\frac{1}{\beta}\ln Q(N+1,V,T) \tag{4.66}$$

Subtracting Eq. (4.18) from (4.66) and invoking Eq. (4.37) for the canonical partition function, we obtain

$$A(N+1,V,T) - A(N,V,T) = -\frac{1}{\beta}\ln\frac{Q(N+1,V,T)}{Q(N,V,T)} =$$

$$-\frac{1}{\beta}\ln\left\{\frac{\left[q^{int}\right]^{N+1}}{(N+1)!\,\Lambda^{3(N+1)}}\;\frac{N!\,\Lambda^{3N}}{\left[q^{int}\right]^{N}}\;\frac{Z(N+1,V,T)}{Z(N,V,T)}\right\} =$$

$$k_B\,T\ln\left[\frac{(N+1)\,\Lambda^3}{V\,q^{int}}\right] - k_B\,T\,\ln\left\{\frac{Z(N+1,V,T)}{V\,Z(N,V,T)}\right\} \tag{4.67}$$

We now focus on the ratio of configurational integrals appearing in Eq. (4.67). By Eq. (4.38),

$$\frac{Z(N+1,V,T)}{V\,Z(N,V,T)} = \frac{\int exp\left[-\beta\mathcal{V}_{N+1}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,\mathbf{r}_{N+1})\right]\,d^3r_1\,d^3r_2\,\cdots\,d^3r_N\,d^3r_{N+1}}{V\int exp\left[-\beta\mathcal{V}_N(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\right]\,d^3r_1\,d^3r_2\,\cdots\,d^3r_N} \tag{4.68}$$

Now, for a given configuration, the $(N+1)$-molecule potential energy of molecules $1, 2, \ldots, N+1$ is related to the N-molecule potential energy of molecules $1, 2, \ldots, N$ as

$$\mathcal{V}_{N+1}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,\mathbf{r}_{N+1}) = \mathcal{V}_N(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) + \mathcal{V}_{test}(\mathbf{r}_{N+1};\,\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \tag{4.69}$$

where $\mathcal{V}_{test}(\mathbf{r};\,\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ is the total potential energy *felt* by a molecule placed at position $\mathbf{r}$ due to N molecules of the fluid in the configuration $(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$. Eq. (4.68) can therefore be rewritten as

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

$$\frac{\int d^3r_{N+1} \int d^3r_1 \cdots d^3r_N \; exp[-\beta \mathcal{V}_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)] \; exp[-\beta \mathcal{V}_{test}(\mathbf{r}_{N+1}; \mathbf{r}_1, \cdots, \mathbf{r}_N)]}{\int d^3r_{N+1} \int d^3r_1 \cdots d^3r_N exp[-\beta \mathcal{V}_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)]} \tag{4.70}$$

The right-hand side of Eq. (4.70) constitutes a canonical ensemble average over all configurations of the N molecules, and also an average over all possible positions of the "test" molecule. The conceptual process considered is the following: Configurations of N interacting molecules in volume V and temperature T are sampled according to the probability density of the canonical ensemble. To each such configuration a "test" molecule is added at a random point. The test molecule "feels" all of the N "real" molecules, but is not felt by them, so it has no effect on their configurational distribution. The Boltzmann factor of the energy $\mathcal{V}_{test}$ "felt" by the test molecule due to the presence of the real molecules is averaged over all configurations of the N real molecules and over all positions of the test molecule. The result equals the ratio of configurational integrals on the left-hand side of Eq. (4.70). We can therefore rewrite this equation as

$$\frac{Z(N+1,V,T)}{V\,Z(N,V,T)} = \langle exp(-\beta \mathcal{V}_{test}) \rangle \tag{4.71}$$

where the brackets denote canonical ensemble averaging over all N-molecule configurations and spatial averaging over all test molecule positions.

We now consider Eq. (4.67) in the thermodynamic limit $N \to \infty$, $V \to \infty$, $\frac{N}{V} = \rho$ = constant. The left-hand side becomes

$$\lim_{\substack{N\to\infty \\ V\to\infty \\ N/V=\rho}} \left\{ \frac{A(N+1,V,T) - A(N,V,T)}{(N+1) - N} \right\} = \lim_{\substack{N\to\infty \\ V\to\infty \\ N/V=\rho}} \left\{ \left(\frac{\partial A}{\partial N} \right)_{T,V} \right\} = \mu(\rho, T) \tag{4.72}$$

Thus, the left-hand side of Eq. (4.67) is equal to the chemical potential of the fluid at the prevailing density and temperature. In view of Eq. (4.45), the first term on the right-hand side of Eq, (4.67) becomes

$$\lim_{\substack{N\to\infty \\ V\to\infty \\ N/V=\rho}} \left\{ k_B\,T \ln\left[\frac{(N+1)\,\Lambda^3}{V\,q^{int}}\right]\right\} = k_B\,T\,\ln\left(\frac{\rho\,\Lambda^3}{q^{int}}\right) = \mu^{ig}(\rho,T) \qquad (4.73)$$

i.e. equal to the chemical potential the fluid would have if it were an ideal gas at the same density and temperature (all intermolecular interactions turned off).

Combining Eqs. (4.67), (4.71) - (4.73) in the thermodynamic limit, we obtain

$$\mu(\rho,T) - \mu^{ig}(\rho,T) \equiv \mu^{ex}(\rho,T) = -k_B\,T\,\ln\langle exp(-\beta\mathcal{V}_{test})\rangle \qquad (4.74)$$

The difference $\mu - \mu^{ig}$, taken at *the same density and temperature*, is referred to as "excess chemical potential". Note that this is *not* the same as the residual molar Gibbs energy of macroscopic thermodynamics, which is a difference between μ and μ^{ig} taken under the same *pressure* and temperature. In terms of the *fugacity* $f(\rho,T)$ of the fluid, the left-hand side of Eq. (4.74) can be written as

$$\mu(\rho,T) - \mu^{ig}(\rho,T) = k_B\,T \ln\left(\frac{f}{\rho\,k_B\,T}\right)$$

The ensemble average on the right-hand side of Eq. (4.74) refers to insertions of a "test" molecule in the fluid at density ρ and temperature T. Clearly, it is an intensive property of the fluid.

Implementations of the Widom test particle method in the microcanonical and isothermal-isobaric ensembles have been developed [Allen and Tildesley 1983, p 50].

4.10 Isothermal-Isobaric Ensemble

The isothermal-isobaric ensemble describes the equilibrium distribution in phase space of a system under constant number of particles, temperature, and pressure. The volume of the system is allowed to fluctuate. Thus, *volume joins the list of microscopic degrees of freedom that comprise phase space.* A point in phase space is specified by specifying $V, \mathbf{q}$, and $\mathbf{p}$. Clearly, the domain from which the components of $\mathbf{q}$ take on values depends on the value of V.

The probability density of the isothermal-isobaric ensemble can be derived from that of the microcanonical ensemble via a procedure analogous to that of section 4.5.1. The only difference is that the bath B acts as both a heat and a work reservoir for the system Σ under study, *i.e.*, fluctuations in both the energy and the volume of Σ are allowed. Here we present without proof the result for the probability density in a classical statistical mechanical formulation:

$$\rho^{NPT}(\mathbf{q}, \mathbf{p}; V) = \frac{exp\{-\beta[\mathcal{H}(\mathbf{q}, \mathbf{p}; V) + PV]\}}{Q_{NPT}(N, P, T)} \tag{4.75}$$

where Q_{NPT} is the *isothermal-isobaric partition function*

$$Q_{NPT} = \frac{1}{N!\,h^{3N}} \frac{1}{V_0} \int dV \int d^{3N}q\, d^{3N}p\, exp\{-\beta[\mathcal{H}(\mathbf{q}, \mathbf{p}; V) + PV]\} \tag{4.76}$$

V_0 denotes some basic unit of volume introduced to make the partition function dimensionless (the exact magnitude of V_0 is immaterial). Note that

$$Q_{NPT} = \frac{1}{V_0} \int dV\ exp(-\beta PV)\ Q(\mathbf{q}, \mathbf{p}; V) \tag{4.77}$$

with Q the canonical partition function of a system at volume V. The operation of Eq. (4.77) is analogous to taking a Legendre transformation to pass from the Helmholtz energy to the Gibbs energy representation of the fundamental equation in macroscopic thermodynamics [Modell and Reid, 1983].

The connection between the formalism of the isothermal-isobaric ensemble and macroscopic thermodynamic properties is established via the Gibbs energy

$$\beta G(N,P,T) = -\ln Q_{NPT}(N,P,T) \tag{4.78}$$

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