Strong Coupling Perturbation Theory of Ionic Fluids

Soft Matter Laboratory, Kochi University of Technology　　Hiroshi Frusawa [1]

ある種のイオン性流体（イミダゾール誘導体などのイオン性溶融体、脱塩されたコロイド分散系など）では、デバイヒュッケル近似（弱結合近似）の適用範囲を超えた強いクーロン相互作用が働く。すなわち、高濃度 (a 小)・高荷電（$Z >> 1$）のために、Bjerrum 長 l_B とイオン間平均距離 a の比に比例するクーロン強度の指標 $\Gamma = z^2 l_B/a$ は、容易に強結合条件 $\Gamma >> 1$ を満たす。ところがこの強結合系においてすら、近距離の強相関性を相互作用に組み入れるだけで、デバイヒュッケル理論 ($\Gamma << 1$ の近似) が良く機能するのである。この背景にある物理は何か？— それを探るために、強結合極限周りでの摂動理論を開発し、修正デバイヒュッケル理論を再導出した。

1 Modified Debye–Hückel Theories

Let us consider the simplest model of ionic fluids, the one component plasma (OCP) which consists of N particles with electric charge Ze embedded in a neutralizing background of its volume Ω. As is well known, the OCP is characterized by the Coulomb-coupling constant $\Gamma = Z^2e^2/(4\pi\epsilon k_B T a)$ and the Coulomb interaction with large coupling constant ($\Gamma >> 1$) has been referred to as "strong coupling", where ϵ is the dielectric permittivity, k_BT the thermal energy, and a the Wigner-Seitz (WS) radius defined by $(4\pi a^3/3)N = \Omega$.

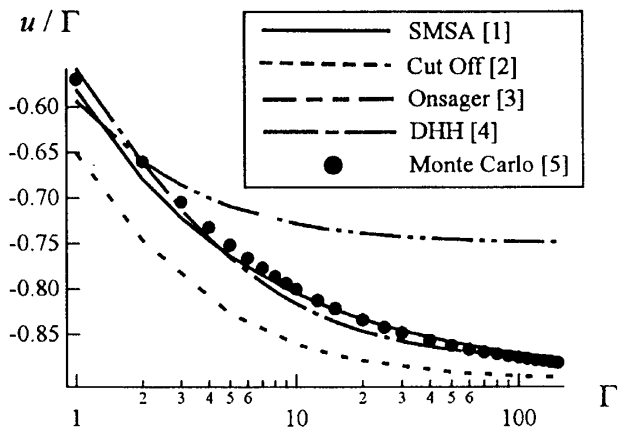
In the strong coupling regime, modified Debye–Hückel (mDH) theories work well as shown in the figure where simulation results of the excess internal energy per ion in the k_BT-unit, $u \equiv U/(Nk_BT)$, is compared with various types of mDH theories [1–4].

How is then the original Debye–Hückel modified? To see this, we give the mDH–forms of u:

$$\begin{aligned} u_{\mathrm{mDH}} &= u_\delta + \frac{\Gamma}{2}\int_{\mathbf{q}} w_q \left(\frac{1}{1+\overline{\rho}\,\Gamma\, w_q} - 1 \right) \\ u_\delta &= \frac{\overline{\rho}\,\Gamma}{2}\int_{\mathbf{r}} h(\mathbf{r})\,\{\, v(\mathbf{r}) - w(\mathbf{r})\,\} \end{aligned} \tag{1}$$

where $w(\mathbf{r})$ is an arbitrary interaction potential which varies according to the models of mDH, $\overline{\rho} = N/\Omega$ is the smeared density, $h(\mathbf{r})$ is the total correlation function expressed by the Fourier–transform of the direct correlation function c_q as $h_q = \overline{\rho}c_q/(1-\overline{\rho}c_q)$, and $v(\mathbf{r}) = 1/|\mathbf{r}|$. Note that the equality $w_q = v_q$ recovers the original Debye-Hückel theory, and that eq. (1) with the replacement, $(1+\overline{\rho}\,\Gamma\, w_q)^{-1} \to (1-\overline{\rho}\,\Gamma\, c_q)^{-1}$, is not an approximation but the identity.

[1] E-mail: frusawa.hiroshi@kochi-tech.ac.jp



2 Perturbation around the solution in the strong coupling limit

Expressing the partition function of strongly–coupled ions by appropriate functional, the saddle–point path satisfying local electrical neutrality becomes exact in the strong coupling limit (SCL). In other words, the mimic SCL system with the w–interactions forbids the emergence of electrostatic interaction as shown by the previous work [6] in a strict but roundabout manner. In the present scheme, perturbation of the finite coupling is considered by the following fluctuation around the SCL:

$$\int_{\phi} e^{-\Delta\mathcal{S}\{\phi\}} = \mathcal{N}^{-1} \int_{\phi,c} \exp\left(-\frac{1}{2}\int_{\mathbf{r},\mathbf{r}'} c(\mathbf{r})w(\mathbf{r}-\mathbf{r}')c(\mathbf{r}') - \frac{\overline{\rho}}{2}\int_{\mathbf{r}} \phi^2(\mathbf{r}) + i\,\frac{c\cdot\phi}{\sqrt{\Gamma}}\right) \tag{2}$$

where $\mathcal{N} = \det(2\pi/w)^{1/2}$. Integrating out the c– and ϕ– fields in eq. (2) leads to the mDH term, the second in the first line of eq. (1). While the weak coupling DH theory is valid due to the predominance of linear c–ϕ coupling, the strong coupling mDH theories are available because the c–ϕ coupling is the perturbation to the independent fluctuations of electrostatic interaction (the first term in the above exponent) and entropic potential (the second), which is the underlying physics of mDH theories.

References

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