Multiscale coarse-grained simulations of ionic liquids: comparison of three approaches to derive effective potentials

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1 The iterative Boltzmann Inversion method

Boltzmann Inversion method (BI) is the simplest method one can use to obtain coarse-grained potentials[1]. BI is structure-based and only requires positions of atoms. It is mostly used for bonded potentials, such as bonds, angles, and torsions. The idea of BI stems from the fact that in a canonical ensemble independent degrees of freedom q obey the Boltzmann distribution, *i.e.*:

$$P(q) = Z^{-1} e^{-\beta U(q)}, \qquad (1)$$

where $Z = \int e^{-\beta U(q)} dq$ is the partition function, and $\beta = 1/k_B T$. Once $P(q)$ is known, one can invert Eq. 1 and obtain the coarse-grained potential, which, in this case, is a potential of mean force:

$$U(q) = -k_B T \ln P(q). \qquad (2)$$

Note that the normalization factor Z is not important since it would only enter the coarse-grained potential $U(q)$ as an irrelevant additive constant.

In practice, $P(q)$ is computed from the trajectory of the reference system, which is sampled either by Monte Carlo, molecular dynamics, stochastic dynamics, or any other integrator that ensures a canonical distribution of states.

Since the goal of the coarse-grained model is to reproduce the distribution functions of the reference system as accurately as possible, one can also iteratively refine the coarse-grained potentials using some numerical scheme. Hence the iterative Boltzmann Inversion (IBI)[2,3] is a natural extension of the BI method.

In the IBI method, the coarse-grained potentials are refined

according to the following scheme:

$$U^{(n+1)} = U^{(n)} + \Delta U^{(n)}, \qquad (3)$$

$$\Delta U^{(n)} = k_B T \ln \frac{P^{(n)}}{P^{ref}} = U_{PMF}^{ref} - U_{PMF}^{(n)}. \qquad (4)$$

One can easily see that convergence is reached as soon as the distribution function $P^{(n)}$ matches the reference distribution function P^{ref}, or, in other words, the potential of mean force, $U_{PMF}^{(n)}$ converges to the reference potential of mean force.

2 The Newton Inversion method

The Newton Inversion method (NI) is another iterative procedure that refines the coarse-grained potentials until the coarse-grained model reproduces a set of reference distribution functions. It is very similar to IBI method except that the update of the potential, ΔU, is calculated using rigorous thermodynamic arguments[4,5].

Herein we briefly recapitulate the more compact version for nonbonded interactions. The primary idea of NI is to express the potential update ΔU in a thermodynamically consistent way in terms of measurable statistical properties, such as the radial distribution function $g(r)$. Considering a simple system of identical particles interacting through a pair potential. The corresponding interaction Hamiltonian is given as

$$H = \sum_{i,j} U(r_{ij}), \qquad (5)$$

where $U(r_{ij})$ is the pair potential. Assuming that all interactions depend only on the relative distance, r_{ij}, between particles i and j. Assume further that this potential is short-ranged, *i.e.*, $U(r_{ij}) = 0$, if $r_{ij} \geq r_{cut}$. With given radial distribution function g(r), one can construct the corresponding interaction potential $U(r_{ij})$.

Initially, one can apply a grid approximation to digitalize the Hamiltonian. By tabulating the potential $U(r)$ on a grid

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of M points with $r_\alpha = \alpha \Delta r$, where $\alpha = 0, 1, \cdots, M$, and $\Delta r = r_{cut}/M$ is the grid spacing, the Hamiltonian can be rewritten as

$$H = \sum_\alpha U_\alpha S_\alpha, \tag{6}$$

where S_α is the number of particle pairs with interparticle distances $r_{ij} = r_\alpha$, which correspond to the tabulated value of the potential U_α.

On one hand, the average value of S_α serves as an estimator of the radial distribution function g(r)

$$\langle S_\alpha \rangle = \frac{N(N-1)}{2} \frac{4\pi r_\alpha^2 \Delta r}{V} g(r_\alpha), \tag{7}$$

where N is the number of atoms in the system, and V is the total volume of the system.

On the other hand, $\langle S_\alpha \rangle$ is a function of the potential U_α, and can be expanded in a Taylor series with respect to small perturbations of U_α, ΔU_α

$$\Delta \langle S_\alpha \rangle = \sum_\gamma \frac{\partial \langle S_\alpha \rangle}{\partial U_\gamma} \Delta U_\gamma + O(\Delta U^2). \tag{8}$$

The derivatives $\frac{\partial \langle S_\alpha \rangle}{\partial U_\gamma}$ can be obtained by using the chain rule

$$\begin{aligned} A_{\alpha\gamma} &= \frac{\partial \langle S_\alpha \rangle}{\partial U_\gamma} \\ &= \frac{\partial}{\partial U_\gamma} \frac{\int S_\alpha(q) e^{-\beta \sum_\lambda U_\lambda S_\lambda(q)} dq}{\int e^{-\beta \sum_\lambda U_\lambda S_\lambda(q)} dq} \\ &= \beta \left(\langle S_\alpha \rangle \langle S_\gamma \rangle - \langle S_\alpha S_\gamma \rangle \right). \end{aligned} \tag{9}$$

Let $U_\alpha^{(0)}$ be some trial potential such as the corresponding potential of mean force

$$U_\alpha^{(0)} = -k_B T \ln g(r_\alpha). \tag{10}$$

Then using standard Monte Carlo simulations, one can evaluate the averages $\langle S_\alpha \rangle$ and their deviations from the reference values S_α^*, defined from given g(r)

$$\Delta \langle S_\alpha \rangle^{(0)} = \langle S_\alpha \rangle^{(0)} - S_\alpha^*. \tag{11}$$

By solving a set of linear Eqs. 8 with the coefficients defined by Eq. 9, and omitting the terms $O(\Delta U^2)$, we can obtain the correction to potential $\Delta U_\alpha^{(0)}$, Then the procedure is repeated with the new potential

$$U_\alpha^{(1)} = U_\alpha^{(0)} + \Delta U_\alpha^{(0)}, \tag{12}$$

until convergence is achieved. The whole procedure is similar to a solution of a multidimensional non-linear equation using the Newton–Rhapson method.

References

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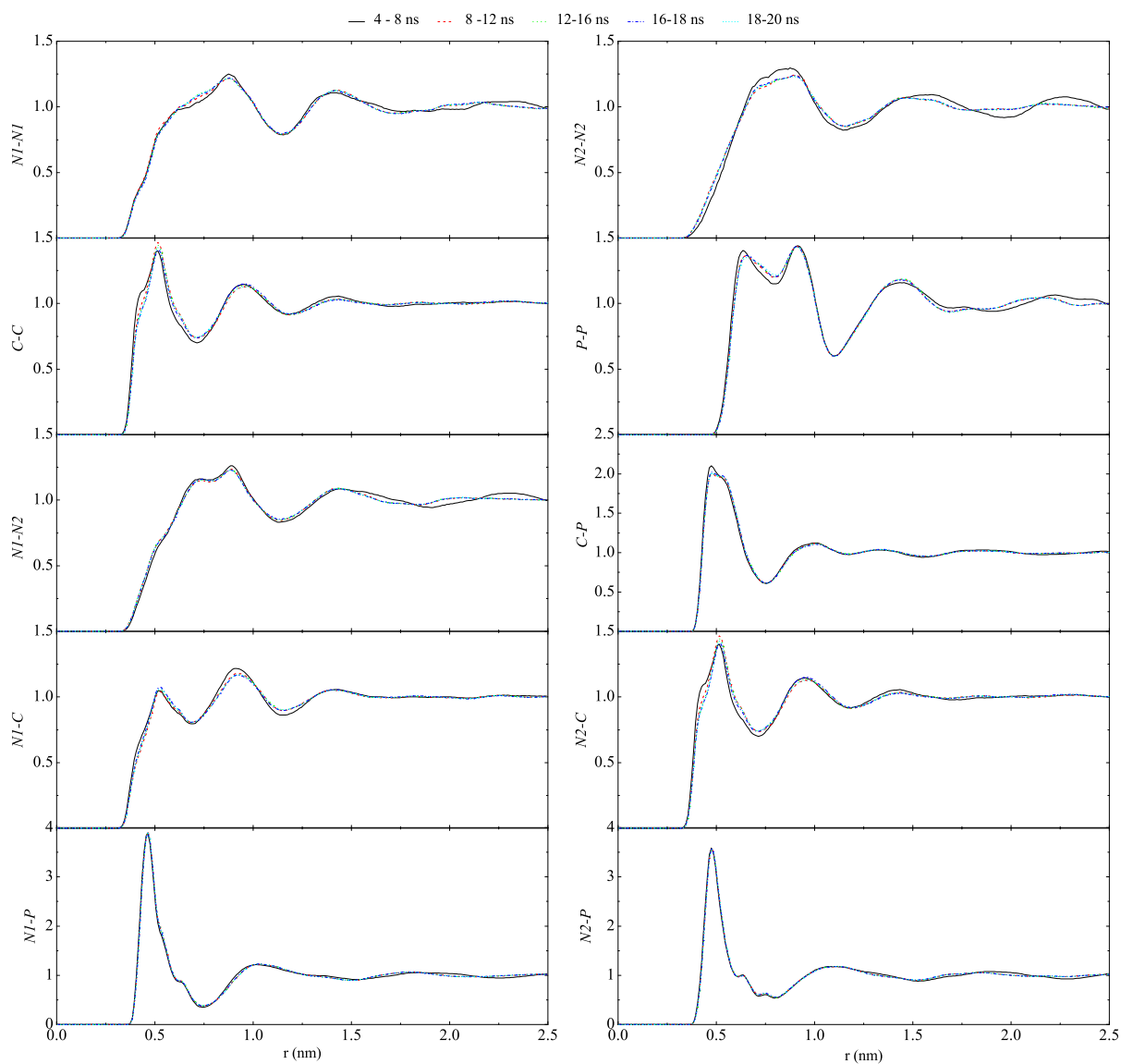5 A. P. Lyubartsev, A. Mirzoev, L. J. Chen and A. Laaksonen, *Faraday Discuss.*, 2009, **144**, 43–56.

Fig. 1 The evolutions of typical intermolecular RDFs calculated from all-atomistic molecular dynamic simulations at different simulation periods.
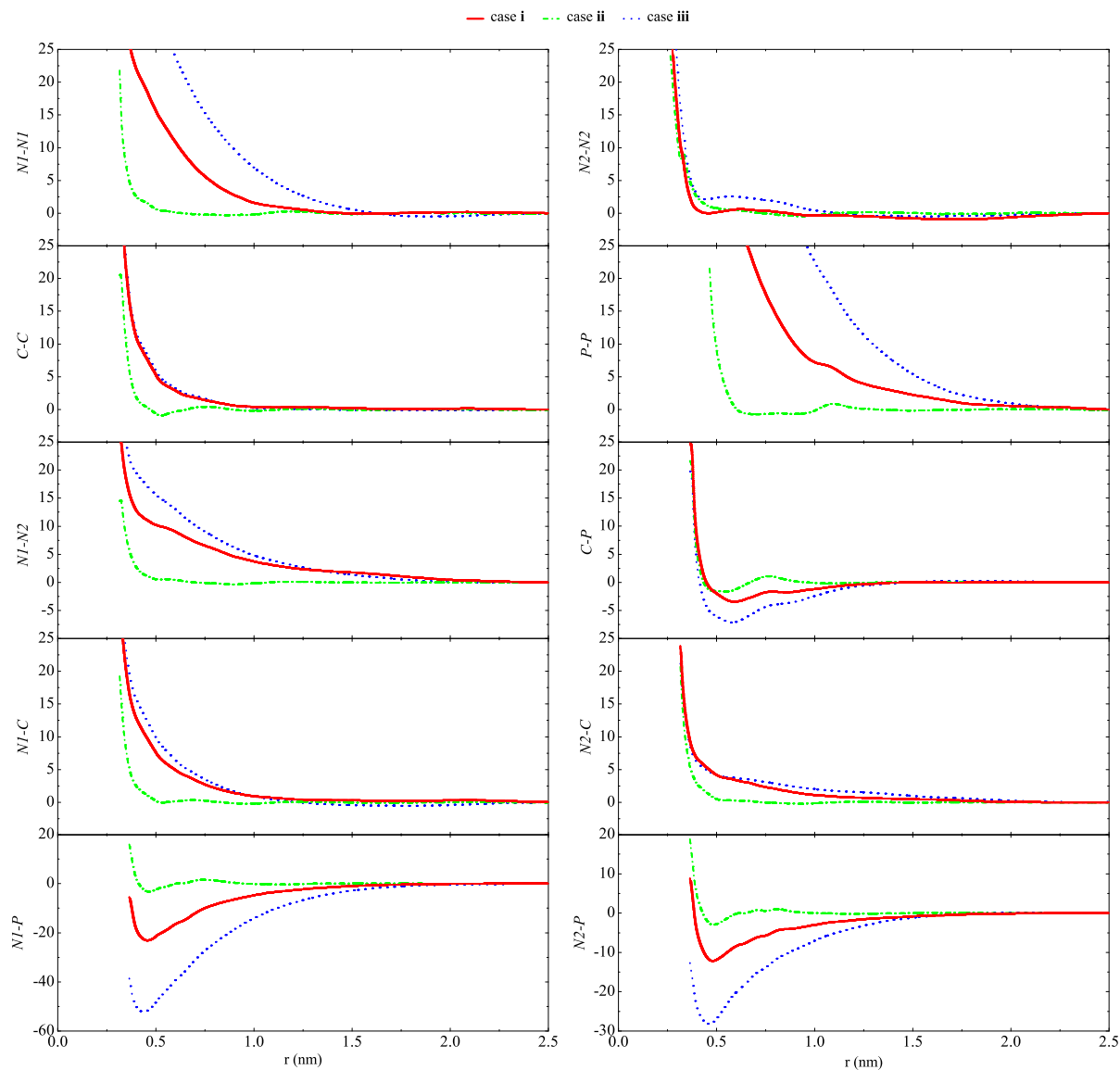
Fig. 2 The comparison of three sets of intermolecular effective potentials obtained from NI and IBI iteration procedures with different treatment fashion of electrostatic interactions. The unit of the intermolecular effective potentials is kJ/mol.
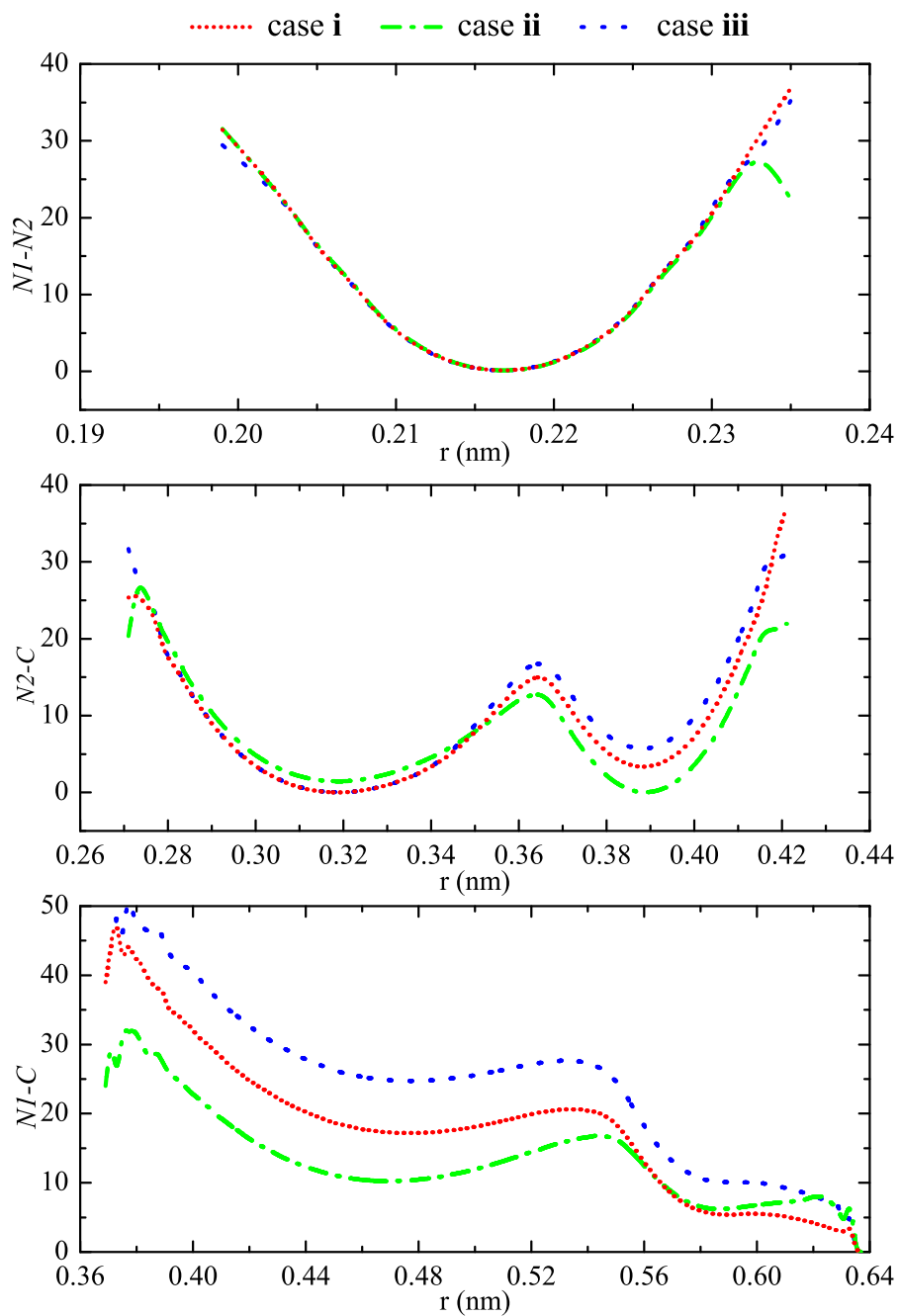
Fig. 3 The comparison of three sets of intramolecular effective potentials obtained from NI and IBI iteration procedures with different treatment fashion of electrostatic interactions. The unit of the intramolecular effective potentials is kJ/mol.
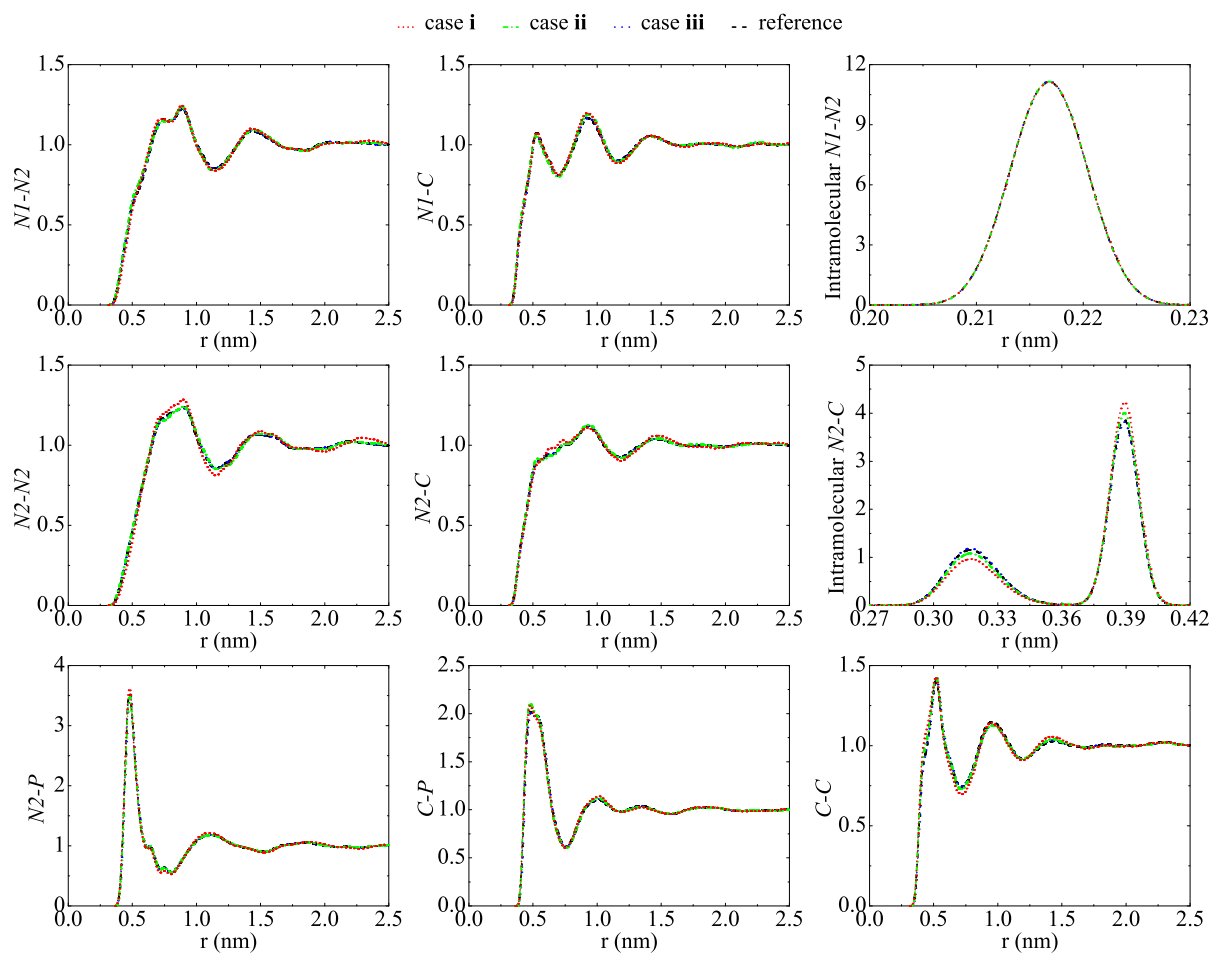
Fig. 4 The comparison of intermolecular RDFs and intramolecular distance distributions between CG beads calculated from coarse-grained simulations to the reference RDFs.
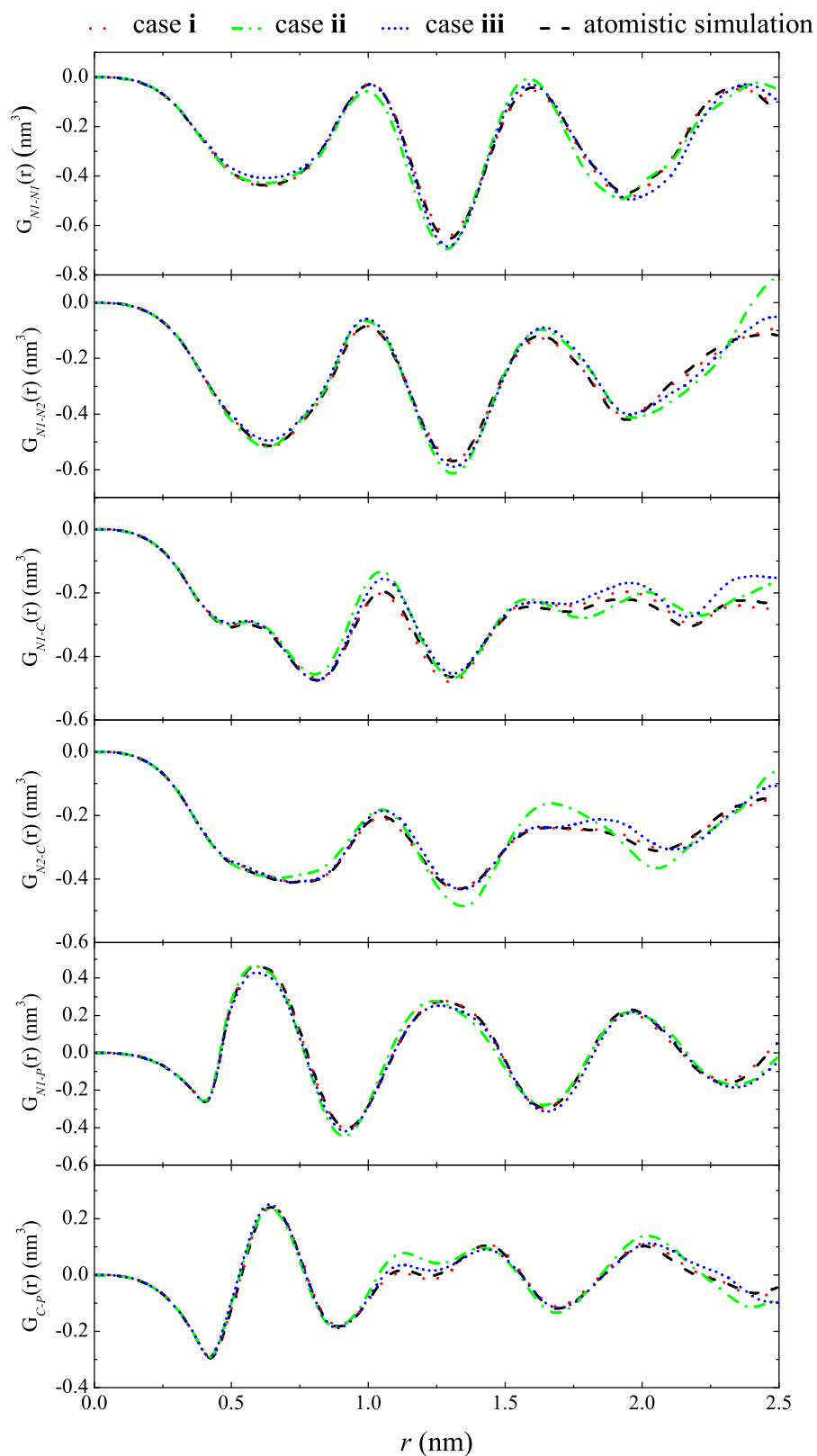
Fig. 5 Kirkwood-Buff integrals calculated from atomistic simulations and three sets of coarse-grained simulations based on corresponding effective potentials.