

Equation of State of Classical Electron Gas

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In a recent paper by Ichikawa,¹⁾ the long range correlation effects of Coulomb interaction are shown to increase the free energy of the Debye-Hückel limiting law by 22%. If this is true, a similar conclusion may be drawn by the usual cluster expansion method, without recourse to the collective coordinate representation. Although Mayer²⁾ has carried out the order estimation of the contributions of complicated clusters other than ring clusters and shown that they are of higher orders, his conclusion is not fully justified in the case of electron gas, since some of terms considered by him diverge for purely Coulomb interactions without hard cores. Thus it will be worth while to investigate the higher order terms in a systematic way, free from the divergence difficulties. We wish here to present an exact evaluation of the free energy term which is expected to be of the next higher orders than the lowest one, i. e., the Debye-Hückel law.

If we define the function $S(\rho)$ by

$$S(\rho) = \sum_{n=1}^{\infty} \frac{\beta_n}{n+1} \rho^{n+1} \quad (1)$$

with β_n the irreducible cluster integral and ρ the particle number density, the equation of state, the Helmholtz free

energy, etc., are easily derived from this function. According to Mayer,²⁾ $S(\rho)$ is expanded as follows,

$$S(\rho) = S_0(\rho) + \sum_{m=2}^{\infty} \frac{\rho^m}{m!} \frac{1}{V} \times \int \sum'_{m \geq i > j \geq 1} \Pi \frac{[-\beta q_{ij}]^{k_{ij}}}{(k_{ij})!} d(m). \quad (2)$$

Here the $S_0(\rho)$ is the contribution of the ring clusters and \sum' implies the summation over prototype graphs with m branch points,³⁾ $d(m)$ the integration over the branch points and k_{ij} the number of bonds between the branch points i and j . The potential function q_{ij} is given by

$$q(r) = \varepsilon^2 e^{-\gamma r} / r \quad (3)$$

in the case of Coulomb interaction. $S_0(\rho)$ is known to lead to the Debye-Hückel law, i. e.,

$$S_0(\rho) / \rho = \lambda / 3 \quad (4)$$

with $\lambda = 2\sqrt{\pi} \beta^{3/2} \rho^{1/2} \varepsilon^3$ which is the non-dimensional parameter characteristic of the classical electron gas. If we further consider the graphs $m=2$ in eq. (2), each term is shown to be divergent. However, if *all* the terms $m=2$, i. e., *all* the graphs of watermelon type,^{4),5)} are summed up, the result is no longer divergent and is given by

$$\frac{S_2(\rho)}{\rho} = 2\pi\rho \int_0^{\infty} \left[e^{-\beta q(r)} - 1 + \beta q(r) - \frac{\beta^2 q^2(r)}{2} \right] r^2 dr.$$

The similar expression was already derived by Yukhnovsky⁶⁾ from another point of view. An analytical evaluation of the integral leads to

$$\begin{aligned} S_2(\rho) / \rho &= 1/2 - \lambda/8 - \lambda^2/6 \\ &\times \sum_{n=0}^{\infty} \sum_{r=0}^n (-1)^r / r!(n-r)! \\ &\times \lambda^{n/2} (r+1)^{n/2} \\ &\times [2/\lambda(r+1) \cdot K_{|n-2|}(2\sqrt{\lambda(r+1)}) \\ &+ 2/(r+1)\sqrt{\lambda(r+1)} \\ &\times K_{|n-3|}(2\sqrt{\lambda(r+1)})], \end{aligned}$$

where $K_n(x)$ is the Neumann function of purely imaginary argument. An explicit calculation yields

$$\begin{aligned} S_2(\rho) / \rho &= \lambda^2(1/12 \cdot \log 3 + \gamma/6 - 11/72) \\ &+ \lambda^2 \log \lambda / 12 + O(\lambda^3) \end{aligned}$$

where γ is Euler's constant. Thus the contribution of graphs with 2 branch points never leads to the term of the order λ and turns out to be of higher orders than that of $S_0(\rho)$. It seems that the more complicated graphs do not lead to the term of the order λ and the Debye-Hückel law is exact with respect to this order for the purely Coulomb interactions as well as for the one with hard cores. The detail of this article will soon be published.

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