Simulation studies of bond-orientational order in charge stabilised colloidal suspensions

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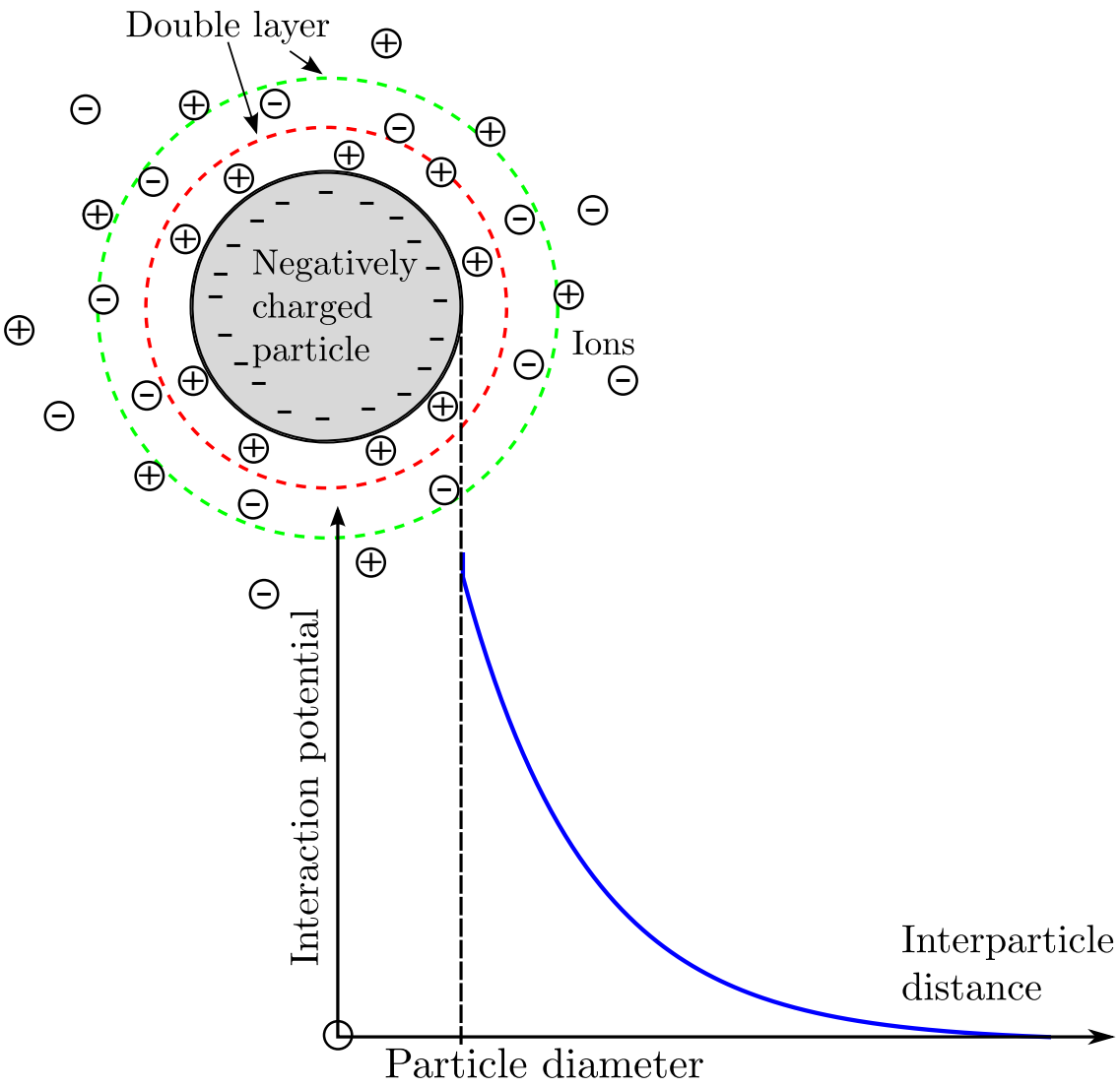
Outline

Pair interaction - DLVO theory



Interaction via hard-core Yukawa (screened coulomb) potential [1]:

$$u(\mathbf{r}_{ij}) = \begin{cases} \infty, & |\mathbf{r}_{ij}| < 1, \\ \frac{u_0}{\beta} \frac{1}{|\mathbf{r}_{ij}|} e^{-\kappa|\mathbf{r}_{ij}|}, & \text{else.} \end{cases}$$

Coupling parameter:

$$u_0 = \frac{\lambda_B}{\sigma} \left(\frac{e^{\kappa/2}}{1+\kappa/2} \right)^2 Z^2$$

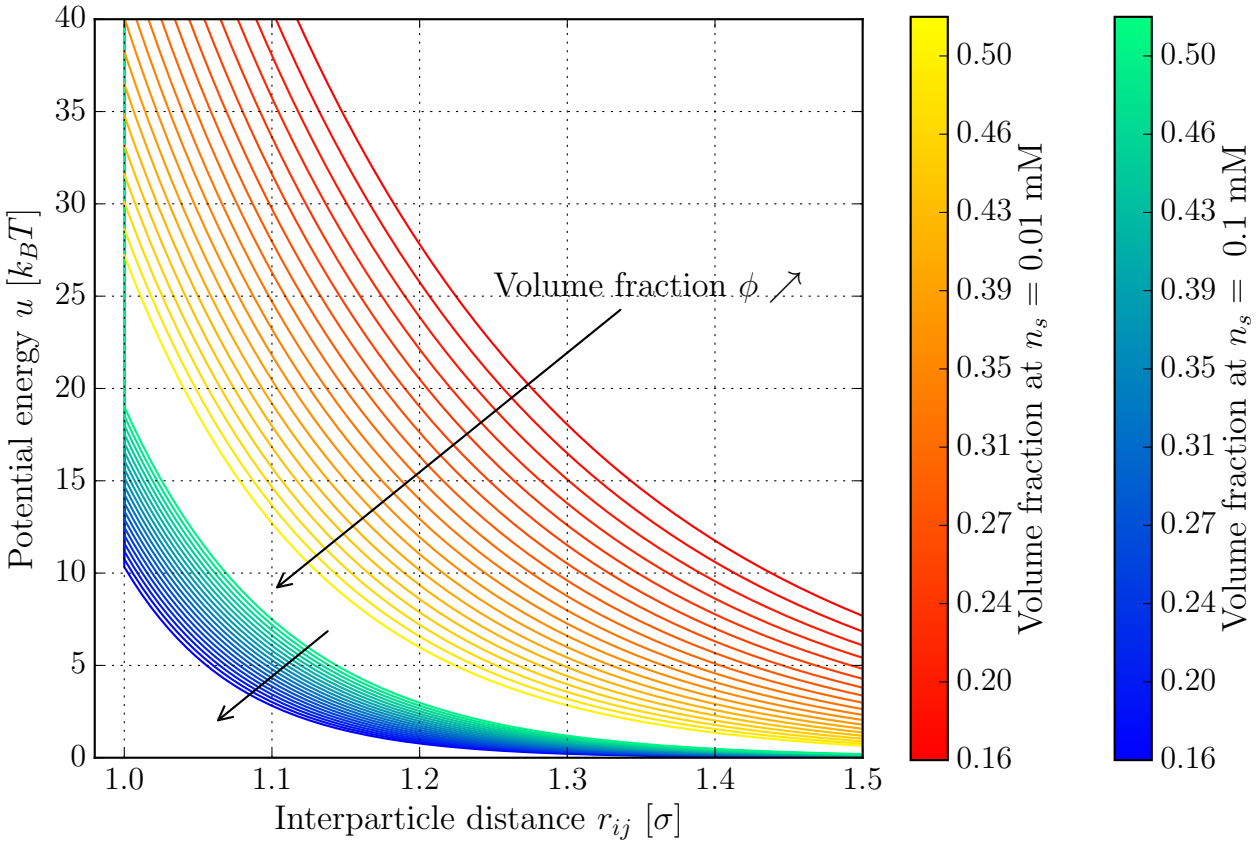
Screening parameter:

$$\kappa^2 = \frac{\lambda_B/\sigma}{1-\phi}(24\phi|Z| + 8\pi n_s \sigma^3).$$

Local Structure:

- **Radial distribution $\mathbf{r}_{ij}$**
- **Bond orientational order θ_{ij}, ϕ_{ij}**
  $\rightarrow$ Only accessible with simulations

Effect of volume fraction and salt concentration



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Thermodynamics and Monte-Carlo

Calculate ensemble average in the canonical ensemble [2]:

$$\langle \mathcal{A} \rangle_{\text{ens}} = \int \rho(\mathbf{\Gamma}) \mathcal{A}(\mathbf{\Gamma}) \, \mathrm{d}\mathbf{\Gamma},$$

using the metropolis Monte-Carlo scheme for generating configurations $\mathbf{\Gamma}$.

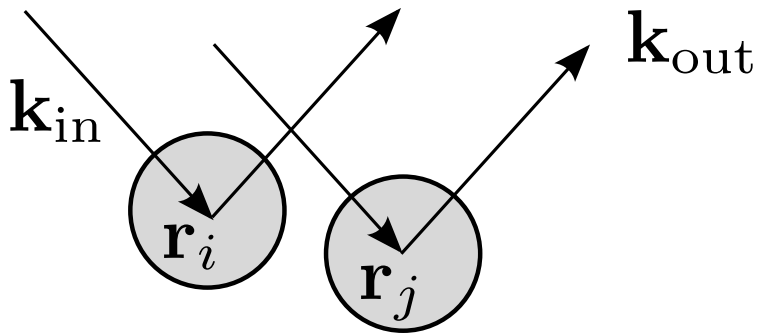
Quantity	Value
particles N	3375
temperature	293 °K
configurations	1000
size σ (momodisperse)	223.4 nm
cutoff	2.5 σ
charge Z	400
ϵ	80

Table : Simulations' parameters

X-ray scattering experiments

The structure factor describes the way the structure scatters light. It is defined as Fourier density correlation[3]

$$S(\mathbf{k}) = 1 + \frac{1}{N}\left\langle \sum_{i \neq j}^{N} e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)} \right\rangle, \quad S(k) = 1 + \rho \int_V e^{ikr} g^{(2)}(r) \mathrm{d}r.$$



$$\mathbf{k} = \mathbf{k}_{\mathrm{out}} - \mathbf{k}_{\mathrm{in}}$$

Experiment's $S(k)$ vs. simulations'

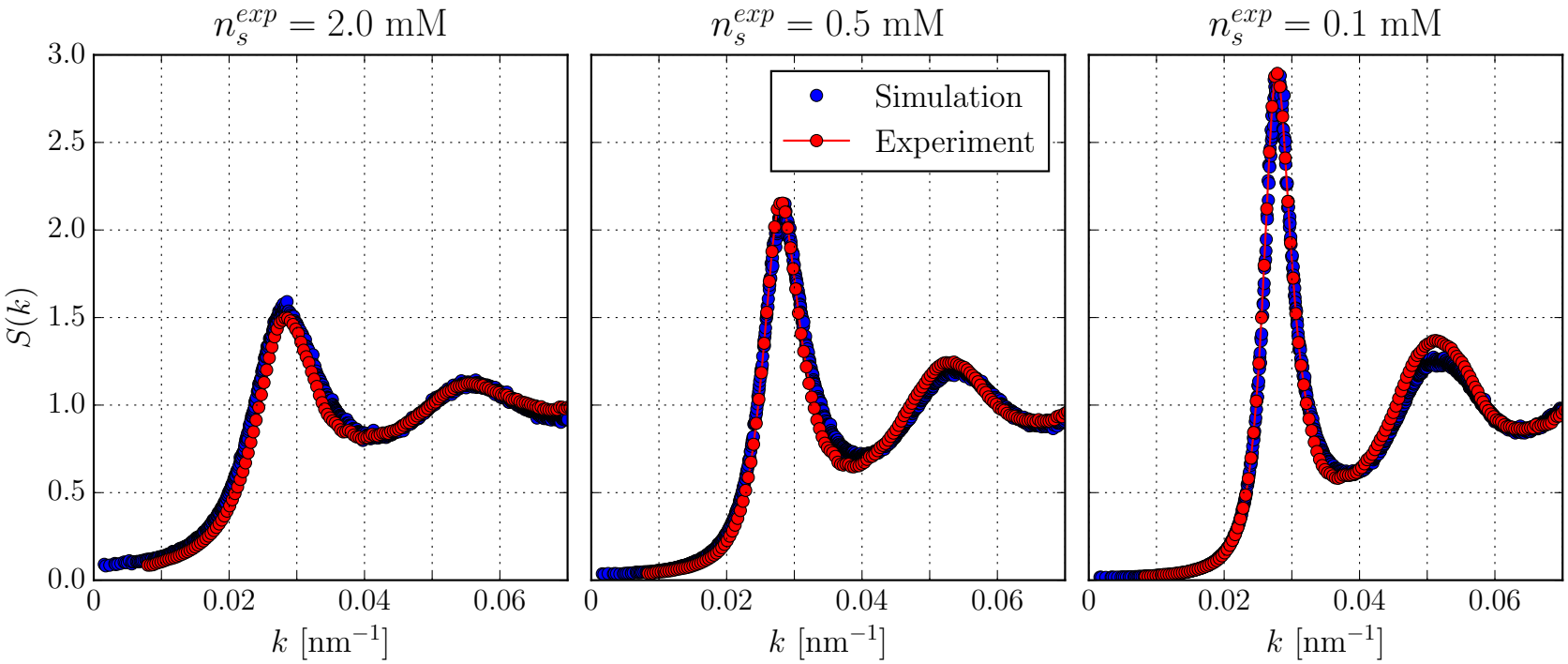


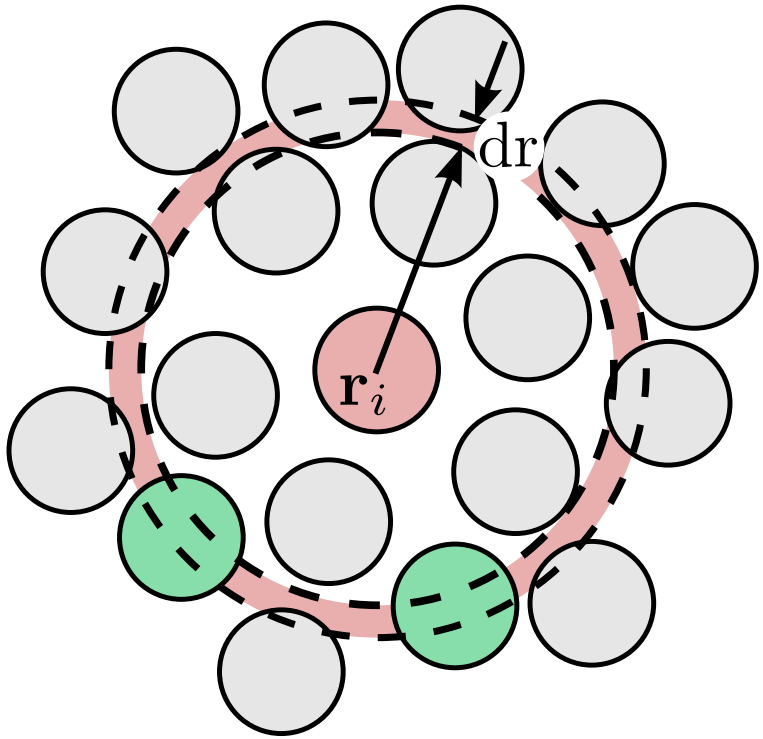
Figure : Structure factors at volume fraction $\phi^{\text{nom}} = 0.32$.
Red circles: Experiments. Blue circles: Simulations.

RMS at volume fraction $\phi^{\text{nom}} = 0.32$ is maximal 5%,
and at $\phi^{\text{nom}} = 0.16$ maximal 3%.

Radial distribution function

Probability $g_N^{(2)}(r)$ of finding a particle at distance r of another particle [4].
Homogeneous and isotropic fluid:

$$\begin{aligned}\rho_N^{(2)}(r) &= \left\langle \sum_{i \neq j} \delta(\, r - |\mathbf{r}_i - \mathbf{r}_j|\,) \right\rangle \\ &= g_N^{(2)}(r)\rho.\end{aligned}$$



Liquid's local structure:
$g_N^{(2)}(r)$ oscillates.

But for $r \nearrow$: $g_N^{(2)}(r) \to 1$.

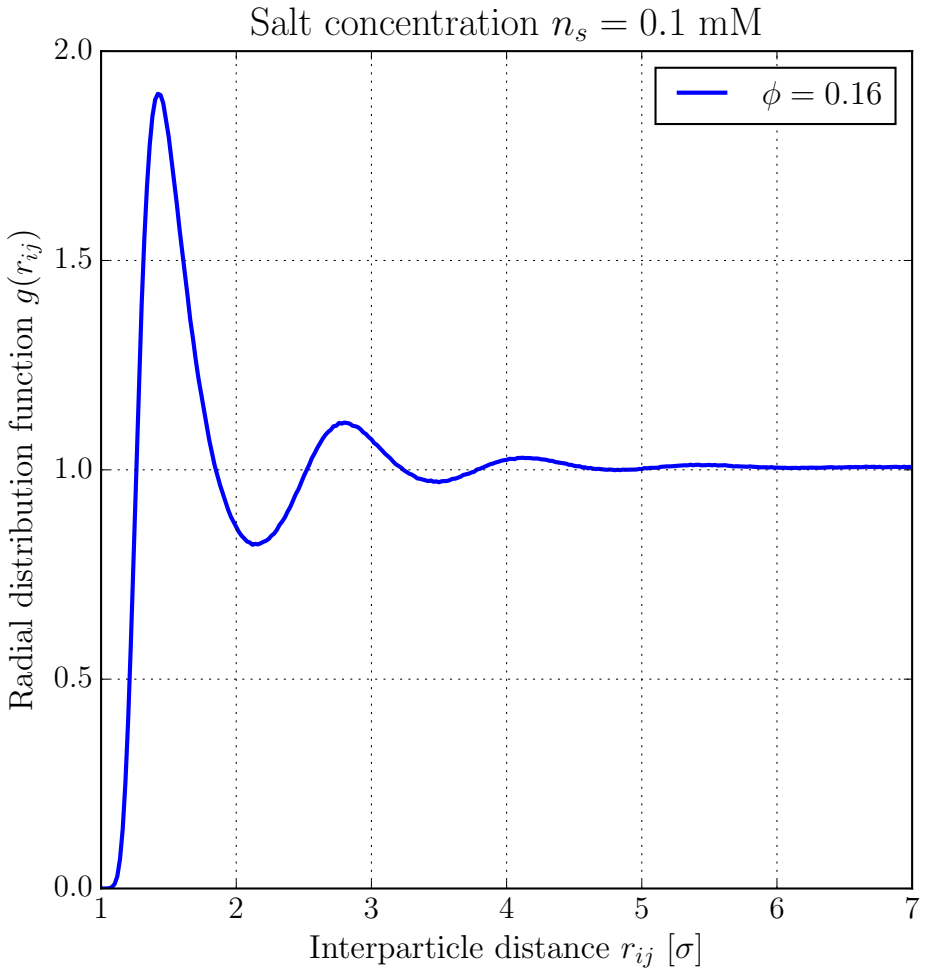


Figure : Typical fluid's radial distribution function, here at salt concentration $n_s^{\text{nom}} = 0.1$.

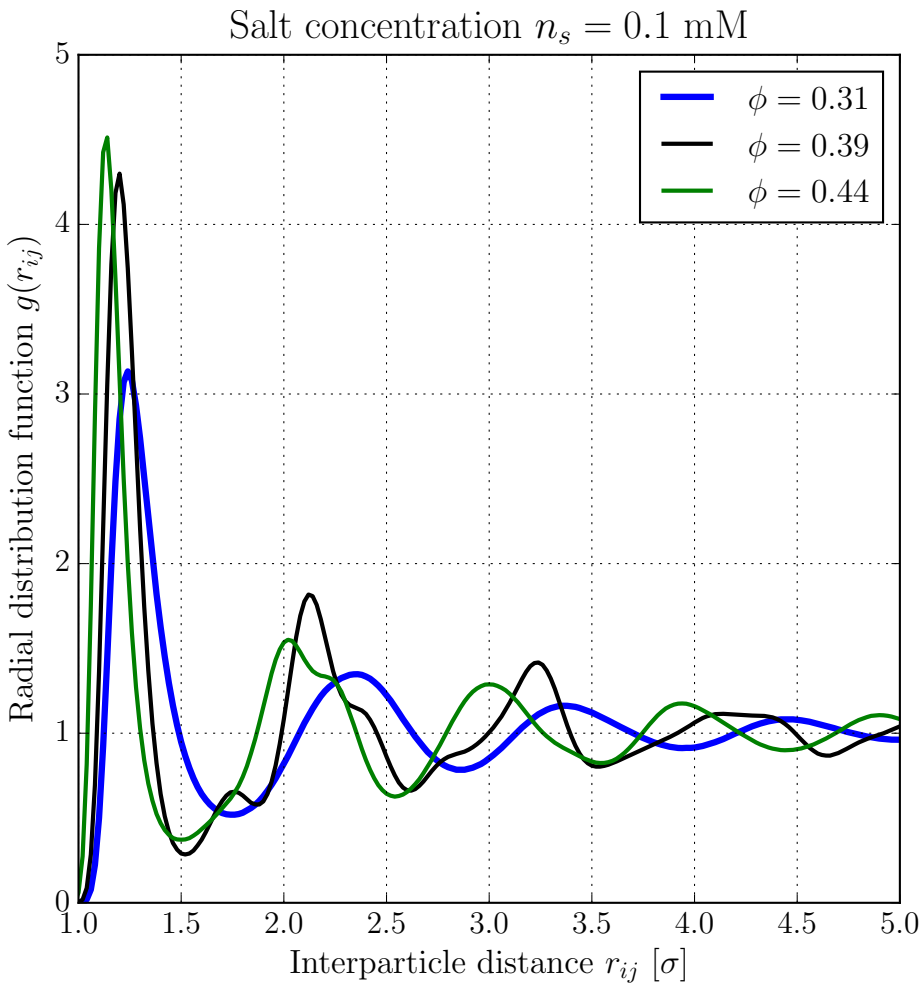
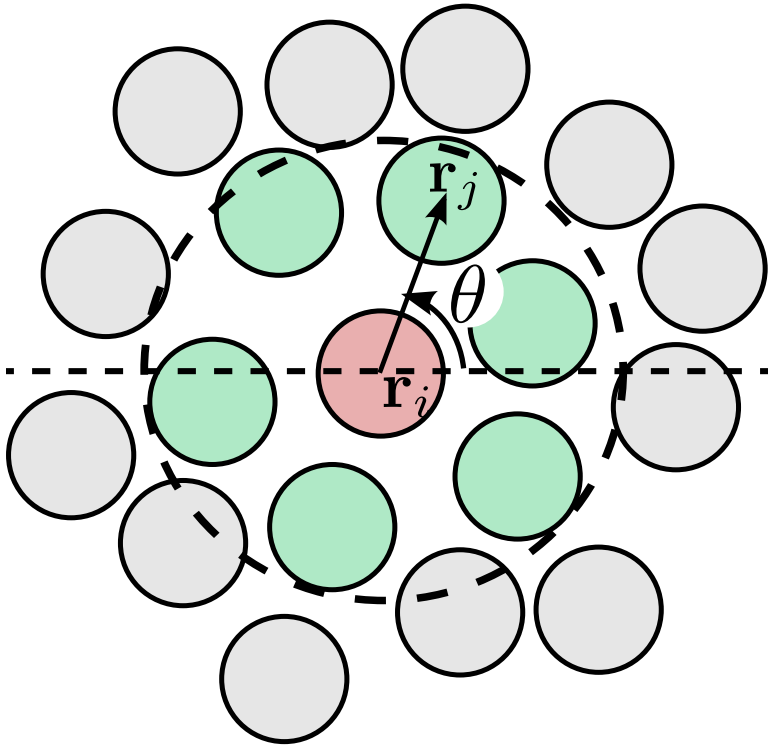


Figure : Radial distribution function at salt concentration $n_s^{\text{nom}} = 0.1$.

Bond orientational order

Local l-fold order of particle i with nearest neighbours $j \in \mathrm{NN}(i)$, defined [5] with l-order spherical harmonics $Y_{lm}(\theta_{ij}, \varphi_{ij})$:

$$q_l(i) = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} \underbrace{\left| \frac{1}{|\mathrm{NN}(i)|} \sum_{j \in \mathrm{NN}(i)} Y_{lm}(\theta_{ij}, \varphi_{ij}) \right|^2}_{q_{lm}(i)} \right]^{1/2}.$$



Correlation between them:

$$c_l(ij) = \frac{\sum_{m=-l}^{l} q_{lm}(i)\, \overline{q_{lm}(j)}}{\left[\sum_{m=-l}^{l} |q_{lm}(i)|^2 \right]^{1/2} \left[\sum_{m=-l}^{l} |q_{lm}(j)|^2 \right]^{1/2}}$$

Bond orientational order for salt concentration $n_s^{\text{nom}} = 0.1$

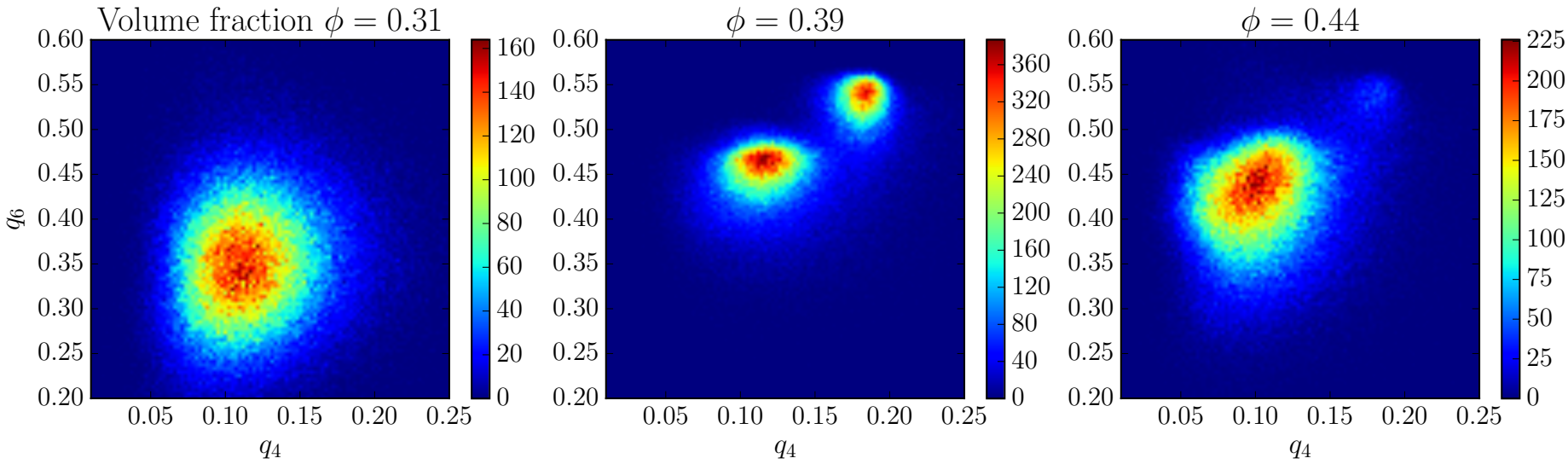


Figure : Scattering plot of q_6/q_4 for different volume fractions ϕ at salt concentration $n_s^{\text{nom}} = 0.1$.

Crystal lattice	q_4	q_6
bcc	0.036	0.511
fcc	0.190	0.575
hcp	0.097	0.484

Table : q_4 and q_6 symmetry values for occurring ideal lattices.

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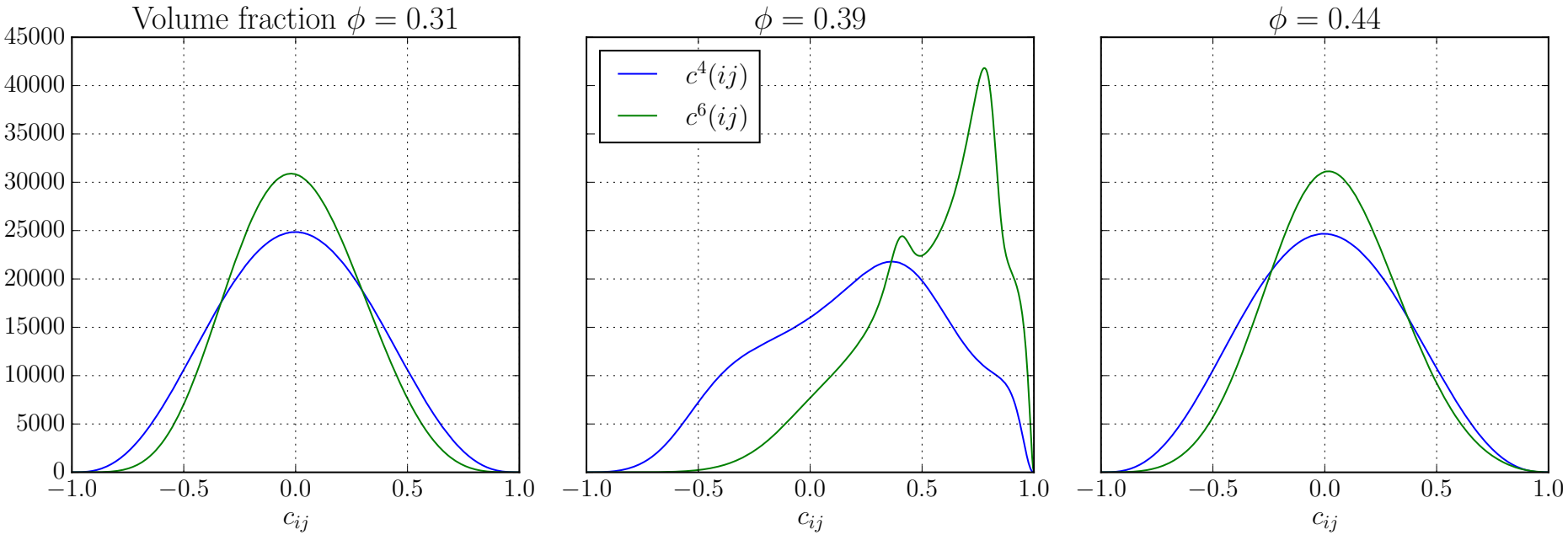
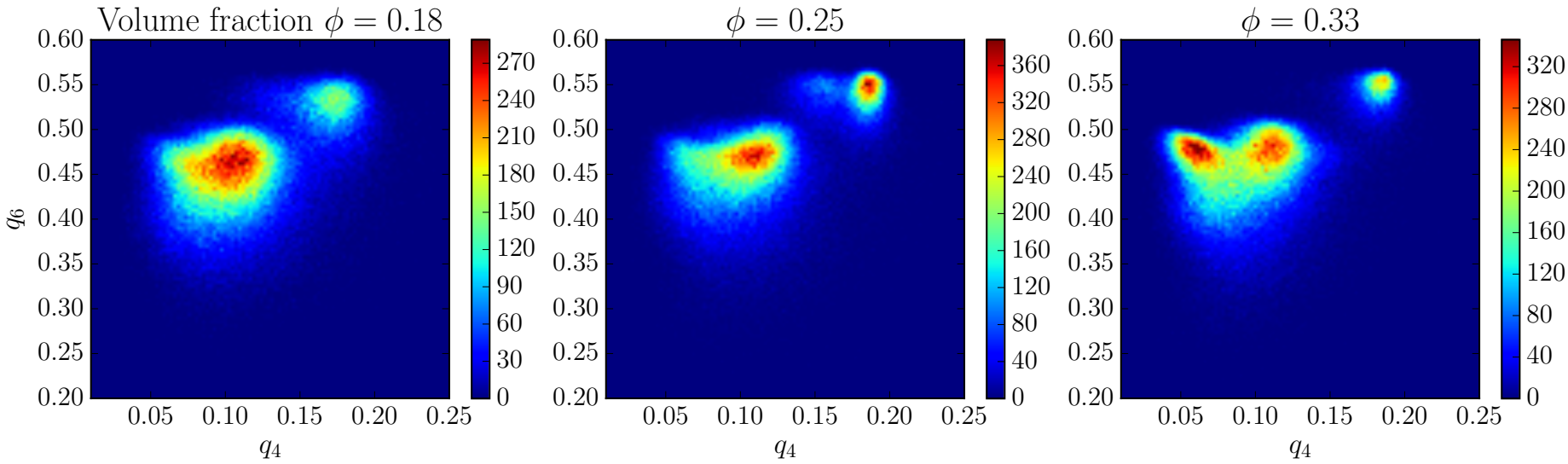


Figure : Plot of $c^l(ij)$ for both symmetries, for different volume fractions ϕ at salt concentration $n_s^{\text{nom}} = 0.1$. Blue: q_3. Green: q_4. Red: q_6.

Bond orientational order for salt concentration $n_s^{\text{nom}} = 0.01$



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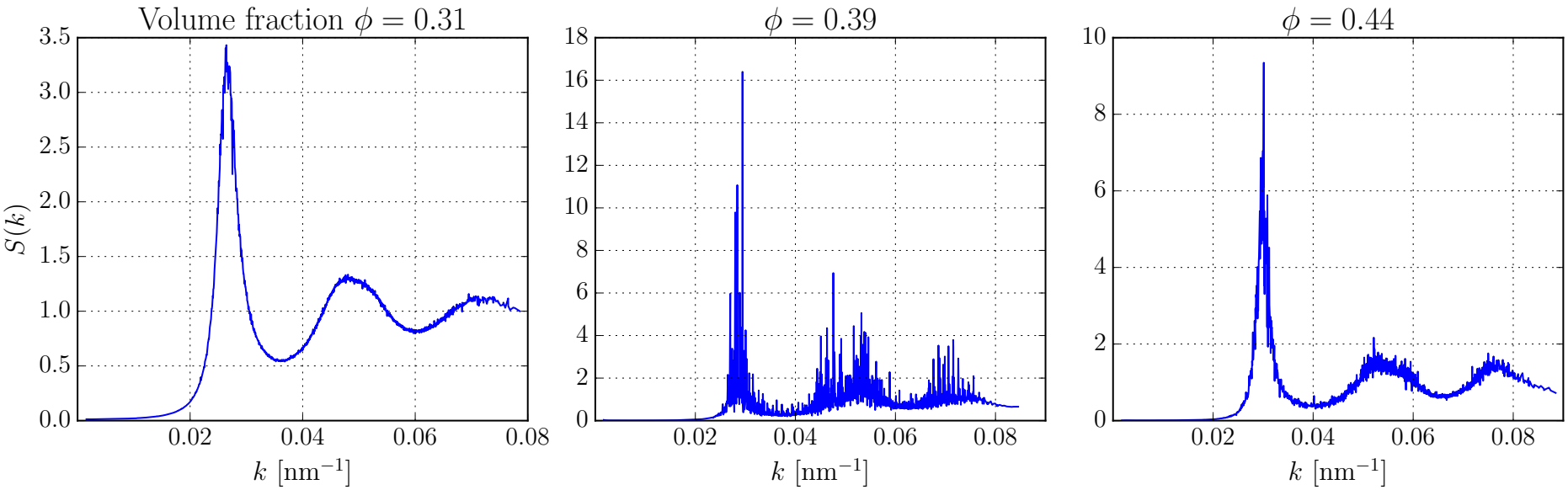

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Conclusion and Outlook

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- The model system compares well to with experiments
- We have tools to measure crystallisation.
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Outlook:

- Find relation of bond orientational order analysis with XCCA.
- Study effect of polydispersity on orientational correlations.

Discussion

Thank you for your attention!

References:

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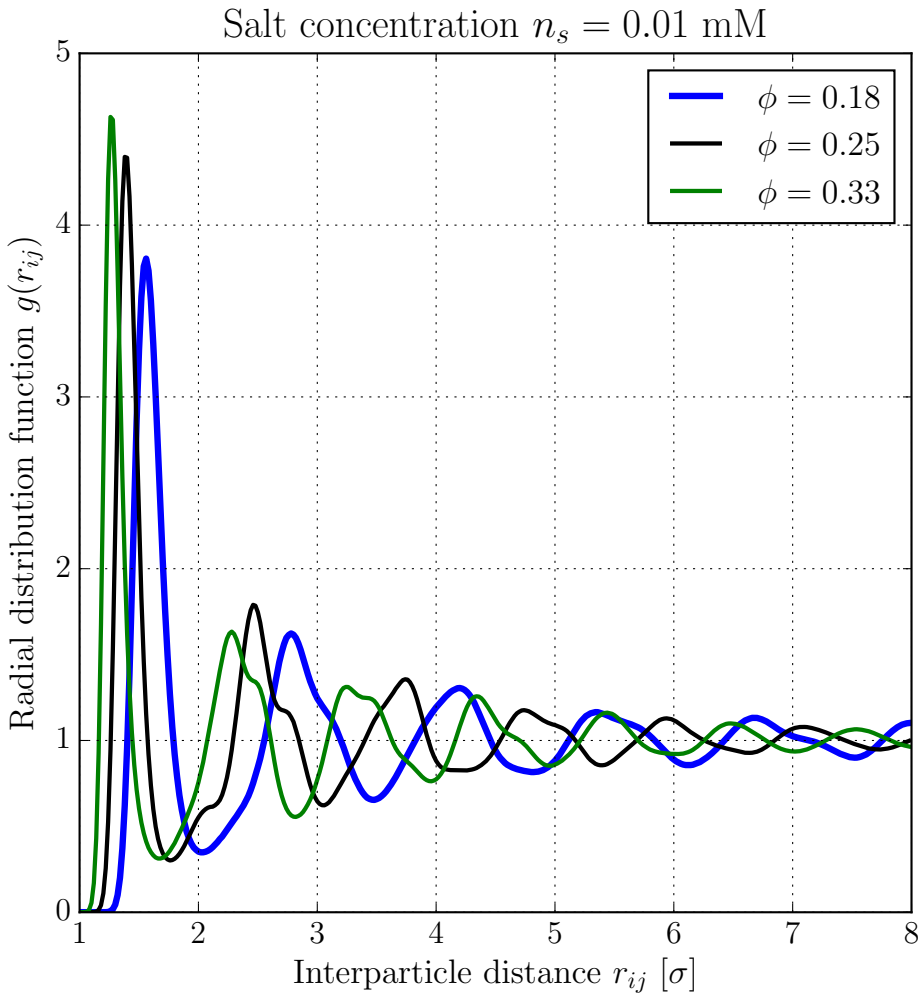

Figure : Radial distribution function at salt concentration $n_s^{\text{nom}} = 0.01$.

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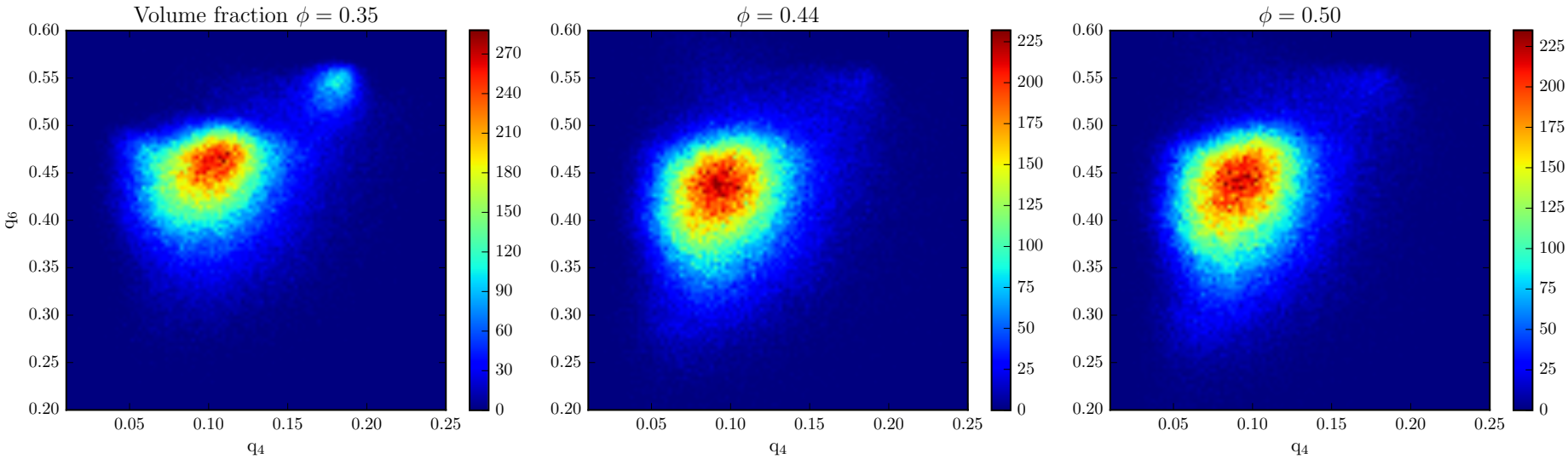

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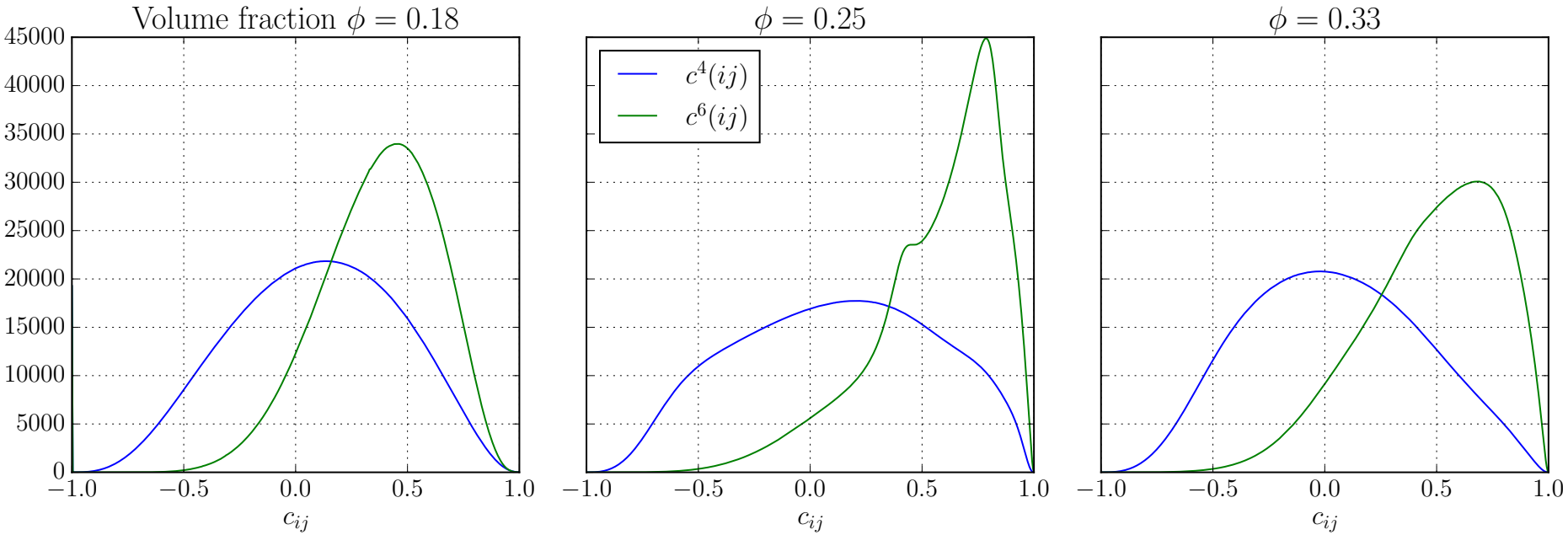

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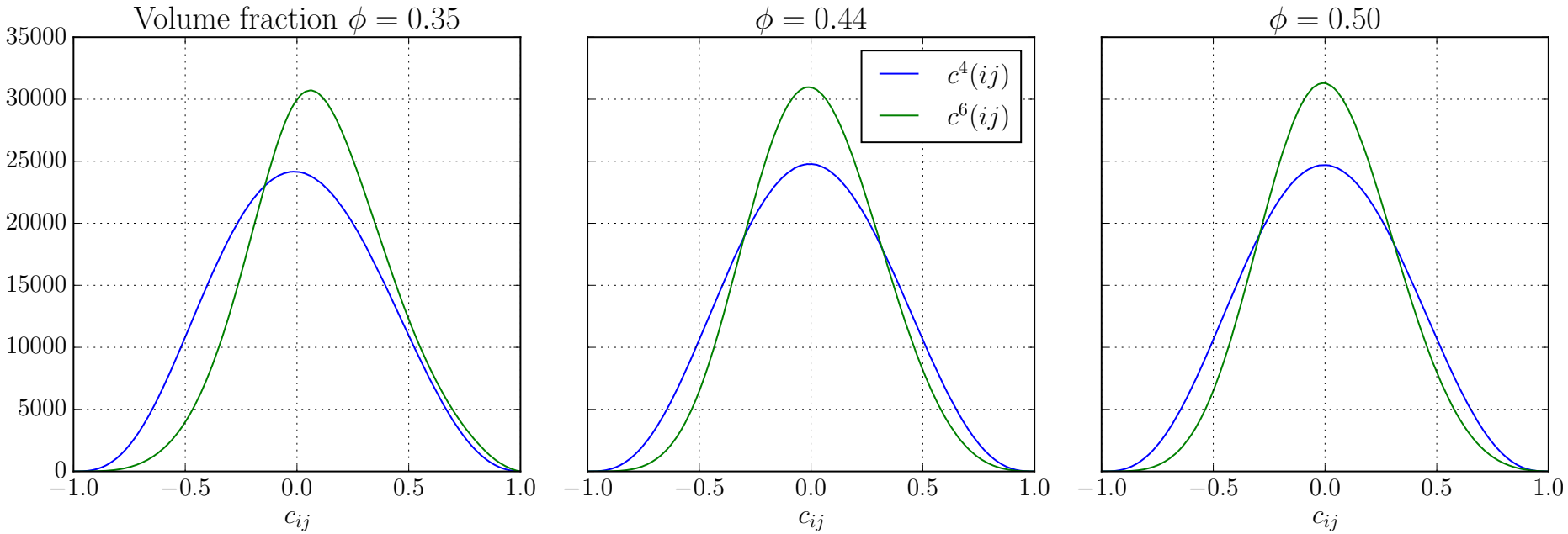

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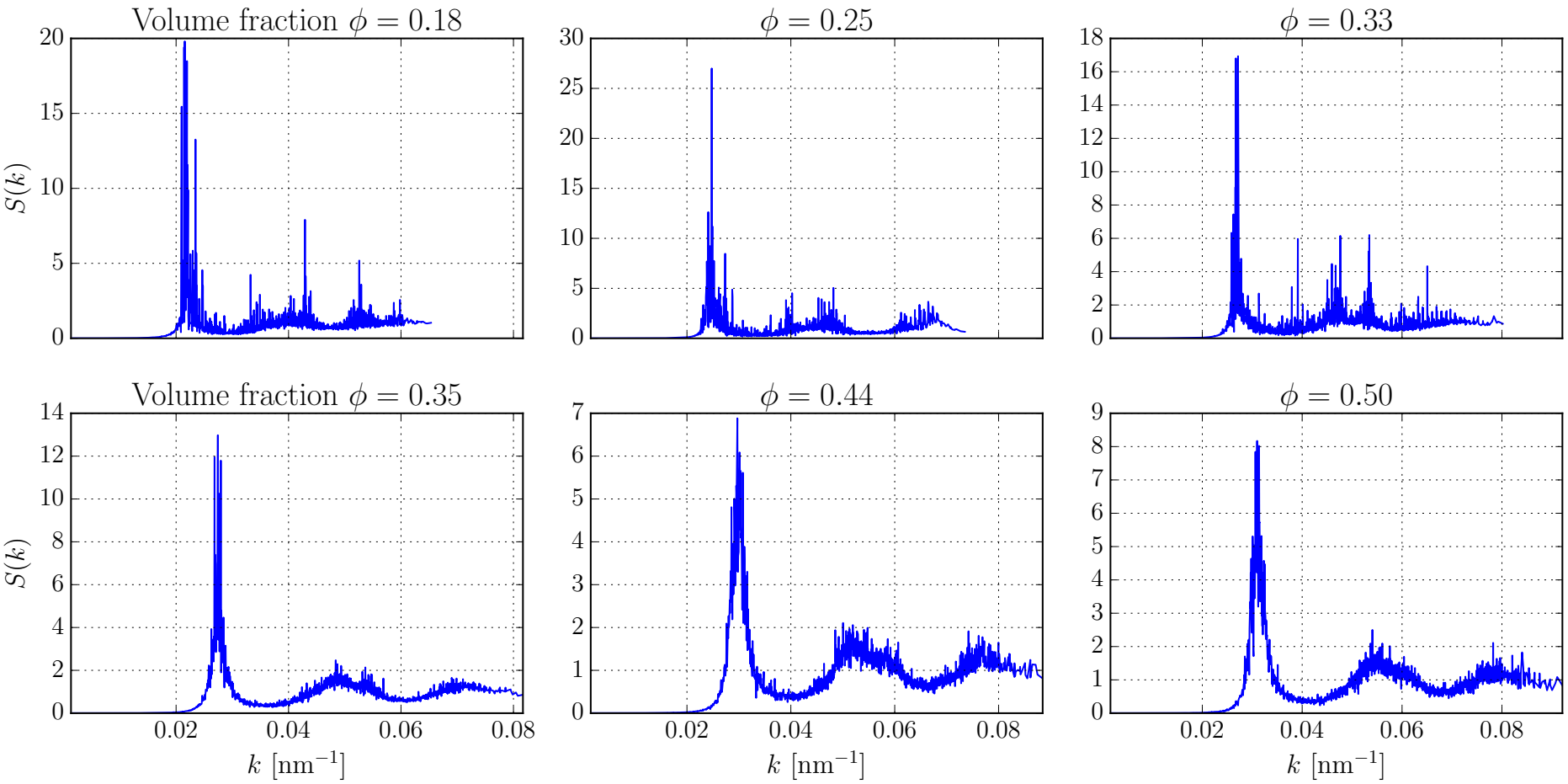

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