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Interpolation method for pair correlations in classical crystals

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ТЕРАГЕРЦОВАЯ ТЕХНИКА Лаборатория Публикации Сотрудники Блог Контакты English

Физика конденсированного состояния

Физика конденсированного состояния – богатейшая область современной физики, важная не только с фундаментальной, но и с прикладной точки зрения. Исследования закономерностей поведения конденсированных сред являют собой основу для технологий управления свойствами веществ, технологий создания новых материалов, а также для создания элементной базы нового поколения в приборостроении.

Оптические сильно-коррелированные системы и методология спектроскопических исследований

Развитие технологий управления светом – актуальная задача современной физики и техники. В последнее время большое внимание в этом направлении привлекают фотонные кристаллы и метаматериалы – среды с периодической в пространстве комплексной диэлектрической и магнитной проницаемостью. Поведение фотонов в таких средах с дальними корреляциями принципиально отличается от обычных однородных сред, что приводит к целому комплексу новых явлений: запрещенным зонам, локализации света и т.д.

ТГц изображающие системы и взаимодействие излучения со структурированными средами

Изображающие системы, работающие в терагерцовом диапазоне электромагнитного излучения, имеют огромную прикладную ценность: они могут использоваться для систем безопасности жизнедеятельности, в биомедицинских приложениях, для технологического и эксплуатационного контроля полимерных конструкций. Для создания таких систем необходимо знать особенности распространения ТГц излучения в различных средах, в т.ч., локально упорядоченных.

Блог Публикации

The presentation plan

1. The general motivation
2. Pair correlations and the shortest graphs in classical crystals
3. Three-body correlations at large distances
4. Thermodynamical properties of simple crystals
5. Account of anharmonicity effects
6. Phase transitions
7. Conclusion and related problems

Classical gases, fluids, and crystals

Usually, to estimate the interaction rate in system of particles, coupling parameter is employed:

$$\Gamma \simeq \frac{\langle U \rangle}{T} = \frac{\text{Interaction energy}}{\text{Kinetic energy}}$$

Then, we have the following different situations:

- $\Gamma \lesssim 1$ — **Gases:**
  Mayer's theory for imperfect gases (1937) – The First-Principle Theory
- $10^2 \gtrsim \Gamma \gtrsim 1$ — **Fluids:**
  BBGKY (1948), Ornstein-Zernike equation for fluids (1914)
  Frenkel's approaches (1947)
  Density-Functional Theory (1927)
- $\Gamma \gtrsim 10^2$ — **Crystals:**
  Density-Functional Theory (1927)

Pair correlation function can be determined in crystals as

$$g(\mathbf{r}) = \frac{V}{N^2} \left\langle \sum_{\alpha,\beta,\alpha\neq\beta} \delta(\mathbf{r} + \mathbf{r}_\alpha - \mathbf{r}_\beta) \right\rangle = \frac{V}{N} \sum_\alpha p_\alpha(\mathbf{r} - \mathbf{r}_\alpha),$$

where V, N stand for volume and number of particle in the system, $\delta(\mathbf{r})$ is Dirac delta-function, and $\langle ... \rangle$ means canonical ensemble averaging, summation is over all the nodes α.

It is amazingly, but the problem of *pair correlations in crystals* has not been solved complementary for a very long time!

The general motivation

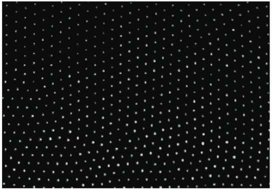
Fundamental problem of condensed matter physics:

Prediction of structure and properties of condensed systems for given thermodynamic conditions, employing only the interaction potentials between the particles.

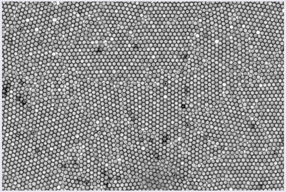
If we know pair correlation functions in classical crystals,

- Thermodynamics of the systems can be obtained.
- The solution is important for broad range of systems: **atomic, molecular, and complex crystals** – in elemental and molecular crystals, in complex media – dusty plasmas, colloidal suspensions, polyelectrolyte ionic microgels, etc.
- Predicting theory of liquid-solid and solid-solid phase transitions can be proposed.

Dusty plasmas

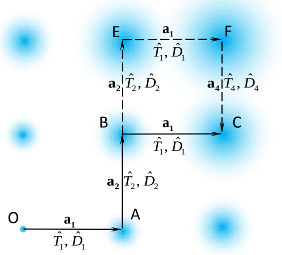


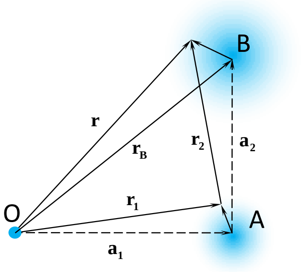
Colloidal systems



Apart from Molecular dynamic (MD) simulations, dusty plasmas and colloidal crystals allow to perform particle-resolved studies of generic phenomena.
The panels demonstrate typical crystals observed in the media.

The shortest graphs in crystals





The shortest graphs define the functions $p_\alpha(\mathbf{r})$ by the corresponding convolutions. In the first approximation, the pair correlations can be *estimated* as

$$\boxed{g(\mathbf{r}) = \frac{1}{n}\sum_\alpha \frac{1}{(\sigma\sqrt{2\pi n_\alpha})^3}\exp\left(-\frac{(\mathbf{r}-\mathbf{r}_\alpha)^2}{2n_\alpha\sigma^2}\right),} \qquad \sigma^2 = \frac{2T}{m\Omega_E^2}, \quad \Omega_E^2 = \frac{1}{3m}\sum_\alpha \Delta\varphi|_{\mathbf{r}=\mathbf{r}_\alpha},$$

where n_α is the number of steps in the corresponding shortest graph to node α.

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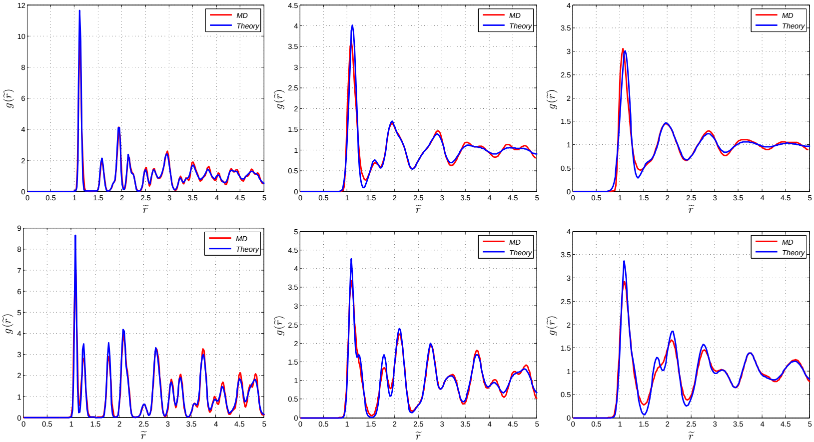
$g(r)$ in Lennard-Jones and Yukawa crystals



Numerical $g(r)$ function (red, MD) and theoretically predicted by the SG method (blue).
Lennard-Jones HCP lattice (top row): Temperature is (from left to right): $T/\epsilon = 0.1,\ 1,\ 1.55$
Yukawa BCC lattice (bottom row): Temperature is (from left to right): $T/\epsilon = (1.0,\ 4.5,\ 8.5) \times 10^{-3}$

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Account of three-body correlations at large distances

In the harmonic approximation, individual peaks are described by the Gaussian functions:

$$\boxed{p_\alpha(\mathbf{r}) \propto \exp\left[-\frac{(\mathbf{e}_\alpha \cdot \mathbf{r})^2}{2\sigma^2_{\parallel\alpha}}\right] \exp\left[-\frac{\mathbf{r}^2 - (\mathbf{e}_\alpha \cdot \mathbf{r})^2}{2\sigma^2_{\perp\alpha}}\right],}$$

where $\sigma^2_{\parallel\alpha}$ and $\sigma^2_{\perp\alpha}$ are the longitudinal and transverse MSDs, respectively, and $\mathbf{e}_\alpha = \mathbf{r}_\alpha/|\mathbf{r}_\alpha|$ is the unit vector. At large distances, $\sigma^2_{\parallel\alpha} \simeq \sigma^2_{\perp\alpha} = \sigma^2_\alpha/D$.

$$\boxed{\widetilde{\sigma}^2_{\alpha+1} = \widetilde{\sigma}^2_\alpha + 1 - 2\phi_\alpha\sqrt{\widetilde{\sigma}^2_\alpha},} \qquad \widetilde{\sigma}^2_\alpha = \frac{\sigma^2_\alpha}{\sigma^2_1}, \quad \phi_\alpha = \frac{\langle(\mathbf{u}_\alpha - \mathbf{u}_0)(\mathbf{u}_\alpha - \mathbf{u}_{\alpha+1})\rangle}{\sqrt{\sigma^2_1\sigma^2_\alpha}},$$

where ϕ_α originates from three-body correlations. At $\alpha \to \infty$ (in 3D crystals) $\phi_\infty = 1/2\sqrt{\widetilde{\sigma}^2_\infty}$ and can be find analytically, as:

$$\sigma^2_1 = \frac{2T}{mN}\sum_{\mathbf{q},j}\frac{1}{\omega^2_j(\mathbf{q})}[1 - \cos(\mathbf{q}\cdot\mathbf{r}_1)], \quad \sigma^2_\infty = \frac{2T}{mN}\sum_{\mathbf{q},j}\frac{1}{\omega^2_j(\mathbf{q})},$$

where j denotes the phonon branch, and the summation is over all $\mathbf{q}$ and j.

In 2D crystals, we obtained $\boxed{\widetilde{\sigma}^2_\alpha \simeq 1 + A\ln n_\alpha}$, where the constant A is found analytically.

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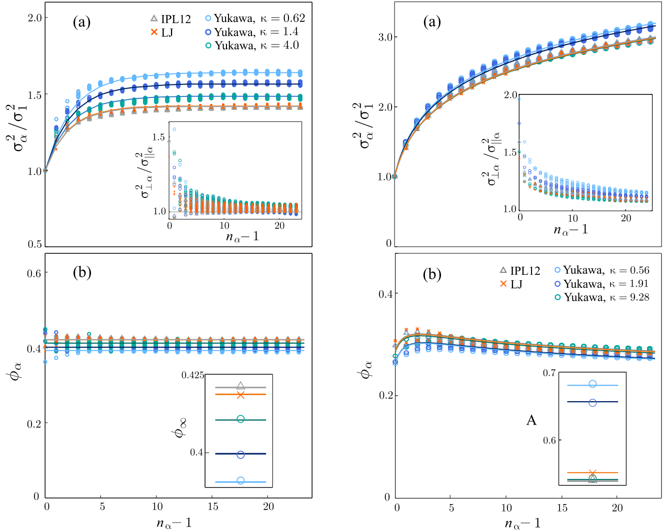
The results for 3D and 2D crystals



Shown are the normalized MSD, $\tilde{\sigma}_\alpha^2 = \sigma_\alpha^2/\sigma_1^2$ (a) and the correlation parameter, ϕ_α (b) versus the shortest-graph length n_α for studied 3D (left column) and 2D (right column) crystals.
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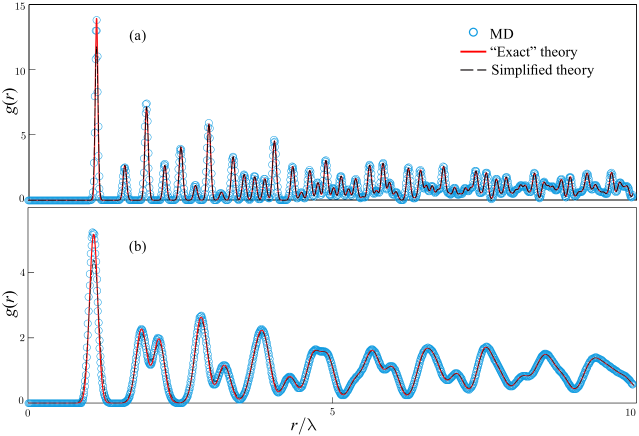
Functions $g(r)$ for "soft" Yukawa crystals



(a) – 3D FCC lattice at $\kappa = 1.4, \tau = 0.1$; (b) – 2D (triangular) lattice at $\kappa = 0.56, \tau = 0.5$. The symbols are the MD results, the solid and dashed lines are the theoretical results from the "exact" (anisotropic Gaussians for close particles) and simplified theories, respectively.

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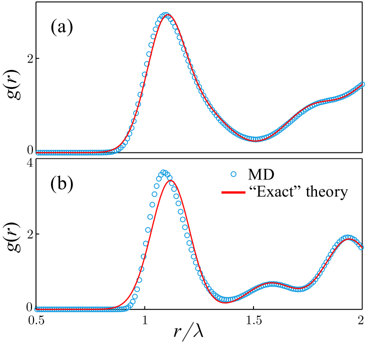
The anharmonicity at short distances



The pair correlation function $g(r)$ at short distances, plotted for Yukawa BCC (a) and IPL12 FCC (b) crystals at $\kappa = 0.62$, $\tau = 0.9$. The first peak is clearly non-Gaussian for the short-range interaction (b).

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From pair correlations to the Helmholtz free energy

Using found pair correlations functions $g(\mathbf{r})$, one can obtain the interaction energy,

$$\boxed{\frac{U_{\text{int}}}{N} = \frac{n}{2}\int d\mathbf{r}\; g(\mathbf{r})\varphi(r)}$$

Then, once can perform thermodynamic integration to find the Helmholtz free energy

$$\boxed{F = F_{\text{ph}} - T\int_0^T \left(\delta U_{\text{int}} - \frac{3}{2}NT\right)\frac{dT}{T^2} + U_0}, \qquad F_{\text{ph}} = T\sum_{\mathbf{q},j}\ln\left[2\sinh\left(\frac{\hbar\omega_j(\mathbf{q})}{2T}\right)\right],$$

where $\delta U_{\text{int}} = U_{\text{int}} - U_0$ is the temperature-dependent part of the internal energy, $U_0 = \frac{1}{2}\sum_{\alpha\neq\beta}\varphi(\mathbf{r}_\alpha - \mathbf{r}_\beta)$ is the static interaction energy, and F_{ph} describes the contribution of phonons.

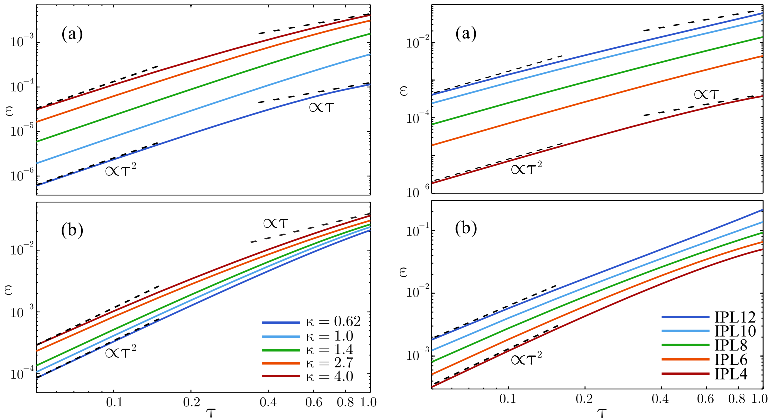
Also, the Helmholtz free energy ($F = E - TS$) can be rewritten using the following expansion (Wallace, 1987),

$$S = -\frac{N}{n}\int d\mathbf{p}\; f_N^{(1)}(\mathbf{p})\ln h^3 f_N^{(1)}(\mathbf{p}) - \frac{n^2}{2}\int d\mathbf{r_1}d\mathbf{r_2}\; g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\ln g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) -$$

$$-\frac{n^3}{3!}\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\; g_N^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\ln\left[\frac{g_N^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)}{g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)g_N^{(2)}(\mathbf{r}_2,\mathbf{r}_3)g_N^{(2)}(\mathbf{r}_1,\mathbf{r}_3)}\right] + \dots$$

D.C. Wallace. JCP **87**, 2282 (1987)
S.O. Yurchenko, N.P. Kryuchkov, A.V. Ivlev. JCP **143**, 034506 (2015)

Thermodynamics of Yukawa and IPL crystals



Left panel: The relative error ε of the Helmholtz free energy (with respect to the MD results), calculated from the "exact" theory for 3D (a) and 2D (b) Yukawa crystals for different dimensionless temperatures τ and screening parameters κ.
Right panel: The relative error ε of the Helmholtz free energy for 3D (a) and 2D (b) IPL crystals with different exponents k.

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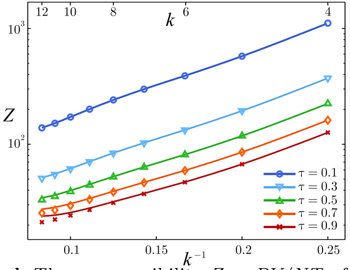
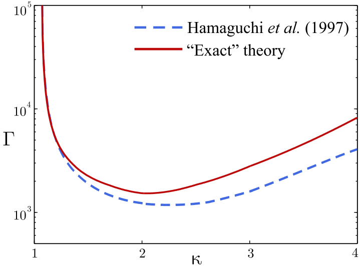
Thermodynamics of crystals





Left panel: The compressibility $Z = PV/NT$ of IPL crystals for different dimensionless temperatures τ and inverse exponents k^{-1}. The symbols and solid lines depict the MD and theoretical results.
Right panel: The solid-solid (BCC-FCC) transition line for Yukawa crystals. The growing deviation from the results by Hamaguchi *et al.* is due to a combined effect of anharmonicity (at lower Γ) and hard-sphere-like interactions (at larger κ).

Theoretical compressibility is obtained from the virial equation of state,

$$Z = 1 - \frac{2\pi n}{3T} \int_0^\infty dr\, r^3 \varphi'(r) g(r).$$

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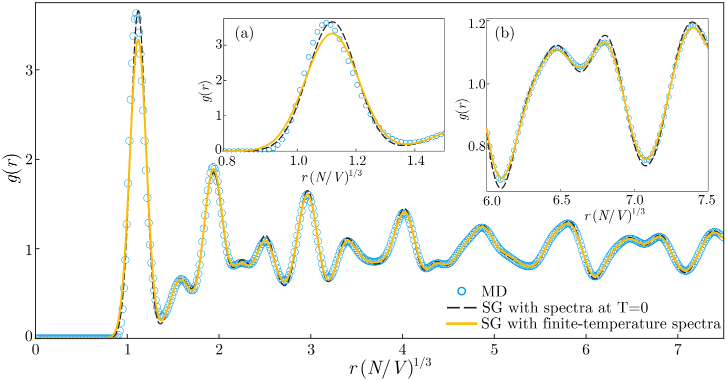
Account of phonon spectra anharmonicity



Pair correlation function for a 3D Yukawa FCC crystal ($\kappa = 4$, near melting line). The insets demonstrate that the use of the finite-temperature spectra substantially improves the analytical results at larger distances, while the results for the first peak become less accurate.

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Interpolation method (IM)

The peak form is

$$\boxed{p_\alpha(\mathbf{r}) \propto \exp\left[-\frac{\varphi(\mathbf{r}+\mathbf{r}_\alpha)}{k_\mathrm{B}T} - b_\alpha(\mathbf{e}_\alpha\cdot\mathbf{r}) - \frac{(\mathbf{e}_\alpha\cdot\mathbf{r})^2}{2a_{\parallel\alpha}^2} - \frac{\mathbf{r}^2-(\mathbf{e}_\alpha\cdot\mathbf{r})^2}{2a_{\perp\alpha}^2}\right]}$$

The normalization constant and constants $a^2_{\parallel,\perp}, b_\alpha$ are found using the conditions

$$\int d\mathbf{r}\; p_\alpha(\mathbf{r}) = 1, \qquad \int d\mathbf{r}\; \mathbf{r}p_\alpha(\mathbf{r}) = 0,$$

$$\int d\mathbf{r}\; (\mathbf{e}_\alpha\cdot\mathbf{r})^2 p_\alpha(\mathbf{r}) = \sigma^2_{\parallel\alpha}, \quad \int d\mathbf{r}\; [\mathbf{r}^2-(\mathbf{e}_\alpha\cdot\mathbf{r})^2]p_\alpha(\mathbf{r}) = (D-1)\sigma^2_{\perp\alpha},$$

where for close particles (with $n_\alpha \leq 4$) the MSDs can be calculated using the finite-temperature phonon spectra $\omega(\mathbf{q},T)$:

$$\sigma^2_{\parallel\alpha} = \frac{2k_\mathrm{B}T}{mN}\sum_{\mathbf{q},j}\frac{(\mathbf{e}_\alpha\cdot\mathbf{e}_\mathbf{q})^2}{\omega_j^2(\mathbf{q},T)}[1-\cos(\mathbf{q}\cdot\mathbf{r}_\alpha)],$$

$$\sigma^2_{\perp\alpha} = \frac{2k_\mathrm{B}T}{mN}\sum_{\mathbf{q},j}\frac{1-(\mathbf{e}_\alpha\cdot\mathbf{e}_\mathbf{q})^2}{(D-1)\omega_j^2(\mathbf{q},T)}[1-\cos(\mathbf{q}\cdot\mathbf{r}_\alpha)].$$

For $n_\alpha > 4$ we use the SG method described before.

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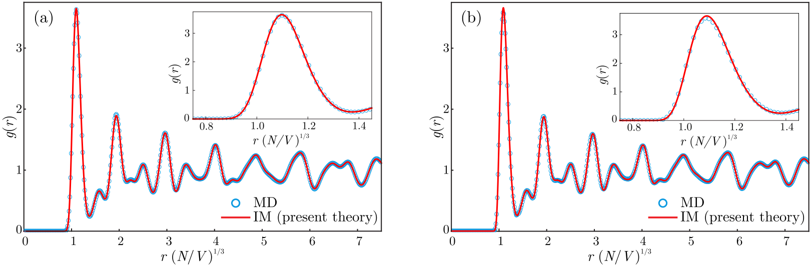
The results: pair correlations in 3D crystals



Pair correlation function for a 3D Yukawa (a) and IPL12 (b) FCC crystal with the screening parameter $\kappa = 4$ and dimensionless temperature (relatively the melting) $\tau = 0.9$. The respective insets show a zoom on the first correlation peak. IM calculations (red lines, include the lattice discreteness effect) demonstrate an excellent agreement with MD results (blue symbols).

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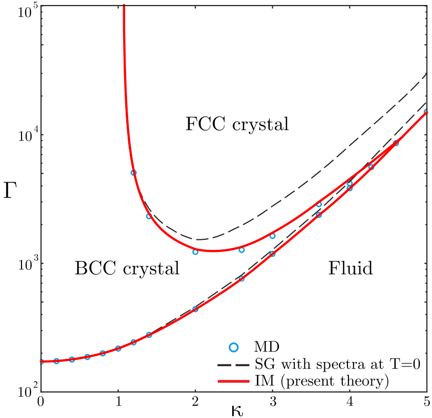
Phase diagram of Yukawa crystal found by IM



Phase diagram of a 3D Yukawa system in the plane spanned by the coupling parameter Γ and screening parameter κ. The black dashed and red solid lines show "semi-analytic" results, obtained for the crystalline phases with the SG and IM approaches, respectively. The blue symbols are our MD results.

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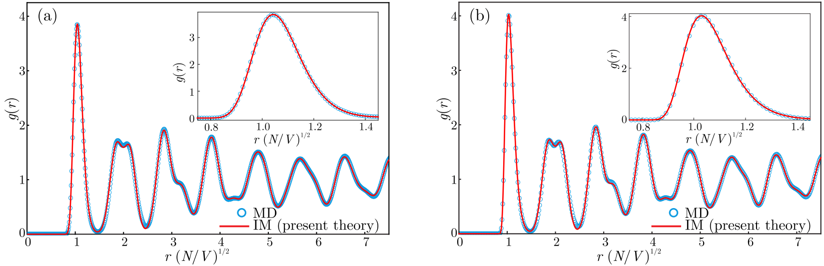
The results: pair correlations in 2D crystals



Pair correlation function for a 2D Yukawa (a) and IPL12 (b) crystal with $\kappa = 4$ and $\tau = 0.9$. The blue symbols are MD results, the red solid lines show IM calculations.

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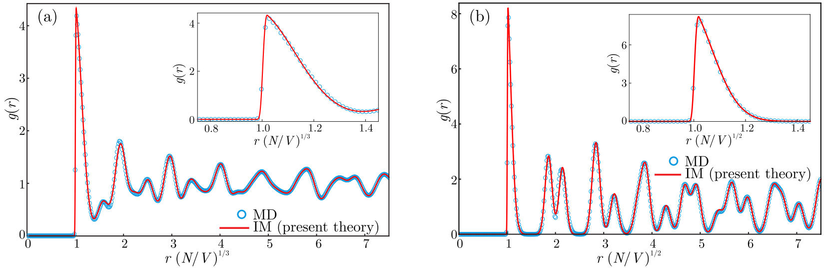
Pseudo-hard-sphere crystal



Pair correlation function for a 3D FCC (a) and 2D (b) crystal with PHS interactions at $N\lambda^D/V = 1$. The blue symbols are MD results, the red solid lines show IM calculations. The insets demonstrate that the IM approach yields accurate results, even for strongly non-Gaussian first peaks.

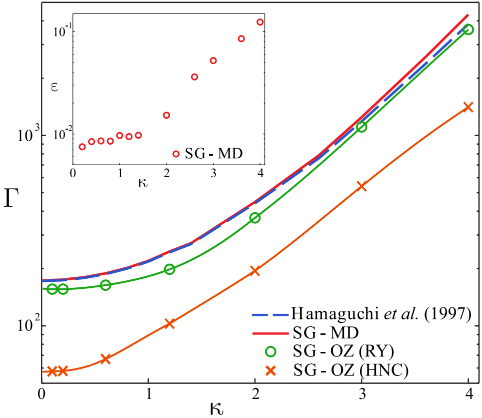
The pseudo-hard-sphere (PHS) potential:

$$\varphi_{\mathrm{PHS}} = \begin{cases} 50\epsilon\left(\frac{50}{49}\right)^{49}\left[\left(\frac{\lambda}{r}\right)^{50} - \left(\frac{\lambda}{r}\right)^{49}\right] + \epsilon, & r \le \frac{50}{49}\lambda; \\ 0, & r > \frac{50}{49}\lambda. \end{cases} \qquad \epsilon = 2k_{\mathrm{B}}T/3$$

S.O. Yurchenko, N.P. Kryuchkov, A.V. Ivlev. J. Phys.: Condens. Matter **28**, 235401 (2016).

Melting – Ornstein-Zernike – Shortest-Graph (OZ - SG) theory

Using Ornstein-Zernike theory for fluid and SG method for solid, one can construct theory quite accurate estimation of melting line.



Melting line calculated using OZ-SG theory for fluid and solid, respectively. One can see that the result strongly depends on the closure relation used in OZ theory.

Conclusion and related problems

The result. — For given interaction potential and finite-temperature phonon spectra, pair correlations are described precisely by proposed IM approach.

Papers about the shortest-graph and interpolation method are

- S.O. Yurchenko // The Journal of Chemical Physics **140**, 134502 (2014).
- S.O. Yurchenko, N.P. Kryuchkov, A.V. Ivlev // The Journal of Chemical Physics **143**, 034506 (2015).
- S.O. Yurchenko, N.P. Kryuchkov, A.V. Ivlev // Journal of Physics: Condensed Matter **28**, 235401 (2016).

Related problems for future studies:

- *Existence of phonon-like excitations in hard-sphere-like systems.* Can phonon spectra be calculated using the proposed IM method ?
- *Quasi-crystalline approach – "crystals" with vanishing correlations ($\phi_\infty \to 0$) at large distances.* Can fluids be described by quasi-crystalline approaches (under the Frenkel's line) ?
- *Predicting theory of melting.* Can we consider the structure of fluid near the melting line ?

Thank you for your attention !

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