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Comparison between Improved Onno's Free Volume Approximation in Cell Theory and Significant Structure Theory of Liquid

by

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액체의 Significant Structure Theory 와 Onno's Cell Theory 와의 이론적 비교

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요 약

액체에 대한 Significant Structure Theory 와 자유부피계산시 수정된 Onno 근사법을 사용한 Cell Theory 와의 통계역학적 분배함수에 대하여 이론적으로 비교 논의하였다.

Abstract

The statistical mechanical basis of the significant structure theory was compared and discussed with the improved Onno's approximation in the cell theory.

So far, the significant structure theory of liquid⁽¹⁾ has been the most widely applied of the various theories of liquids⁽²⁾. It yields excellent results⁽³⁾ for the prediction of thermodynamic, transport, surface, and dielectric properties of various liquids ranging from simple monoatomic liquids to complicated liquid mixtures. Among the advantages of the significant structure theory are its mathematical simplicity and its wide application to the liquid state. One of the defects of this theory is that it has not been derived from an exact partition function by any mathematically well-defined approximations, but it is a result of intuition. On the contrary, the cell theory has been given a firm statistical mechanical foundation by Kirkwood⁽⁴⁾. It is instructive to find out the relation between those two models. Here, the author will discuss the analogy between the improved Onno's approximation ⁽⁵⁾,⁽⁶⁾ in cell theory and the significant structure theory; and also explain that the latter gives better agreement with experiment than the former.

The partition function of the cell theory for an assembly of N identical monoatomic molecules randomly distributed over L lattice cells subject to the conditions of $N \leq L$ is given by

$$f_{C\cdot T}=\left[\frac{L!}{N!(L-N)!}\right]\lambda^{-3N}\times$$

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$$\exp\left[-yNz\phi(0)/2kT\right]\left[V_f\right]^N \tag{1}$$

Where $y=\frac{N}{L}$ is the average function of occupied nearest neighbor cells, $\lambda^{-1}=\left(\frac{2\pi^m kT}{h_2}\right)^{\frac{3}{2}}$, Z is the coordination number, $\phi(0)$ is the pair potential energy of a molecule at a distance equal to the equilibrium distance between molecules, and the free volume, V_f is defined as

$$V_f=\int_{cell}\exp\left[-yz\frac{\phi(r)-\phi(o)}{kT}\right]4\pi r^2 dr \tag{2}$$

Here γ is the distance from the potential minimum in the cell to a point γ in the cell, and $\phi(r)$ is the average pair potential energy at γ.

Following the Ree, Ree and Eyring's approximation (6) for free volume (improved Onno's approximation), we can express V_f as follows:

$$V_f=(V_o g)^y (V_g)^{1-y} \tag{3}$$

Where the factor g is the Eyring, s degeneracy factor, and V_o is the free volume at $y=1$ while V_g is the free volume at $y=0$.

Substituting of Eq. (3) into Eq. (1) and rearranging yields

$$f_{C\cdot T}=(\lambda^{-3}V_o g\ \exp(-z\phi(o)/2kT))^{yN}$$
$$\times(\lambda^{-3}V_g)^{(1-y)N}\ \frac{L!}{N!(L-N)!} \tag{4}$$

The first parentheses in Eq. (4) represent the classical solid partition function, while the second parentheses contain the partition function of molecules in an ideal gas occupying the average free volume v_g.

Now, substituting $y=\frac{N}{L}=\frac{V_s}{V}$ into Eq. (4), and using the notation of f_s for solid partition function, and of f_g for ideal gas partition function, and using Stirling's approximation we obtain

$$f_{C\cdot T}=(f_s g)^{N\frac{V_s}{V}}(f_g)^{N\frac{V-V_s}{V}}$$
$$\times\left(\frac{V^V}{V_s^{V_s}(V-V_s)^{(V-V_s)}}\right)^{N/V_s} \tag{5}$$

According to the significant structure theory, the partition function is given by

$$f_{s\cdot s}=(f_s g)^{N\frac{V_s}{V}}(f_g)^{N\frac{V-V_s}{V}}\Big/\left(N\left(\frac{V-V_s}{V}\right)\right)! \tag{6}$$

Here V is the molar volume of the liquid, V_s is the molar volume of the solid at the melting point.

The significant structure theory has several mathematical expressions to represent "solid like" partition function. Originally, f_s was represented by an Einstein Oscillator(3) for ordinary liquid and by a Debye Oscillator(3) for quantum liquid. Later, this model was also represented by the Lennard-Jones and Devonshire solid partition function to eliminate several disadvantages(6) of the original expressions.

The Eqs. (5) and (7) are of the same form, and only differ in the combinatorial factor. This difference is due to the assumption made in the formulation of the partition function. The significant structure theory assumes that some molecules possess solid like and some possess gas like degrees of freedom, and the combinatorial factor was introduced for the indistinguishability of gas like molecules. On the otherhand, in the cell theory the combinatorial factor was introduced to account for the random distribution of N particles in L cells.

Henderson(7) applied the $f_{s\cdot s}$ to hard sphere molecules with good success, while Ree et al(6) obtained good results by using improved Onno's approximation in the cell theory.

From Eq. (6) and (7), we can easily see that the calculated results for thermodynamic quantities are the same for both theories, but differ in volume dependent properties as PV/NkT or P because of combinatorial factor. The significant structure theory gives better results(6),(7) for the calculation of PV/NkT and P.

It is very natural to think of the fact that f_{ss} gives the limiting value of an ideal gas as V goes to infinity.

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