6. THE GRAND CANONICAL ENSEMBLE

6.1 Probability Density in the Grand Canonical $(\mu V T)$ Ensemble

The grand canonical ensemble provides a statistical microscopic description of an *open* equilibrium system of given volume or spatial extent, capable of exchanging energy and particles with its surroundings. This ensemble is particularly useful in the study of sorption equilibria and surface thermodynamic properties of fluids.

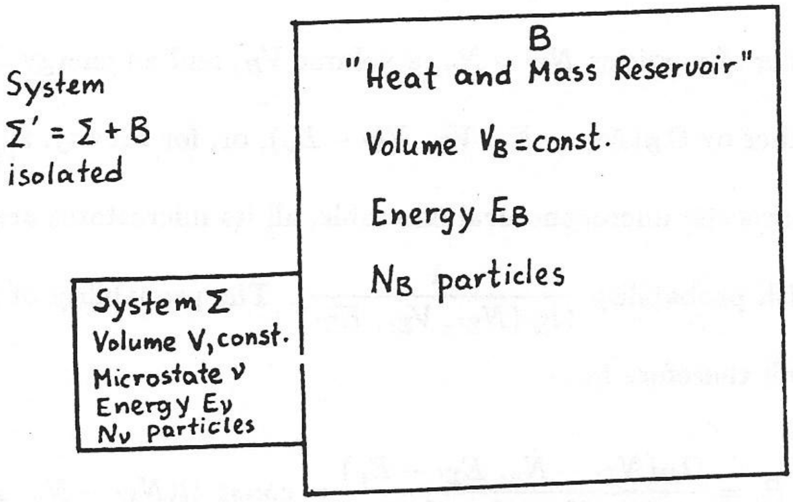

Figure 6.1 Derivation of the probability distribution of the grand canonical ensemble

To derive the probability density governing the distribution of microstates in the grand canonical ensemble, consider a system Σ, of given volume V, that is capable of exchanging energy and particles with a much larger system B, whose volume is also constant. The composite system $\Sigma' = \Sigma + B$ will be assumed isolated. The total number of particles $N_{\Sigma'} = N + N_B$, the total energy $E_{\Sigma'} = E + E_B$, and the total volume

$V_{\Sigma'} = V + V_B$ of the composite system Σ' are fixed; therefore, the probability distribution of Σ' among the microstates accessible to it is governed by the microcanonical ensemble. The number of particles and the energy of systems Σ and B fluctuate. Specifying the microstate of Σ entails specifying both the number of particles it contains and the quantum state in which this set of particles finds itself.

Consider that Σ is in a *particular* microstate ν, in which the number of particles is N_ν and the energy E_ν (see Fig. 6.1). Since the microstate of Σ is fixed, the number of microstates accessible to Σ' equals the number of microstates of B that are compatible with a number of particles $N_{\Sigma'} - N_\nu$, a volume V_B, and an energy $E_{\Sigma'} - E_\nu$. We symbolize this number by $\Omega_B(N_{\Sigma'} - N_\nu, V_B, E_{\Sigma'} - E_\nu)$, or, for brevity, $\underset{B}{\Omega}(N_{\Sigma'} - N_\nu, E_{\Sigma'} - E_\nu)$. Since Σ' follows the microcanonical ensemble, all its microstates are equiprobable, each occurring with probability $\dfrac{1}{\Omega_{\Sigma'}(N_{\Sigma'}, V_{\Sigma'}, E_{\Sigma'})}$. The probability of finding Σ in the microstate ν will therefore be

$$P_\nu = \frac{\Omega_B(N_{\Sigma'} - N_\nu, E_{\Sigma'} - E_\nu)}{\Omega_{\Sigma'}(N_{\Sigma'}, V_{\Sigma'}, E_{\Sigma'})} = const\ \underset{B}{\Omega}(N_{\Sigma'} - N_\nu, E_{\Sigma'} - E_\nu) \tag{6.1}$$

Using the fact that B is much larger than Σ, we can approximate the right-hand side of Eq. (6.1) as follows:

$$P_\nu = const\ \underset{B}{\Omega}(N_{\Sigma'}, E_{\Sigma'})\ exp\left[\ln \Omega_B(N_{\Sigma'} - N_\nu, E_{\Sigma'} - E_\nu) - \ln \Omega_B(N_{\Sigma'}, E_{\Sigma'})\right] =$$

$$const'\ exp\left[-E_\nu \left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)_{N_B = N_{\Sigma'},\, V_B} - N_\nu \left(\frac{\partial \ln \Omega_B}{\partial N_B}\right)_{E_B = E_{\Sigma'},\, V_B}\right] \tag{6.2}$$

Now, from the microcanonical ensemble formalism [Eq. (4.5)]:

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

with T_B the temperature of the bath. We also set

$$\left(\frac{\partial \ln \Omega_B}{\partial N_B}\right)_{E_B,\, V_B} = \frac{1}{k_B}\left(\frac{\partial S_B}{\partial N_B}\right)_{E_B, V_B} = -\frac{\mu_B}{k_B\, T_B} \tag{6.3}$$

Eq. (6.3) can be viewed as a definition of the particle chemical potential in the bath B. Note that this definition is consistent with what we know from macroscopic thermodynamics: For a 1-component system, the fundamental equation of thermodynamics in the internal energy representation gives

$$dU = T\, dS - P\, dV + \mu\, dn, \text{ hence } \left(\frac{\partial S}{\partial n}\right)_{U,V} = -\frac{\mu}{T}$$

The reader is reminded that the chemical potential of statistical mechanics is absolute, rather than relative, and is defined as a partial molecular, rather than as a molar property. The quantities T_B and μ_B are characteristic of the "heat and mass" reservoir. Setting $\beta = \dfrac{1}{k_B\, T_B} = \dfrac{1}{k_B\, T}$ and $\mu = \mu_B$, we obtain

$$P_\nu^{\mu VT} = const'\ exp\left[-\beta\, E_\nu + \beta\, \mu\, N_\nu\right], \text{ or}$$

$$\text{Probability} \quad P_\nu^{\mu VT} = \frac{exp\left[-\beta\, E_\nu + \beta\, \mu\, N_\nu\right]}{\Xi(\mu,\, V,\, T)} \tag{6.4}$$

$$\text{where} \quad \Xi(\mu,\, V,\, T) = \sum_\nu exp\left[-\beta\, E_\nu + \beta\, \mu\, N_\nu\right] \tag{6.5}$$

The normalizing factor Ξ is the *grand partition function.* Note that the summation in Eq. (6.5) is taking place over *all numbers of particles* N_ν and over *all quantum microstates* accessible to the system for each N_ν.

In a *classical formulation,* a microstate in the grand canonical ensemble is specified through the number of particles N and the generalized coordinates and momenta $\mathbf{q}^N$,

$\mathbf{p}^N$ of all particles. The superscript N is used here to emphasize that the dimensionality of the $\mathbf{q}$ and $\mathbf{p}$ vectors depends on the value of N. The probability distribution is discrete in N and continuous in $\mathbf{q}^N$, $\mathbf{p}^N$. The probability density is given by

$$\rho^{\mu VT}(N;\, \mathbf{q}^N, \mathbf{p}^N) = \frac{1}{\Xi(\mu,\, V,\, T)}\, \frac{1}{h^{3N}\, N!}\, exp\left[-\beta\, \mathcal{H}_N(\mathbf{q}^N, \mathbf{p}^N) + \beta\, \mu\, N\right] =$$

$$\frac{1}{\Xi(\mu,\, V,\, T)}\, \frac{1}{h^{3N}\, N!}\, z^N\, exp\left[-\beta\, \mathcal{H}_N(\mathbf{q}^N, \mathbf{p}^N)\right] \qquad (6.6)$$

where the *grand partition function* is

$$\Xi(\mu,\, V,\, T) = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int_{\substack{\text{all phase space}\\ \text{accessible to}\\ N \text{ particles}}} d^{3N}q\; d^{3N}p\; exp\left[-\beta\, \mathcal{H}_N(\mathbf{q}^N, \mathbf{p}^N) + \beta\, \mu\, N\right] =$$

$$\sum_{N=0}^{\infty} \frac{z^N}{h^{3N}\, N!} \int_{\substack{\text{all phase space}\\ \text{accessible to}\\ N \text{ particles}}} d^{3N}q\; d^{3N}p\; exp\left[-\beta\, \mathcal{H}_N(\mathbf{q}^N, \mathbf{p}^N)\right] =$$

$$\sum_{N=0}^{\infty} z^N\, Q(N,\, V,\, T) \qquad (6.7)$$

with z the *activity*, defined as

$$z = exp(\beta\, \mu) \qquad (6.8)$$

Observe that Eq. (6.8) is consistent with the macroscopic thermodynamic definition of activity,

$$\mu - \mu^0 = RT\, \ln z$$

the only differences being that μ here is expressed per molecule and that the reference state chemical potential is zero, since an absolute scale of chemical potentials is used.

6.2. Connection with Thermodynamics

The quantity $\Omega(\mu, V, T) \equiv -k_B T \ln \Xi(\mu, V, T)$ is called *grand potential.* In a homogeneous system, the connection between the grand potential and macroscopic thermodynamics is

$$-P\,V = \Omega(\mu, V, T) = -k_B T \ln \Xi(\mu, V, T) \tag{6.9}$$

Note that this connection is consistent with what we know from macroscopic thermodynamics. Invoking the maximum term approximation for the relation between grand and canonical partition functions, Eq. (6.7), we are led to

$$-k_B T \ln \Xi(\mu, V, T) = -k_B T \,\langle N\rangle \ln z - k_B T \ln Q(\langle N\rangle\,, V\,T) =$$

$$-\langle N\rangle\,\mu + A = -G + A = -P\,V$$

The average number of particles we expect to find in the system under given chemical potential, volume, and temperature is determined as

$$\langle N\rangle_{\mu V T} = \sum_{N=0}^{\infty} N \int d^{3N}q\; d^{3N}p\; \rho^{\mu V T}(N;\, \mathbf{q}^N, \mathbf{p}^N) =$$

$$\frac{\sum\limits_{N=0}^{\infty} N z^N Q(N, V, T)}{\Xi(\mu,\, V\,T)} = \frac{\sum\limits_{N=0}^{\infty} N z^N Q(N, V, T)}{\sum\limits_{N=0}^{\infty} z^N Q(N, V, T)} =$$

$$z\left(\frac{\partial \ln \Xi}{\partial z}\right)_{V,T} = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V} \tag{6.10}$$

Eliminating μ between Eqs. (6.9) and (6.10) leads to an equation of state for the system.

The Gibbs energy is found as

$$G = \langle N\rangle\;\mu = \langle N\rangle\; k_B T \ln z = k_B T \left(\frac{\partial \ln \Xi}{\partial \ln \mu}\right)_{T,V} \tag{6.11}$$

and the Helmholtz energy as

$$A = G - PV = \langle N \rangle \, \mu - k_B T \ln \Xi = k_B T \left[\left(\frac{\partial \ln \Xi}{\partial \ln \mu} \right)_{T,V} - \ln \Xi \right] \tag{6.12}$$

The grand canonical formulation is readily extended to *multicomponent* systems. For a system of n components under the macroscopic co~~m~~nstraints of fixed total volume V, fixed temperature T, and fixed chemical potentials $\mu_1, \mu_2 \ldots, \mu_n$ of all species, the probability density is

$$\rho^{\mu_1 \mu_2 \ldots \mu_n VT} \left(N_1, N_2, \ldots, N_n; \mathbf{q}^N, \mathbf{p}^N \right) =$$

$$\frac{1}{\Xi(\mu_1, \mu_2, \ldots, \mu_n, V, T)} \; \frac{e^{-\beta \mathcal{H}_{N_1 N_2 \ldots N_n}(\mathbf{q}^N, \mathbf{p}^N) + \beta(\mu_1 N_1 + \mu_2 N_2 + \cdots + \mu_n N_n)}}{h^{3N} \; N_1! \, N_2! \ldots N_n!} \tag{6.13}$$

where $N = N_1 + N_2 + \cdots + N_n$ and

$$\Xi(\mu_1, \mu_2, \ldots, \mu_n, V\, T) = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \cdots \sum_{N_n=0}^{\infty} \frac{1}{h^{3N} \; N_1! \, N_2! \ldots N_n!} \times$$

$$\int d^{3N}q \; d^{3N}p \, exp \left[-\beta \mathcal{H}_{N_1 N_2 \ldots N_n}(\mathbf{q}^N, \mathbf{p}^N) + \beta(\mu_1 N_1 + \cdots + \mu_n N_n) \right]$$

6.3 Density Fluctuations in the Grand Canonical Ensemble

The grand canonical ensemble offers itself for studying density or concentration fluctuations in a system of given temperature and spatial extent, capable of exchanging particles with an environment in which the chemical potentials of all species are specified. Of particular interest is how the magnitude of density fluctuations scales with the size of the system. To quantify density fluctuations, we introduce the variance in the number of particles:

$$\left\langle (\delta N)^2 \right\rangle \equiv \left\langle (N - \langle N \rangle)^2 \right\rangle = \left\langle N^2 \right\rangle - \langle N \rangle^2 \tag{6.14}$$

where all angular brackets denote averages under constant μ, V, and T. From Eq. (6.10) we obtain

$$\langle N \rangle = k_B\, T \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{T,V} \tag{6.15}$$

hence

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{1}{\beta} \left(\frac{\partial^2 \ln \Xi}{\partial \mu^2} \right)_{T,V} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \left[\frac{1}{\Xi} \left(\frac{\partial \Xi}{\partial \mu} \right)_{T,V} \right]_{T,V} =$$

$$\beta \left[\frac{1}{\beta^2\, \Xi} \left(\frac{\partial^2 \Xi}{\partial \mu^2} \right)_{\beta,V} - \left\{ \frac{1}{\beta \Xi} \left(\frac{\partial \Xi}{\partial \mu} \right)_{\beta,V} \right\}^2 \right] \tag{6.16}$$

Now, from Eq. (6.7),

$$\frac{1}{\Xi} \left(\frac{\partial^2 \Xi}{\partial \mu^2} \right)_{\beta,V} = \frac{\sum\limits_{N=0}^{\infty} N^2\, exp(N \beta \mu)\, Q(N\, V\, T)}{\Xi(\mu, V, T)} =$$

$$\sum_{N=0}^{\infty} N^2 \int d^{3N}q\, d^{3N}p\, \rho^{\mu V T}(N; \mathbf{q}^N, \mathbf{p}^N) = \left\langle N^2 \right\rangle \tag{6.17}$$

Using Eqs. (5.15) and (6.17) in (6.16), we obtain

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \beta \left[\left\langle N^2 \right\rangle - \langle N \rangle^2 \right] \tag{6.18}$$

The left-hand side of Eq. (6.18) is easily calculated from macroscopic thermodynamics:

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{N_{Avo}^2}{\left(\dfrac{\partial (\mu\, N_{Avo})}{\partial \left(\frac{\langle N \rangle}{N_{Avo}} \right)} \right)_{T,V}} = \frac{N_{Avo}^2}{\left(\dfrac{-s\, \partial T + v\, \partial P}{\partial n} \right)_{T,V}} =$$

$$\frac{N_{Avo}^2}{v\left(\frac{\partial P}{\partial n}\right)_{T,V}} = -\frac{N_{Avo}^2\left(\frac{\partial V}{\partial P}\right)_{T,n}}{v\left(\frac{\partial V}{\partial n}\right)_{T,P}} =$$

$$-\frac{N_{Avo}^2}{v}\,\frac{n\left(\frac{\partial v}{\partial P}\right)_T}{v} = \frac{\langle N\rangle^2}{v\,n}\left[-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\right]$$

$$\text{or}\quad \left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{\langle N\rangle^2}{V}\,\kappa_T \qquad (6.19)$$

where v the molar volume and $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$ the isothermal compressibility of the material. Combining Eqs. (6.18) and (6.19) we obtain

$$\left\langle(\delta N)^2\right\rangle \equiv k_B\,T\,\frac{\langle N\rangle^2}{V}\,\kappa_T,\ \text{or}$$

$$\frac{\left\langle(\delta N)^2\right\rangle^{\frac{1}{2}}}{\langle N\rangle} = \left(\frac{R\,T}{v}\,\kappa_T\right)^{\frac{1}{2}}\,\frac{1}{\langle N\rangle^{\frac{1}{2}}} \qquad (6.20)$$

Eq. (6.20) is one form of the *compressibility equation.* The fluctuation in the *molecular density* $\rho = \frac{\langle N\rangle}{V}$ can be expressed on the basis of Eq. (6.20) as

$$\left\langle(\delta\rho)^2\right\rangle^{\frac{1}{2}} = \rho\left(\frac{k_B\,T}{V}\,\kappa_T\right)^{\frac{1}{2}} \qquad (6.21)$$

A number of interesting conclusions can be derived from Eqs. (6.20) and (6.21). First, the isothermal compressibility must be a nonnegative quantity for a thermodynamically stable system. Second, the ratio $\frac{\left\langle(\delta N)^2\right\rangle^{\frac{1}{2}}}{\langle N\rangle}$ equals an intensive thermodynamic quantity times the inverse square root of the number of particles in the system. In the thermodynamic limit, this ratio goes to zero. In other words, the distribution of particle numbers becomes extremely peaked at $\langle N\rangle$. This explains why the grand canonical ensemble formalism yields the same results for the system thermodynamics as the canonical ensemble. Third, fluctuations in density in a one-component system become very large when the isothermal compressibility tends to infinity. The condition $\kappa_T \to \infty$ is realized at the critical point of a pure substance. Near the critical point, therefore, density fluctuations become unbounded. Inasmuch density fluctuations cause index of refraction fluctuations within a material, we expect that light will be scattered strongly by pure fluids in the vicinity of their critical point. This is actually observed, and constitutes the phenomenon of *critical opalescence.*

6.4 An Application of the Grand Canonical Ensemble: Derivation of the BET Isotherm for Multilayer Adsorption

The formalism of the grand canonical ensemble is particularly convenient for predicting sorption isotherms from molecular-level information. Sorption involves an equilibrium between a solid (sorbent + sorbate) phase and a fluid phase. The fluid chemical potential in the solid phase equals that in the fluid phase. In many cases, the spatial extent and configuration of the sorbent (*e.g.* a microporous solid or a face of a metal crystallite) is not significantly affected by the presence of fluid molecules; *i.e.*, the sorbent can be viewed merely as a source of an external potential energy field on the fluid molecules. Under these conditions, the sorbed phase constitutes a system at fixed temperature, volume, and chemical potential, and can be treated naturally by the grand canonical ensemble. Even in cases where the sorbent responds to the presence of sorbate (*e.g.*, swelling of glassy polymer matrices, reconstruction of solid surfaces) one can extend the ideas discussed here and formulate ensembles for the realistic treatment of sorption equilibria.

As a simple example of the application of the grand canonical ensemble to the prediction of sorption equilibria we consider the prediction of the BET isotherm for multilayer adsorption on a solid surface [Brunauer, Emmett, and Teller 1938]. Our derivation follows Hill's approach [Hill 1946, 1956].

The BET isotherm treats the phenomenon of physisorption of a gas on a solid surface, wherein the fluid can form multiple molecular layers on the surface. It provides a functional relation between the amount sorbed and the ambient gas pressure at given temperature. This relation is of the form

$$\frac{c}{c_m} = \frac{b\left(\frac{P}{P_s}\right)}{\left(1-\frac{P}{P_s}\right)\left(1-\frac{P}{P_s}+b\frac{P}{P_s}\right)} \qquad (\mathrm{P} < \mathrm{P_s}) \tag{6.22}$$

where

c : adsorbed amount per unit mass of sorbent, mol/g.

c_m : adsorbed amount that would correspond to full coverage of the surface by a monolayer, mol/g.

P: gas phase pressure.

P_s: vapor pressure of saturated liquid sorbate at the prevailing temperature.

The BET isotherm is very useful in determining the specific surface areas of porous solids. For the surface area determination, one typically performs a series of measurements of the sorbed amount c of a nonpolar gas (N_2, Ar) at cryogenic temperature over a range of reduced pressures $0.05 < \frac{P}{P_s} < 0.35$. The experimental results are plotted as $\frac{P}{c(P-P_s)}$ *vs.* $\frac{P}{P_s}$. In these coordinates, the BET Eq. (6.22) gives a straight line:

$$\frac{P}{c(P_s - P)} = \frac{1}{c_m\, b}\left[(b-1)\left(\frac{P}{P_s}\right) + 1\right] \tag{6.23}$$

The quantities c_m and b are obtained from the slope and intercept of the plot. Knowing the area occupied by a molecule on the surface, one can readily translate c_m (mol sorbate/g sorbent) into a specific surface area (cm^2 of internal or external surface/g sorbent). Absolute specific surface areas can be determined to within 20% by this method.

To derive the BET isotherm, we will use the following microscopic model and approximations (see Fig. 6.2).

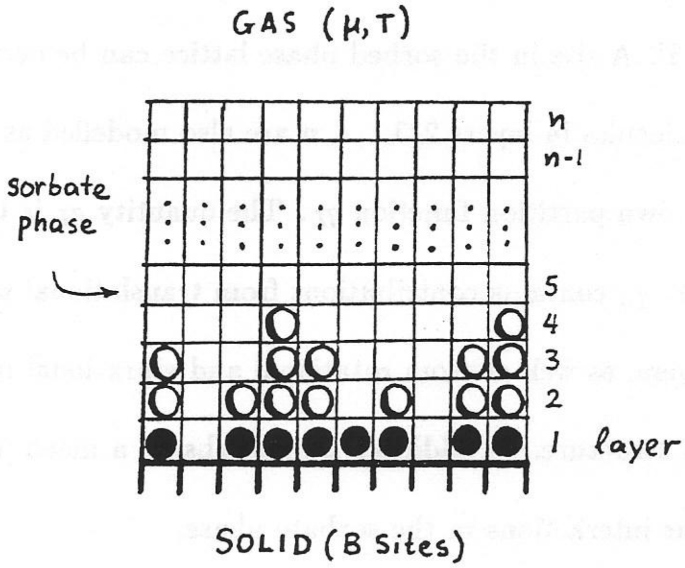

Figure 6.2 Microscopic model used for the derivation of the BET isotherm. Fluid molecules adsorbed directly on the solid surface are shown as black spheres, molecules adsorbed on other molecules as white spheres. The maximum number of layers that can form is n.

1. The surface consists of a regular two-dimensional array of identical sorption sites.
2. The gas molecules occupy sites in a three-dimensional lattice extending above the solid surface. Gas molecules can adsorb directly on the surface to form the first layer. Gas molecules can also adsorb on top of already adsorbed gas molecules, thereby forming layers $2, 3, \ldots, n$. We will assume that up to n layers of adsorbed molecules can form on the surface.
3. Within layer 1 there is no lateral interaction between sorbed molecules, apart from the requirement that no two molecules can occupy the same sorption site. In the statistical mechanical formulation, all molecules in the first layer will be modelled as independent entities, each characterized by its own partition function q_1.
4. Molecules in layers $2, 3, \ldots, n$ form a phase that is similar to a saturated liquid at temperature T. A site in the sorbed phase lattice can be occupied by at most one molecule. Molecules in layers $2, 3, \ldots, n$ are also modelled as independent entities, each with its own partition function q_L. The quantity q_L is the same for all layers $2, 3, \ldots, n$. q_L contains contributions from translational motion within a site of the upper layers, as well as from rotational and vibrational motion, if the molecules have internal structure. In addition, q_L absorbs, in a mean field sense, the effects of intermolecular interactions in the sorbate phase.
5. The pressure in the gas phase is sufficiently low that the gas can be treated as ideal. If the sorbate molecules have internal structure, we will denote their internal partition function by q_G^{int}. [compare Eq. (4.37)].

Some clarification of what goes into the partition function q_1 of molecules in the first sorbed layer is in order. For molecules with internal structure, q_1 will contain contributions from internal vibrational motion of bonds and bond angles, as well as from torsional and overall rotational motion while the molecule is attached to a sorption site; in other words, q_1 will contain contributions from the same degrees of freedom that go into q_G^{int}. Note, however, that the values of these "internal" contributions from vibration, torsion, and rotation, may be quite different in the sorbed state than they are in the free gas state, as internal motions are strongly influenced by the field that keeps the molecule sorbed at a site. In addition to the contribution of internal motions in the sorbed state, factors that shape q_1 are *(i)* the potential energy of adsorptive interactions between a molecule and the solid substrate; *(ii)* the vibrational motion of the molecule's center of mass about its equilibrium position in the sorption site. Note that this center-of-mass vibration replaces the uninhibited translational motion that the molecule is capable of executing in the gas phase.

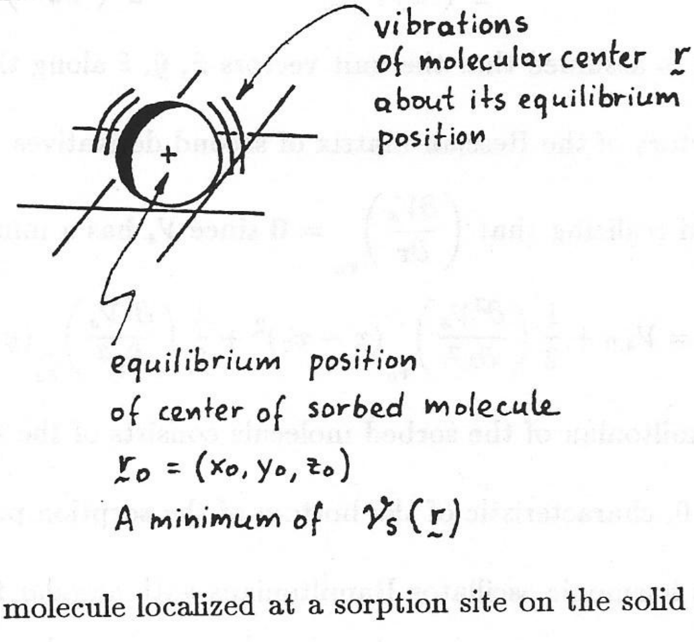

Figure 6.2 Schematic of a single molecule localized at a sorption site on the solid surface, for the explanation of the partition function q_1.

To clarify factors *(i)* and *(ii)* mentioned in the last paragraph, consider a spherical (structureless) molecule sorbed at a site on the solid surface (Fig. 6.3). In the gas phase, the internal partition function of this molecule is $q_G^{int} = 1$ (compare section 4.6). In the sorbed state, the molecule spends most of its time localized at a site under the influence of a potential $\mathcal{V}_s(\mathbf{r})$, exerted on it by the solid.

The equilibrium position $\mathbf{r_0} = (x_0, y_0, z_0)$ of the molecule center of mass above the surface corresponds to a minimum of $\mathcal{V}_s$. Excursions away from $\mathbf{r_0}$ undertaken by the center of mass in the course of its vibrational motion within the site are expected to be small. For the purpose of analyzing this motion, therefore, it is sufficient to approximate $\mathcal{V}_s(\mathbf{r})$ by its Taylor expansion around $\mathbf{r_0}$ truncated at the second order terms (*harmonic approximation*):

$$\mathcal{V}_s(\mathbf{r}) = \mathcal{V}_s(\mathbf{r}_0) + \left(\frac{\partial \mathcal{V}_s}{\partial \mathbf{r}}\right)_{\mathbf{r}_0} \cdot (\mathbf{r} - \mathbf{r}_0) + \frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial x^2}\right)_{\mathbf{r}_0} (x - x_0)^2 +$$
$$\frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial y^2}\right)_{\mathbf{r}_0} (y - y_0)^2 + \frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial z^2}\right)_{\mathbf{r}_0} (z - z_0)^2$$

where it is assumed that the unit vectors $\hat{x}$, $\hat{y}$, $\hat{z}$ along the three coordinate axes are eigenvectors of the Hessian matrix of second derivatives $\left(\frac{\partial^2 \mathcal{V}}{\partial \mathbf{r}\, \partial \mathbf{r}^T}\right)_{\mathbf{r}_0}$. Setting $\mathcal{V}_s(\mathbf{r}_0) = \mathcal{V}_{s,0}$, and realizing that $\left(\frac{\partial \mathcal{V}_s}{\partial \mathbf{r}}\right)_{\mathbf{r}_0} = \mathbf{0}$ since $\mathcal{V}_s$ has a minimum at $\mathbf{r}_0$, we can write

$$\mathcal{V}_s(\mathbf{r}) = \mathcal{V}_{s,0} + \frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial x^2}\right)_{\mathbf{r}_0} (x - x_0)^2 + \frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial y^2}\right)_{\mathbf{r}_0} (y - y_0)^2 + \frac{1}{2}\left(\frac{\partial^2 \mathcal{V}_s}{\partial z^2}\right)_{\mathbf{r}_0} (z - z_0)^2$$

The Hamiltonian of the sorbed molecule consists of the attractive potential energy $\mathcal{V}_{s,0} < 0$, characteristic of the bottom of the sorption potential well, plus three independent harmonic oscillator Hamiltonians with angular frequencies

$$\omega_x = \left(\frac{1}{m}\frac{\partial^2 \mathcal{V}_s}{\partial x^2}\right)_{\mathbf{r}_0}^{\frac{1}{2}}, \quad \omega_y = \left(\frac{1}{m}\frac{\partial^2 \mathcal{V}_s}{\partial y^2}\right)_{\mathbf{r}_0}^{\frac{1}{2}}, \quad \omega_z = \left(\frac{1}{m}\frac{\partial^2 \mathcal{V}_s}{\partial z^2}\right)_{\mathbf{r}_0}^{\frac{1}{2}}$$

A quantum statistical mechanical analysis of a harmonic oscillator of frequency ω leads to the canonical partition function $\dfrac{exp(-\beta\hbar\omega/2)}{1-exp(-\beta\hbar\omega)}$ [McQuarrie 1976, p.96]. Consequently, the partition function of the sorbed molecule will be

$$q_1 = exp\left(-\beta \mathcal{V}_{s,0}\right) \frac{exp(-\beta\hbar\omega_x/2)}{1-exp(-\beta\hbar\omega_x)} \frac{exp(-\beta\hbar\omega_y/2)}{1-exp(-\beta\hbar\omega_y)} \frac{exp(-\beta\hbar\omega_z/2)}{1-exp(-\beta\hbar\omega_z)} \tag{6.24}$$

If the vibrational frequencies $\omega_x, \omega_y, \omega_z$ are low compared to $\dfrac{k_B T}{\hbar}$, then q_1 assumes its classical form

$$q_1 = exp\left(-\beta \mathcal{V}_{s,0}\right) \left(\frac{k_B T}{\hbar}\right)^3 \frac{1}{\omega_x\,\omega_y\,\omega_z}$$

The above discussion gives us an idea of what shapes the internal partition function q_1.

We now return to the problem of predicting the adsorption isotherm based on the simple model of multilayer adsorption we introduced above. Consider the sorbate phase in equilibrium with the gas phase at temperature T and chemical potential μ. The chemical potential of the sorbed species is the same in the gas and sorbate phases. By the ideal gas assumption 5, it is related to the gas-phase pressure P and the temperature T by Eq. (4.45):

$$\mu = k_B T \ln\left(\frac{\rho_G \Lambda^3}{q_G^{int}}\right) = k_B T \ln\left(\frac{P \Lambda^3}{k_B T\, q_G^{int}}\right) \tag{4.45}$$

We focus on a macroscopic patch of surface containing B sites and pick the sorbate above this patch as our system. This is a one- component system of given spatial extent (B surface sites × n lattice layers), temperature T , and chemical potential μ. Therefore, the distribution of its microstates is governed by the grand canonical ensemble. We proceed to formulate the grand partition function $\Xi(\mu, B, n, T)$ for this system.

Let N_1, N_2 ..., N_n be the number of molecules in the 1^{st}, 2^{nd} ..., n^{th} layer of the sorbate phase lattice. These numbers fluctuate from configuration to configuration in such a way as to maintain a fixed chemical potential. For all physically acceptable configurations, the following inequalities hold:

$$0 \leq N_n \leq N_{n-1} \leq \ldots \leq N_2 \leq N_1 \leq B$$

This is because a molecule in layer i of the sorbate phase necessarily sits on top of an uninterrupted column of molecules in layers $1, 2, \ldots, i-1$ (compare Fig.6.2). A given set of layer occupancies, $\{N_1, N_2, \ldots, N_n\}$ can be realized in

$$\frac{B!}{(B-N_1)!\,N_1!}\,\frac{N_1!}{(N_1-N_2)!\,N_2!}\cdots\frac{N_{n-1}!}{(N_{n-1}-N_n)!\,N_n!}$$

ways. This is because there are $\frac{B!}{(B-N_1)!\,N_1!}$ ways of arranging N_1 first-layer molecules on B sorption sites; there are $\frac{N_1!}{(N_1-N_2)!\,N_2!}$ ways of arranging N_2 second-layer molecules on top of N_1 first layer molecules, *etc.* In the grand partition function, each one such configuration will carry a weight

$$q_1^{N_1}\, q_L^{N_2+N_3+\cdots+N_n}\, exp\left[(N_1+N_2+N_3+\cdots+N_n)\,\beta\mu\right]$$

as each molecule in the first layer is independently contributing a partition function q_1 (assumption 3 above), each molecule in the subsequent layers is independently contributing a partition function q_L (assumption 4 above), and the chemical potential is everywhere μ. The grand partition function becomes [compare Eqs. (6.5), (6.7)]:

$$\Xi(\mu, B, n, T) = \sum_{N_1=0}^{B}\sum_{N_2=0}^{N_1}\sum_{N_3=0}^{N_2}\cdots\times$$

$$\sum_{N_n=0}^{N_{n-1}} \left\{ \frac{B!}{(B-N_1)!\,N_1!}\,\frac{N_1!}{(N_1-N_2)!\,N_2!}\,\frac{N_2!}{(N_2-N_3)!\,N_3!}\cdots\frac{N_{n-1}!}{(N_{n-1}-N_n)!\,N_n!}\times \right.$$

$$\left. q_1^{N_1}\, q_L^{N_2+\cdots+N_n}\, exp\left[(N_1+N_2+\cdots+N_n)\,\beta\mu\right] \right\} \qquad (6.25)$$

For the analytical expression of $\Xi(\mu, B, n, T)$ it is convenient to introduce the following notation:

$$q_L\, exp(\beta\mu) = x \ , \qquad \frac{q_1}{q_L} = \lambda \qquad (6.26)$$

Eq. (6.25) becomes

$$\Xi(\mu, B, n, T) = \sum_{N_1=0}^{B} \sum_{N_2=0}^{N_1} \sum_{N_3=0}^{N_2} \cdots \times$$

$$\sum_{N_n=0}^{N_{n-1}} \left\{ \frac{B!}{(B-N_1)!\,N_1!}\,\frac{N_1!}{(N_1-N_2)!\,N_2!}\cdots\frac{N_{n-1}!}{(N_{n-1}-N_n)!\,N_n!}\times \right.$$

$$\left. (\lambda x)^{N_1}\, x^{N_2+\cdots+N_n} \right\} \qquad (6.27)$$

We focus on the innermost summation over N_n first. Invoking the binomial theorem, we obtain

$$\sum_{N_n=0}^{N_{n-1}} \frac{N_{n-1}!}{(N_{n-1}-N_n)!\,N_n!}\, x^{N_n} = \sum_{N_n=0}^{N_{n-1}} \binom{N_{n-1}}{N_n} x^{N_n} = (1+x)^{N_{n-1}}$$

Next we perform the summation over N_{n-1}. Again by the binomial theorem, this gives

$$\sum_{N_{n-1}=0}^{N_{n-2}} \frac{N_{n-2}!}{(N_{n-2}-N_{n-1})!\,N_{n-1}!}\, x^{N_{n-1}}\,(1+x)^{N_{n-1}} =$$

$$\sum_{N_{n-1}=0}^{N_{n-2}} \frac{N_{n-2}!}{(N_{n-2}-N_{n-1})!\,N_{n-1}!}\, \left[x\,(1+x)\right]^{N_{n-1}} =$$

$$\left[1 + x\,(1+x)\right]^{N_{n-2}} = \left[1 + x + x^2\right]^{N_{n-2}}$$

The sums over $N_{n-2}, N_{n-3}, \ldots$ are performed in the same way. In each case the result collapses into a power of a polynomial of x, by virtue of the binomial theorem. The sum over N_2 gives

$$\sum_{N_2=0}^{N_1} \frac{N_1!}{(N_1 - N_2)!\, N_2!} x^{N_2} \left(1 + x + x^2 + \cdots + x^{n-2}\right)^{N_2} = \left(1 + x + x^2 + \cdots + x^{n-1}\right)^{N_1}$$

Finally, the outermost summation over N_1 yields

$$\Xi(\mu, B, n, T) = \sum_{N_1=0}^{B} \frac{B!}{(B - N_1)!\, N_1!} (\lambda\, x)^{N_1} \left(1 + x + x^2 + \cdots + x^{n-1}\right)^{N_1} =$$

$$\left[1 + \lambda\, x \left(1 + x + x^2 + \cdots + x^{n-1}\right)\right]^B \quad \text{or}$$

$$\Xi(\mu, B, n, T) = \left[1 + \lambda\, x \left(\frac{1 - x^n}{1 - x}\right)\right]^B \tag{6.28}$$

The grand partition function has been determined in closed form. From Eqs. (6.25) and (6.26), the average number of adsorbed molecules at equilibrium can be found as

$$\langle N \rangle \equiv \langle N_1 + N_2 + \cdots + N_n \rangle = k_B\, T \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{B,\overset{n}{\cancel{N}},T} =$$

$$\frac{1}{\beta} \frac{\partial \ln \Xi}{\frac{1}{\beta}\left(\frac{\partial x}{x}\right)_{B,n,T}} = x \left(\frac{\partial \ln \Xi}{\partial x}\right)_{B,n,T}, \quad \text{or}$$

$$\langle N \rangle = x\, B \left[1 + \lambda\, x \left(\frac{1 - x^n}{1 - x}\right)\right]^{-1} \lambda\, \frac{n\, x^{n+1} - (n+1)\, x^n + 1}{(1 - x)^2}, \quad \text{or}$$

$$\frac{\langle N \rangle}{B} = \frac{\lambda\, x \left[1 - (n+1)\, x^n + n\, x^{n+1}\right]}{(1 - x)\,(1 - x + \lambda\, x - \lambda\, x^{n+1})} \tag{6.29}$$

Eq. (6.29) is in fact an adsorption isotherm. By definition, we can identify

$$\frac{\langle N \rangle}{B} = \frac{c}{c_m} \tag{6.30}$$

As regards the quantity x appearing in Eq. (6.29), in order to give it a more tangible physical interpretation we think as follows: The average number of sorbate molecules in layer 1, N_1, can be found by differentiation of the grand partition function. From Eq. (6.27) it is clear that

$$\langle N_1 \rangle = \lambda \frac{1}{\Xi} \left(\frac{\partial \Xi}{\partial \lambda} \right)_{x,B,n} = \lambda \left(\frac{\partial \ln \Xi}{\partial \lambda} \right)_{x,B,n}$$

Substituting for Ξ the closed-form expression (6.28), we obtain

$$\frac{\langle N_1 \rangle}{B} = \frac{\lambda\, x\,(1 - x^n)}{1 - x + \lambda x - \lambda x^{n+1}} \tag{6.31}$$

Combining Eqs. (6.29) and (6.31),

$$\frac{\langle N \rangle}{\langle N_1 \rangle} = \frac{1 - (n+1)\, x^n + n\, x^{n+1}}{(1 - x)\,(1 - x^n)}$$

Consider, now, the sorbate phase as the gas-phase pressure tends towards the saturation pressure P_s. In this limit all layers will be filled with saturated liquid, and therefore

$$\text{As } P \to P_s, \quad \frac{\langle N \rangle}{\langle N_1 \rangle} = n \ , \quad \text{or} \quad 1 - (n+1)\, x^n + n x^{n+1} = n(1 - x - x^n + x^{n+1}) \ , \quad \text{or}$$

$$1 - x^n = n\,(1 - x) \ , \quad \text{or} \quad (1 - x)\,\left[1 + x + \cdots + x^{n-1} - n\right] = 0$$

The only real solution to the above equation is $x = 1$. Therefore, we conclude that

$$\text{As } P \to P_s, \quad x \to 1 \tag{6.32}$$

Eqs. (6.26) and (4.45) give

$$x = q_L \frac{P \Lambda^3}{k_B\, T\, q_G^{int}} \tag{6.33}$$

Taking the limit (6.32), we obtain from Eq. (6.33)

$$1 = q_L \frac{P_s \Lambda^3}{k_B\, T\, q_G^{int}}\,, \quad \text{or} \quad q_L = \frac{k_B\, T\, q_G^{int}}{P_s\, \Lambda^3} \tag{6.34}$$

Eq. (6.34) attributes a concrete molecular meaning to the partition function q_L, which we introduced in a rather *ad hoc* fashion for the description of the state of molecules in layers $2, 3, \ldots, n$. Combining Eqs. (6.33) and (6.44), we obtain

$$x = \frac{P}{P_s} < 1 \tag{6.35}$$

The parameter x, therefore, is none else than the reduced pressure P/P_s. In view of Eqs. (6.30) and (6.35), Eq. (6.29) can be recast in the form

$$\frac{c}{c_m} = \frac{\lambda \left(\frac{P}{P_s}\right) \left[1 - (n+1)\left(\frac{P}{P_s}\right)^n + n\left(\frac{P}{P_s}\right)^{n+1}\right]}{\left(1 - \frac{P}{P_s}\right)\left[1 - \frac{P}{P_s} + \lambda \frac{P}{P_s} - \lambda \left(\frac{P}{P_s}\right)^{n+1}\right]} \quad \text{with} \quad \lambda = \frac{q_1\, P_s\, \Lambda^3}{k_B\, T\, q_G^{int}} \tag{6.36}$$

(*BET isotherm for sorption limited to n layers*).

Letting the number of layers n go to infinity, we obtain from Eq. (6.36) the simpler equation

$$\frac{c}{c_m} = \frac{b\left(\frac{P}{P_s}\right)}{\left(1 - \frac{P}{P_s}\right)\left(1 - \frac{P}{P_s} + b\frac{P}{P_s}\right)} \quad \text{with} \quad b \equiv \lambda = \frac{q_1\, P_s\, \Lambda^3}{k_B\, T\, q_G^{int}} \tag{6.22}$$

which is the BET equation stated at the beginning of this section. Note that the statistical mechanical analysis has clearly pointed out the microscopic model and approximations on which the BET equation is based and has provided us with a molecular interpretation of the coefficient b. [compare Eqs. (6.22), (6.24)]. The coefficient b is a function of temperature. For a structureless (spherical) sorbate, b is shaped by the depth and curvature of the potential energy well experienced by the molecule at the sorption site. If the sorbate has rotational, torsional, and vibrational degrees of freedom, perturbations in these degrees of freedom upon sorption also affect b.

If we restrict the sorption to a monomolecular layer ($n = 1$), the general equation (6.36) reduces to

$$\frac{c}{c_m} = \frac{b\left(\dfrac{P}{P_s}\right)}{1 + b\left(\dfrac{P}{P_s}\right)} \quad \text{with} \quad b = \frac{q_1\, P_s\, \Lambda^3}{k_B\, T\, q_G^{int}} \quad \text{or}$$

$$\frac{c}{c_m} = \frac{K\,P}{1 + K\,P} \quad \text{with} \quad K = \frac{q_1\, \Lambda^3}{k_B\, T\, q_G^{int}} \tag{6.37}$$

which is the *Langmuir isotherm* for monolayer adsorption. Note that, in the limit of low pressures, isotherms (6.22), (6.36), and (6.37) reduce to a *linear* relationship between $\dfrac{c}{c_m}$ and P, with proportionality constant $K = b/P_s$. The coefficient K (low-occupancy slope of the isotherm) is known as the *Henry's law constant* for sorption.

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