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On the Quasi-Chemical Theory of Solutions

J. P. Stark[1]

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The classical canonical partition function for a one-dimensional, two-component system is examined for the case of nearest-neighbor interactions. The quasi-chemical model of solid solutions is found to be a natural consequence of the definition of the partition function when one replaces the normal configurational energy with a configurational free energy. Consequently, the quasi-chemical theory may be viewed as a consequence of the definition of the partition function and not as merely a physically pleasing model.

KEY WORDS: Classical partition function; quasi-chemical model; Ising model; nearest-neighbor interactions; one dimension; exact solution; configurational degeneracy.

1. INTRODUCTION

The theoretical description of phase transformations has proven to be one of the most interesting and mathematically difficult aspects of statistical mechanics. As a consequence of the mathematical difficulty, a great number of physically pleasing models have been introduced in the literature. One of the more frequently used models originated with Ising(1) as an attempt to explain ferromagnetism; his model is also often used to explain solid-state segregation and order–disorder phenomena. One recent example is the work of Dunn and McLelann,(2) who use the term "quasi-chemical model" to describe the introduction of a configurational entropy. Excellent reviews(3) are available of the progress with the Ising and other models.

The purpose of this work is to prove that the physical basis for the introduction of configurational entropy as used in the quasi-chemical theory is a direct manifestation of the definition of the partition function and thus is not merely an attractive model: It will be shown that the classical partition function for a two-component, one-dimensional system with nearest-neighbor interactions contains a contribution to the free energy from configurational degeneracy, and consequently, the model is an exact

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[1] Materials Science Laboratory, Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas.

description of physical reality to the degree to which the above approximations are valid.

2. DESCRIPTION OF THE PROBLEM

Consider a system of length L in which N_A A-type atoms and $N - N_A$ B-type atoms are confined. The potential energy is restricted to nearest-neighbor interactions only; however, the exact mathematical form will be left somewhat arbitrary. Obviously, the form of the potential will depend upon the elemental species, e.g., the A–A bond may differ in form from the A–B bond, etc.

The following assumptions are applicable to all interactions, independent of the species involved: (1) The atoms have a impenetrable core of diameter a, i.e., $U_{ij}(r_i - r_j) = \infty$ for $| r_i - r_j | \leqslant a$; a may be considered to be infinitesimal. (2) The potentials are otherwise bounded.

Consequently, the total potential energy of the system must be

$$\begin{aligned} KT\phi &= \sum_{i=1}^{N-1} U_{i,i+1}(r_{i+1} - r_i) \\ &= f(N_{AB}, N, N_A) \end{aligned} \tag{1}$$

where N_{AB} is the number of AB interactions, and the potential is dependent upon concentration, configuration, and interparticle spacing. The canonical ensemble partition function is defined as

$$\begin{gathered} Z = \Lambda_A^{N_A} \Lambda_B^{N-N_A} Q_{N,N_A} / [N_A!(N - N_A)!] \\ \Lambda_i = \{2\pi m_i KT/h^2\}^{1/2}, \qquad Q_{N,N_A} = \int_0^L dr_1 \cdots \int_0^L dr_N \, e^{-\phi} \end{gathered} \tag{2}$$

The hard-core potential of infinitesimal diameter imposes a linear ordering in the system. Consequently, the evaluation of Eq. (2) incorporates all possible arrangements of the atoms; there are $N!$ of them. If one associates the variable r_i with the position of the ith particle in the array and the variable λ with the permutation, Eq. (2) can be expressed as

$$Q_{N,N_A} = \sum_{\{\lambda\}} \int \cdots \int_{0<r_1<r_2 \ldots <r_{N-1}<r_N<L} dr_1 \cdots dr_N \, e^{-\phi(\lambda)} \tag{3}$$

where the sum over λ extends over all $N!$ permutations of the particles.

Now one can prove by induction that the entire volume of phase space is incorporated when Eq. (3) is given in the explicit form

$$Q_{N,N_A} = \sum_{\{\lambda\}} \int_0^L dr_1 \int_{r_1}^L dr_2 \cdots \int_{r_{N-2}}^L dr_{N-1} \int_{r_{N-1}}^L dr_N \, e^{-\phi(\lambda)} \tag{4}$$

With the isothermal–isobaric(3) partition function in mind, consider the Laplace transform of any one of the integrals in Eq. (4):

$$\int_0^\infty e^{-sL} \int_0^L dr_1 \cdots \int_{r_{N-1}}^L dr_N \, e^{-\phi(\lambda)} \, dL$$

$$= \int_0^\infty dr_1 \int_{r_1}^\infty dr_2 \cdots \int_{r_{N-1}}^\infty dr_N \int_{r_N}^\infty e^{-sL} e^{-\phi(\lambda)} \, dL \tag{5}$$

Consider the following set of reduced coordinates:

$$r_i - r_{i-1} = x_i\,, \quad i = 2,\ldots, N; \qquad r_1 = x_1$$

The Jacobian for the transformation is easily shown to be unity,

$$\partial r_m/\partial x_n = \begin{cases} 1 & \text{if} \quad m \geqslant n \\ 0 & \text{if} \quad m < n \end{cases}$$

Thus,

$$\partial(r_1\,,\ldots, r_N)/\partial(x_1\,,\ldots, x_N)$$

is the determinant of a lower triangular matrix whose nonzero elements are unity. Expansion by minors easily proves the assertion. The use of these coordinates in Eq. (5) leads to the following:

$$Q_{N,N_A} = \sum_{\{\lambda\}} \frac{1}{S} \int_0^\infty dx_1 \int_0^\infty dx_2 \cdots \int_0^\infty dx_N \exp - \left\{ S \sum_{i=1}^{N} x_i + \phi(x_1\,,\ldots, x_N\,, \lambda) \right\} \tag{6}$$

Now, since

$$\phi(x_1\,,\ldots, x_N\,, \lambda) = (1/KT) \sum_i U(x_i\,, \lambda)$$

from the definition of the potential energy, Eq. (6) can be written in the following form:

$$\varDelta(N, s, T) = L[Q_{N,NA}] = \sum_{\{\lambda\}} \left[\prod_{i=1}^{N-1} \psi_i(\lambda)/s^2 \right] \tag{7}$$

$$\psi_i = \int_0^\infty dx_i \, e^{-sx_i} e^{-U_{ii+1}/KT} \tag{8}$$

Upon inserting $s = p/KT$ into Eqs. (7) and (8), one can recognize the fact that $\varDelta(N, P, T) = \exp[-G(N, p, T)/KT]$, where $\varDelta$ is the isothermal–isobaric partition function and G is the Gibbs free energy excluding the $\varLambda_i$ and factorial terms, Eq. (2).

Consider the following modification of Eq. (7):

$$\varDelta(N, p, T) = (p/KT)^{N-3} \sum_{\{\lambda\}} \prod_{i=1}^{N-1} (KT/p)\, \psi_i \tag{9}$$

From Laplace transform theory,

$$(KT/p)\, \psi_i = \int_0^\infty e^{-px_i/KT} \, dx_i \int_0^{x_i} e^{-U_{ii+1}/KT} \, dx \tag{10}$$

Equation (10) is the transform of a single particle in a volume x_i. The particle interacts with one "wall" of its container with a potential $U_{i,i+1}$. From prior discussion, the source of this potential is a neighboring particle in a particular configuration. Such a Laplace transform as in Eq. (10) has in the past been interpreted as the negative exponential of a "chemical potential" divided by $KT^{(3-5)}$. Such an interpretation is of interest here. Furthermore, Eq. (9) and (10) may be interpreted as the isothermal–isobaric partition function of the system; the sum over all of the permutations carries the interpretation of configurational entropy.

If one relables

$$(KT/p)\,\psi_i = e^{-\mu_{0i}/KT}$$

Eq. (9) takes the form

$$\varDelta(N, p, T) = (p/KT)^{N-3} \sum_{\{\lambda\}} \prod_{i=1}^{N-1} \exp[-\mu_{0i}(\lambda)/KT] \tag{11}$$

With the above interpretations, Eq. (11) carries the configurational entropy of the Ising model and an energy of particle interaction given by $\mu_{0i}(\lambda)$. This energy takes the place of the usual potential energy as used in the Ising model or quasi-chemical model.

Phase transformations in one-component, one-dimensional systems have been discussed elsewhere.(3–6) It is known that a phase transformation of the van der Waals type is possible in one dimension.(5) Fluctuations can be discussed on the basis of continuity of the equation of state.(7) Consequently, with the exception of the two-phase region of the van der Waals gas, the system properties are well-behaved. As an example, upon setting the potential equal to zero and using Eqs. (2), (10), and (11), one can easily attain the free energy of the two-component ideal gas.

Now, the two- or three-dimensional system presents a different problem altogether. No two- or three-dimensional system has been studied exactly. The majority of the knowledge about phase transformations comes from the cluster expansions(3) or the use of models such as Ising's. The two-dimensional Ising model is known to have a first-order phase change, a critical point, etc. The evaluation of the partition function for two- or three-dimensional systems is usually approximate, involving the exclusion of a portion of phase space.

In a two-component system, such an exclusion leads to the quasi-chemical theory, as the density is usually restricted to the range for solids. Since an exact evaluation has not been accomplished, the physical validity of the model remains open to question except for the one-dimensional system treated here. From this work, the quasi-chemical theory is an exact manifestation of the one-dimensional partition function when the interactions are restricted to nearest-neighbor interactions and the configurational energy is replaced by a configurational free energy.

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