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<th>Strong Coupling Perturbation Theory of Ionic Fluids (poster presentation, Soft Matter as Structured Materials)</th>
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<tr>
<td>Author(s)</td>
<td>Frusawa, Hiroshi</td>
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<tr>
<td>Citation</td>
<td>物性研究 京都大学学術情報リポジトリ 科学技術 84(6): 952-953</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2005-09-20</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/110283">http://hdl.handle.net/2433/110283</a></td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
<tr>
<td>Institution</td>
<td>Kyoto University</td>
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Strong Coupling Perturbation Theory of Ionic Fluids

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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 $\Omega$. As is well known, the OCP is characterized by the Coulomb-coupling constant $\Gamma = Z^2e^2/(4\pi\epsilon k_BT a)$ and the Coulomb interaction with large coupling constant ($\Gamma \gg 1$) has been referred to as "strong coupling", where $\epsilon$ is the dielectric permittivity, $k_BT$ the thermal energy, and $a$ the Wigner-Seitz (WS) radius defined by $(4\pi a^3/3)\Omega = N$.

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, $u \equiv U/(N k_BT)$, 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 $u$:

$$u_{\text{mDH}} = u_\delta + \frac{\Gamma}{2} \int w_q \left( \frac{1}{1 + \bar{\rho}_q} - 1 \right)$$
$$u_\delta = \frac{\bar{\rho} \Gamma}{2} \int h(r) \{ v(r) - w(r) \}$$

(1)

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

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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 $u$–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:

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

where $\mathcal{N} = \det(2\pi/w)^{1/2}$. Integrating out the $c$– and $\phi$– 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 $c$–$\phi$ coupling, the strong coupling mDH theories are available because the $c$–$\phi$ 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