摘　要

溶液中离子的关联效应可以描述离子间的相互作用，包括尺寸效应和静电关联作用等。在溶液体系模拟中，它可以对离子浓度、静电势能以及其他一些相关物理性质现象等给出合理有效的实验预测。在本文中，我们介绍溶液中的离子关联效应，将其加入到传统连续模型中，通过模型分析和数值模拟研究其对溶剂化能、电流、浓度分布以及离子选择性的影响与作用。

尺寸修正 Poisson-Nernst-Planck (SMPNP) 或尺寸修正 Poisson-Boltzmann (SMPB) 模型在传统连续模型中加入了尺寸效应。分析表明在平衡态下, 尺寸修正模型中根据自由能泛函推导出的溶剂化能存在一个简单的近似计算公式，与 Poisson-Boltzmann (PB) 模型中广泛应用的近似公式完全相同。模拟结果发现, 加入尺寸效应后溶剂化能的绝对值和电流都会减小 (实际溶剂化能值升高)。溶剂化能的近似计算与准确计算结果相差不大，因此尺寸效应对溶剂化能的影响主要体现在近似计算部分；对电流各部分的数值结果表示其降低主要体现在电场驱动项。

我们从统计力学出发新导出了一个局域近似的三维 LHSPNP 模型。在自由能泛函中增加超额 Helmholtz 自由能,结合密度泛函理论 (DFT) ,运用 Rosenfeld 的 FMT 表示硬球之间的排斥作用，并对积分形式的硬球超额化学势进行局域近似就得到简化的 LHSPNP 模型。在均匀分布的单组分溶液中，通过状态方程的研究发现，FMT 可以成功预测前三项维里系数，推导得出的 LHS 模型能够精确给出前两项，而 SMPNP 模型则只能精确确定第一项。对带电球形粒子的模拟结果表明，LHSPNP 和 SMPNP 的结果在很多情形下都比较接近，但是与传统连续模型的结果相差很大。

在尺寸修正模型和 LHSPNP 模型的数值计算方面, 我们将电势分解为三部分加和处理与固定电荷对应的 Dirac-delta 函数项, 用有限元方法和 Gummel 方法对耦合偏微分方程迭代求解，结合并行自适应有限元程序包 PHG 对大规模计算进行并行加快计算速度。同时为了保证收敛性，在迭代过程中加入对电势和浓度的松弛算法。

在平板、圆柱和球形对称构型中，FMT 及 MFMT 中相应的加权密度和硬

球超额化学势表达式中的积分都可以进行简化计算，对此我们给出了严格的推导。在平衡态下圆柱构型中，我们结合 Poisson 方程，MFMT 和静电关联作用模拟离子分布，研究其中的离子选择性。根据对称性，电势和浓度都只与一个自变量即到中轴的径向距离有关，此时 Poisson 方程可以约化为常微分方程，结合平衡态下浓度的表达式进行耦合求解。我们发现对于只有尺寸差异的两种反离子，在圆柱半径小的时候尺寸大的离子选择性通过的机会更大，而圆柱半径大时则恰恰相反。

关键词： 离子关联效应，尺寸修正 PNP 模型，密度泛函理论，静电关联作用，溶剂化能，选择性通透

Abstract

Ion correlation in solution, including size effects, electrostatic correlation, etc. can describe the interactions between ions. It provides physically reasonable simulation results for ion concentrations, electrostatic potentials and some other physical properties and phenomena. In this paper, we investigate the ion correlation in solution, incorporate it into the traditional continuum model, and study its effects on solvation energy, ion current, ion concentrations and ion selectivity.

In the size modified Poisson-Nernst-Planck (SMPNP) or size modifie
Boltzmann (SMPB) model, the ionic size effects are incorporated into the traditional continuum model. At equilibrium state, the solvation energy in the size modified model has a simple approximate expression, which is exactly the same as the widely used one in Poisson-Boltzmann (PB) community. Numerical results indicate that the size effects tend to negate the solvation effe
to a reduced ion current. The diff
results of solvation energy is small, so the size eff
originates from the approximation part. For ion current, the decrease is mainly due to the electrostatic drift component.

Three dimensional local hard sphere Poisson-Nernst-Planck (LHSPNP) model is generated on the basis of statistical mechanics by considering the excess Helmholtz free energy and incorporating density functional theory (DFT). Rosenfeld's fundamental measure theory (FMT) is employed to present the hard sphere repulsions and the excess chemical potential from hard sphere interactions in integral form is locally approximated to get the final local hard sphere (LHS) model. For the equation of state in one component homogeneous fluid, FMT can predict the first three virial coeffic
accurately, but the SMPNP can only give the first term accurately. In a charged spherical system, it is found that the results of LHSPNP and SMPNP are close to each other, but are quite different from the PB results.

For numerical calculation in the SMPNP and LHSPNP model, the potential is devided into three parts to deal with the Dirac-delta functional resulted from the fi
Gummel method to iteratively solve the coupled partial differential equations, and use the parallel adaptive finite element package PHG to accelerate the calculation. To obtain converged results, relaxation of potential and concentration is implemented during the iterations.

In symmetric geometries of planar, cylindrical and spherical systems, ion concentration only depends on one variable, and thus the weighted densities in FMT and the corresponding excess hard sphere chemical potential can be simplifi
the ion selectivity in a charged cylindrical geometry by incorporating the modifi
FMT and electrostatic correlations into the Poisson equation. According to the symmetry, the potential and concentrations only depend on the radial distance to the center of the cylinder, and the three dimensional Poisson equation can be reduced to an ordinary differential equation. By coupling the expression of equilibrium concentration, the potential and concentration can be solved. It is found that for two counterion species with the only difference in radius, the cylindrical pore with small radius has high ion selectivity while the pore with large radius is with low ion selectivity.

Keywords: Ion correlation, Size modified PNP model, Density functional theory, Electrostatic correlation, Solvation energy, Ion selectivity