A CANONICAL ENSEMBLE DERIVATION OF THE McMILLAN-MAYER SOLUTION THEORY

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A special free energy function is defined for a solution in the osmotic equilibrium with pure solvent. The partition function of the solution is derived at the McMillan–Mayer level and it is related to this special function in the same manner as the common partition function of the system to its Helmholtz free energy.

Earlier theories of electrolyte solutions[1] were developed by the canonical ensemble method, formally at the Born–Oppenheimer (BO) level, however, they were based on simplified models in which the molecular character was being taken into account only for solute species, whereas the solvent was being treated as a continuous medium characterized solely by its permittivity. The exact formulation and generalization of this approach has been enabled through the McMillan-Mayer theory of solutions, which forms a special case of the generalized method of the grand canonical ensemble[2,3]. Modern theories of electrolyte solutions[4,5] are being developed within the frame of this method. However, the method of canonical ensemble represents even at the McMillan–Mayer (MM) level an adequate alternative[3]. Due to this reason, we shall outline a simple derivation of fundamental equations for the canonical ensemble at the MM level. We shall limit ourselves to a system containing one solute in a single component solvent, since the extension to more complex system is a formal question only.

Formulation of the Problem

The partition function of a single component thermodynamic system at the BO level (a set of molecules in vacuum) is in the usual classical limit expressed through the relation

$$Q_{\mathrm{BO}}(T, V, N) = (\Lambda^{3N} N!)^{-1} \int_V \exp(-\beta U_N)\, \mathrm{d}\{N\}\,, \tag{1}$$

where T is temperature, V is the volume of the system, N is the number of molecules of a system component, Λ is a function[3] of temperature only, $\beta = 1/kT$, k is Boltzmann's constant, U_N is the potential energy of intermolecular forces in a system containing N molecules and $\{N\}$ is the set of coordinates of these molecules. The partition function (*1*) is related to the Helmholtz free energy of the system $F(T, V, N)$, by

$$\beta F = -\ln Q_{\mathrm{BO}}\,. \tag{2}$$

For a thermodynamic system at the MM level (a set of solute molecules with the solvent-averaged hamiltonian) we will find functions analogous to the Q_{BO} and F functions as well as relations formally identical with Eqs (*1*) and (*2*).

Helmholtz Free Energy of MM *System*

Let us consider a vessel of a volume v separated into two parts by a partition permeable to solvent 0, but impermeable to the solute 1. This partition plays no role if the vessel contains the solvent only. Let us denote the number of molecules of the solvent in the system by N_0, its chemical potential related to one molecule by μ_0 and the pressure of the system in the state (T, v, N_0) by P_0. Now let us consider that we add N_1 molecules of substance 1 into a part of the system of a volume V (see Fig. 1*c*) and that we let establish the osmotic equilibrium between the solution in this part and the pure solvent in the other part of the system whose volume is $v - V$. In the equilibrium state, the pressure of the pure solvent is P_0' and the solution pressure is then $p = P_0' + P'$, where P' is the osmotic pressure of the solution. If the volume v

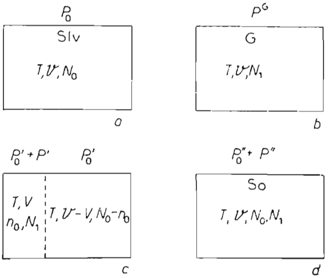

FIG. 1

The schematic illustration of systems relating to the outlined derivation. Our aim is to describe the part of system (*c*) of a volume V which is in an osmotic equilibrium with the pure solvent in the other part of system (*c*) in the limiting case of $v \to \infty$ at a constant volume V, the number of molecules of the solute N_1 and the number density of solvent molecules N_0/v

of the system grows to infinity at constant

$$V, N_1, N_0/v \tag{3}$$

(and temperature), P'_0 approaches P_0. The Helmholtz free energy of the system before the addition of substance *1* will be denoted by $F(T, v, N_0)$ and the corresponding Helmholtz free energy after this addition will be denoted by $F(T, v, V, N_0, N_1)$, where the second volume term expresses the volume accesibile to molecules of the solute *1*. Let us define the function A by

$$A = \lim_{v \to \infty} [F(T, v, V, N_0, N_1) - F(T, v, N_0)] . \tag{4}$$

We find easily that it holds

$$A = N_1\mu_1 - PV , \tag{5}$$

where μ_1 is the chemical potential of the solute *1* and P is the osmotic pressure of the solution being in the osmotic equilibrium with the pure solvent at pressure P_0. (Solutions with this property are denoted as MM systems). Function A possesses usual properties of the free energy and we shall call it the Helmholtz free energy of the MM system. Eq. (5) does not contain quantities referring to the solvent and function A describes the MM system formally exactly as it were the Helmholtz free energy $F(T, V, N_1)$ of a one-component system at pressure P.

Partition Function at the MM *Level*

The canonical ensemble method serves for the description of closed systems. In our case, however, the system is closed only with respect to dissolved substances (we could speak about a closed system at the MM level). Such a system can be described to advantage[3] in terms of an ensemble defined by the variables (T, V, N_1, μ_0) and with the partition function

$$\psi = \sum_{n_0 \geqq 0} \exp(\beta n_0 \mu_0)\, Q_{BO}(T, V, V, n_0, N_1) , \tag{6}$$

where $Q_{BO}(T, V, V, n_0, N_1)$ is the canonical partition function at the BO level of the system with a volume V (see Fig. *1c*) containing n_0 molecules of the solvent and N_1 molecules of the dissolved substance *1*. It is obvious that the function Q_{MM} defined by the relation*

$$Q_{MM} = \psi/\Xi_0 , \tag{7}$$

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* The method outlined here may also be used in derivation of the expression for the grand partition function at the MM level which is defined by Eq. (*33*) of ref.[5].

where Ξ_0 is the grand partition function of the system containing the pure solvent and defined by the variables (T, V, μ_0), satisfies the relation

$$\beta A = -\ln Q_{\mathrm{MM}} \,. \tag{8}$$

Now let us show that the function Q_{MM} can be expressed in the form

$$Q_{\mathrm{MM}} = (\lambda_1^{3\mathrm{N}_1} N_1!)^{-1} \int_{\mathrm{V}} \exp\left(-\beta \overline{U_{\mathrm{N}_1}}\right) \mathrm{d}\{N_1\} \tag{9}$$

which agrees formally with (*1*) and which entitles us to employ usual formal canonical ensemble procedures also for the MM systems. (However, we must remember[5] that $\overline{U}_{\mathrm{N}_1}$ depends on temperature and pressure P_0). In Eq. (*9*), λ_1 is a function of temperature and pressure P_0 and it is defined by the relation

$$\lambda_1^3 = \Lambda_1^3 / K_1 \,, \tag{10}$$

where K_1 is the equilibrium constant for the transfer of substance *1* from the gaseous phase into its solution in solvent 0 defined by the relation

$$K_1^{-\mathrm{N}_1} = \lim_{\mathrm{v}\to\infty} \frac{Q_{\mathrm{BO}}(T, v, N_0)\, Q_{\mathrm{BO}}(T, v, N_1)}{Q_{\mathrm{BO}}(T, v, v, N_0, N_1)} \,. \tag{11}$$

The quantity $\overline{U}_{\mathrm{N}1}$ is the potential energy of average forces acting among N_1 molecules of substance *1* in the solvent at infinite dilution (solvent-averaged potential energy):

$$\exp\left(-\beta\overline{U_{\mathrm{N}_1}}(\{N_1\})\right) = \lim_{v\to\infty} \frac{v^{\mathrm{N}_1} \int_{\mathrm{v}} \exp\left[-\beta U_{\mathrm{N}_0,\mathrm{N}_1}(\{N_0\}, \{N_1\})\right] \mathrm{d}\{N_0\}}{\int_{\mathrm{v}} \int_{\mathrm{v}} \exp\left[-\beta U_{\mathrm{N}_0,\mathrm{N}_1}(\{N_0\}, \{N_1\})\right] \mathrm{d}\{N_0\}\, \mathrm{d}\{N_1\}} \,. \tag{12}$$

In the limiting cases, quantities (*3*) in Eqs (*11*) and (*12*) remain constant. It holds

$$\int_{\mathrm{v}} \exp\left(-\beta U_{\mathrm{N}_0,\mathrm{N}_1}\right) \mathrm{d}\{N_0\} = \sum_{\mathrm{n}_0 \geqq 0} \binom{N_0}{n_0} \int_{\mathrm{V}} \exp\left(-\beta U_{\mathrm{n}_0,\mathrm{N}_1}\right) \mathrm{d}\{n_0\} \times$$

$$\times \int_{\mathrm{v}-\mathrm{V}} \exp\left(-\beta U_{\mathrm{N}_0-\mathrm{n}_0}\right) \mathrm{d}\{N_0 - n_0\} \,. \tag{13}$$

By inserting from (*13*) into (*12*) and (*9*) and after a rearrangement using (*10*) and (*11*) we obtain

$$Q_{\mathrm{MM}} = \lim_{v \to \infty} \sum_{n_0 \geqq 0} Q_{\mathrm{BO}}(T, V, V, n_0, N_1) \frac{Q_{\mathrm{BO}}(T, v - V, N_0 - n_0)}{Q_{\mathrm{BO}}(T, v, N_0)} =$$

$$= \exp\left(-\beta P_0 V\right) \sum_{n_0 \geqq 0} \exp\left(\beta n_0 \mu_0\right) Q_{\mathrm{BO}}(T, V, V, n_0, N_1) \qquad (14)$$

which is identical with (*7*).

Eq. (*9*) can also be derived extremely simply in a „thermodynamic" manner. The constant K_1 can be defined within the frame of thermodynamics in terms of Helmholtz free energies of systems illustrated in Fig. 1*a*, *b* and *d*. Then by inserting into (*4*), we obtain

$$A = -\beta^{-1} N_1 \ln K_1 + \lim_{v \to \infty} \left[F(T, v, V, N_0, N_1) + \right.$$

$$\left. + F(T, v, N_1) - F(T, v, v, N_0, N_1)\right]. \qquad (15)$$

By inserting functions F of systems (*b*) to (*d*) from Eq. (*2*) into Eq. (*15*) and introducing the function Q_{MM} through relation (*8*), we obtain Eq. (*9*) directly.

Note added in proof: *a*) As far as liquid solutions are concerned, one can find the function A to be comparable to the entire Gibbs free energy rather than to the entire Helmholtz free energy. Thus it is misleading to give this function the name of the latter and we shall call it the McMillan–Mayer free energy instead.

b) To establish the present theory more rigorously we must recognize that the logarithm of the canonical partition function, $Q(T, v, N_0)$, is asymptotically a first order homogeneous function of v and N_0. Then we have for any finite values of V and n_0,

$$\exp\left(\beta P_0 V\right) = \exp\left(\beta n_0 \mu_0\right) \lim_{v, N_0 \to \infty} \frac{Q(T, v, N_0)}{Q(T, v - V, N_0 - n_0)}, \qquad (16)$$

where P_0 and μ_0 are the values of the pressure and the chemical potential at $(T, N_0/v)$.

It is interesting to note that even the most general result of the MM theory, Eq. (*38*) in^2, can easily be obtained from Eqs (*16*) and (*13*), where in this case $N_1 = 0$ and N_0, n_0 and μ_0 are s-component vectors for an s-component system.

REFERENCES

1. Kirkwood J. G.: J. Chem. Phys., *2*, 767 (1934); Chem. Rev. *19*, 275 (1936).
2. McMillan W. G., Mayer J. E.: J. Chem. Phys. *13*, 276 (1945).
3. Hill T. L.: *Statistical Mechanics*. McGraw Hill, New York 1956.
4. Friedman H. L.: *Ionic Solution Theory*, Interscience, New York 1962.
5. Friedman H. L., Dale W. D. T., in the book: *Modern Theoretical Chemistry*, (B. J. Berne, Ed.) Vol. 5. Plenum Press, New York 1977.

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