Analysis of three-dimensional classical liquids via density functional flow equations

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RIKEN RQC → Osaka Institute of Technology (April~)

Collaborators

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Abstract

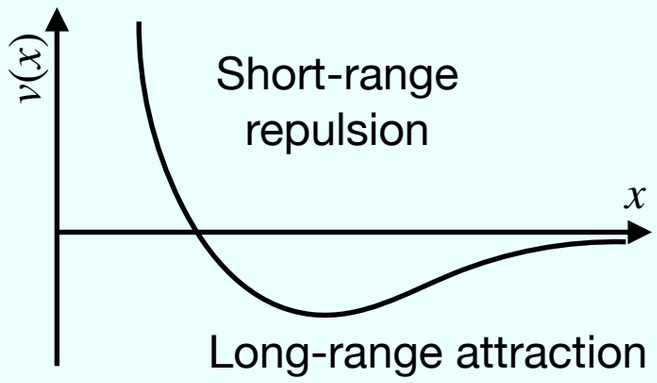
- **The classical version of the density functional framework is a fundamental framework in classical liquid theory.**
  - Application of classical liquid theory: Chemical reaction (solvent)
  - A platform for developing more efficient methods than **molecule dynamics**
    - Integral equation (Hypernetted chain…), BBGKY hierarchy…
- **Method for including higher-order correlation (e.g.): One-parameter evolution equation (Flow equation)**
  - Hierarchical reference theory (HRT): renormalization group *Parola, Reatto, PRA (1985)*
    - But hard-core references are needed.
- **Previous work: Flow equation without hard-core references**

  TY, Haruyama, Sugino, PRE (2021), Talk in DFT2024
  - Flow equation for treating hard cores on an equal footing with attractions
  - 1D numerical demonstration
- **This talk: analysis of 3D classical liquid**
  - To achieve this, an efficient method for evaluating spatial integrals is developed.

Classical liquids

- Consider liquids within statistical mechanics of interacting classical particles

$$H_N = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i} + \sum_{i<j} v_{ij}(\boldsymbol{x}_i, \boldsymbol{x}_j)$$



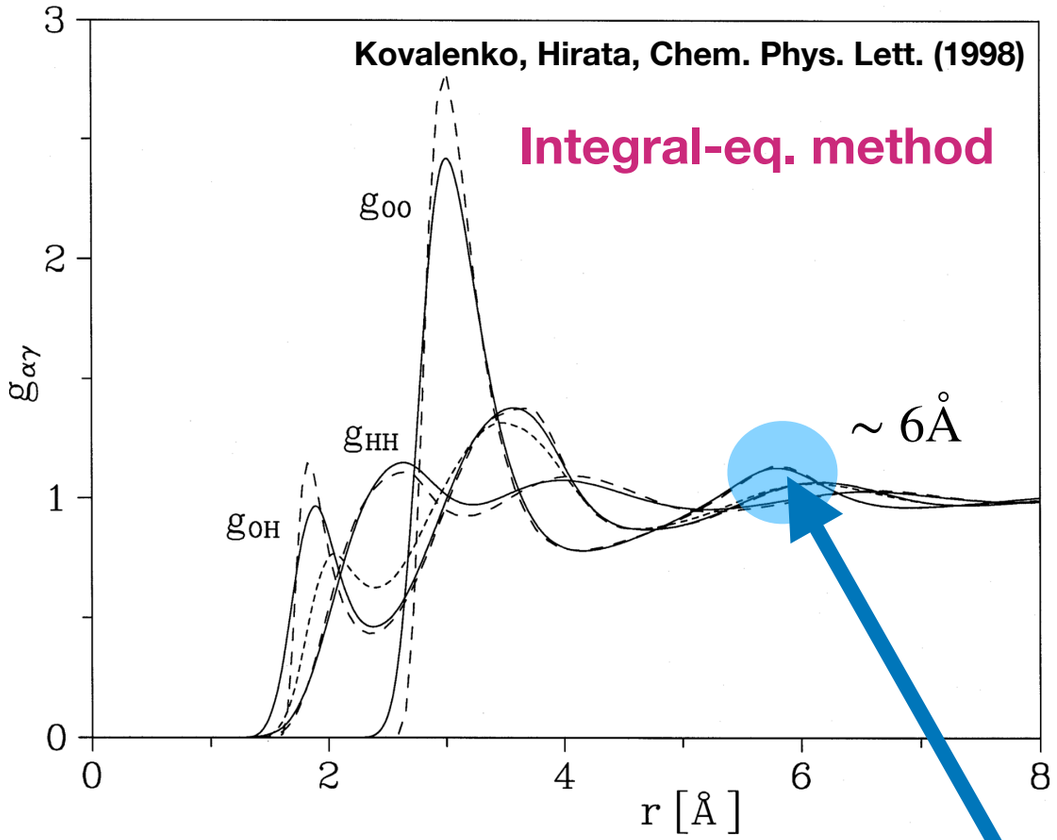
  - E.g., solvent in chemical reactions (water, …)

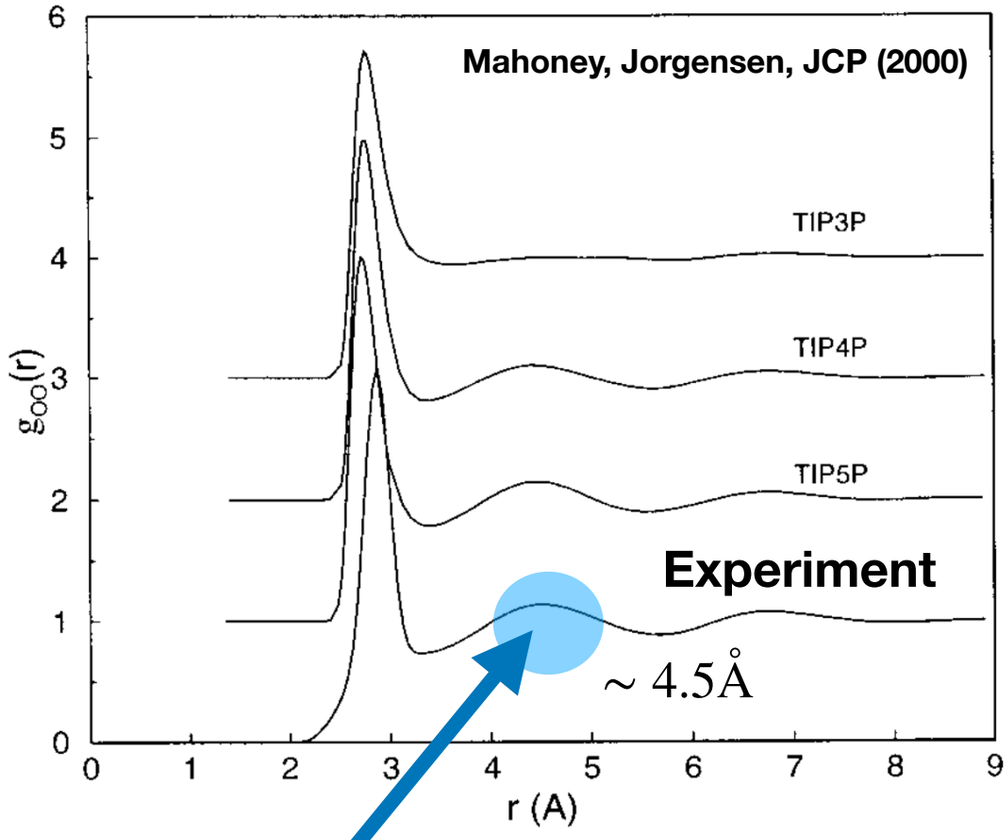
- **Molecular dynamics** is a well-established method but can be inefficient in some cases.
  - E.g., multi-scale analysis, such as combination w/ electronic DFT (e.g., battery)

- **The density functional framework** serves as a platform for alternative methods.
  - DOF of the system: $\{\boldsymbol{x}_i\}_{i=1}^{N} \Leftrightarrow \rho(\boldsymbol{x}) = \sum_{i=1}^{N} \delta(\boldsymbol{x} - \boldsymbol{x}_i)$
    - Thermodynamics & correlations: **Free-energy density functional** $F[\rho]$
  - Integral equation method (hypernetted chain, Percus-Yevick), BBGKY hierarchy, fundamental measure theory, renormalization group, machine learning…

Classical liquids

How much accuracy can be achieved with the density functional framework remains an open question.





The position of the second peak of g_{OO} is missed.

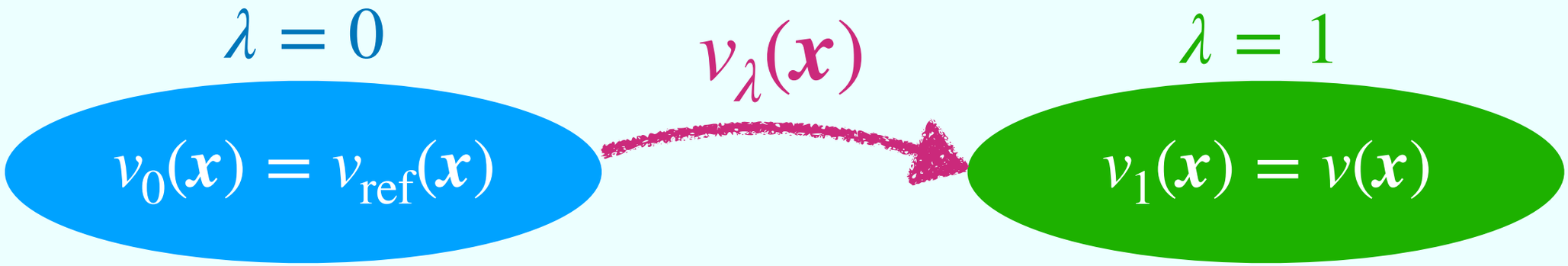
- Thermodynamics & correlations: **Free-energy density functional** $F[\rho]$

- Integral equation method (hypernetted chain, Percus-Yevick), BBGKY hierarchy, fundamental measure theory, renormalization group, machine learning…

One-parameter exact flow equation

I will consider simple liquid cases: $v_{ij}(\boldsymbol{x}_i, \boldsymbol{x}_j) = v(\boldsymbol{x}_i - \boldsymbol{x}_j)$, $m_i = m$.

- **One-parameter flow of $v(\boldsymbol{x})$: Many-body effects are incorporated through differential equations.**



- **Density functional formalism provides an exact & closed description!**

Flow eq. for free-energy density functional $F[\rho]$ w/ temperature β^{-1}

$$\partial_\lambda \beta F_\lambda[\rho] = \frac{1}{2}\int_{\boldsymbol{x},\boldsymbol{x}'} \partial_\lambda \beta v_\lambda(\boldsymbol{x}-\boldsymbol{x}')\left[\rho(\boldsymbol{x})\rho(\boldsymbol{x}') + \left(\frac{\delta^2 \beta F_\lambda[\rho]}{\delta\rho\delta\rho}\right)^{-1}(\boldsymbol{x},\boldsymbol{x}') - \rho(\boldsymbol{x})\delta(\boldsymbol{x}-\boldsymbol{x}')\right]$$

Parola, Reatto, PRA (1985), TY, Haruyama, Sugino, PRE (2021)

***quantum cases:** Polonyi, Sailer (2002), Schwenk, Polonyi (2004), Kemler, Braun (2013), Liang, Niu, Hatsuda (2018), Kemler, Pospiech, Braun (2017), TY, Yoshida, Kunihiro (2019), TY, Yoshida, Kunihiro (2019), TY, Naito (2019), TY, Naito (2021), TY, Kasuya, Yoshida, Kunihiro(2021), TY, Naito (2022)

Hierarchical reference theory (HRT)

Parola, Reatto, PRA (1985)

- **Renormalization-group (RG) inspired flow equation method**
  - $v(\boldsymbol{x})$ is included in an RG-like manner to analyze critical-point properties.

- **The repulsive core has a divergently large UV component;** therefore, it should be considered as the initial reference.
  - $v_\lambda(x) = v_{\text{repulsive}}(x) + v_{\text{att},\lambda}(x)$ Only the attractive part is evolved.
  - Knowledge about the repulsive-core system is needed.

- In general, methods that do not rely on the knowledge of hard-core references are preferred.

→ We have developed a flow-equation method **w/o hard-core references.**

TY, Haruyama, Sugino, PRE (2021), Talk in DFT 2024

Functional Taylor expansion

$$\partial_\lambda \beta F_\lambda[\rho] = \frac{1}{2}\int_{\boldsymbol{x},\boldsymbol{x}'} \partial_\lambda \beta v_\lambda(\boldsymbol{x}-\boldsymbol{x}')\left[\rho(\boldsymbol{x})\rho(\boldsymbol{x}') + \left(\frac{\delta^2 \beta F_\lambda[\rho]}{\delta\rho\delta\rho}\right)^{-1}(\boldsymbol{x},\boldsymbol{x}') - \rho(\boldsymbol{x})\delta(\boldsymbol{x}-\boldsymbol{x}')\right]$$

Functional Taylor expansion for $F_\lambda[\rho]$

Hierarchical eq. for distribution functions

0th order

Free energy

$$\partial_\lambda \frac{\beta F_\lambda}{N} = -\frac{\rho_{\mathrm{hom}}}{2}\int_{\mathbf{r}} \partial_\lambda \beta v_\lambda(\mathbf{r}) g_\lambda^{(2)}(\mathbf{r})$$

Divergent from hard core

1st order

Chemical potential

$$\partial_\lambda \beta\mu_\lambda = \frac{\rho_{\mathrm{hom}}\int_{\mathbf{r}} \partial_\lambda \beta v_\lambda(\mathbf{r}) g_\lambda^{(2)}(\mathbf{r}) + \frac{\rho_{\mathrm{hom}}^2}{2}\int_{\mathbf{r},\mathbf{r}'} \partial_\lambda \beta v_\lambda(\mathbf{r}-\mathbf{r}')\left[g_\lambda^{(3)}(\mathbf{r},\mathbf{r}') - g_\lambda^{(2)}(\mathbf{r}-\mathbf{r}')\right]}{1+\rho_{\mathrm{hom}}\int_{\mathbf{r}}\left[g_\lambda^{(2)}(\mathbf{r})-1\right]}$$

$n(\geq 2)$th order

***n*-particle distribution function**

$$\begin{aligned}\partial_\lambda g_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) = &-\sum_{i<j}^{n}\partial_\lambda\left[\beta v_\lambda(\mathbf{r}_i-\mathbf{r}_j)\right] g_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) \\ &+ n g_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})\partial_\lambda\mu_\lambda + \rho_{\mathrm{hom}}\partial_\lambda\mu_\lambda\int_{\mathbf{r}}\left[g_\lambda^{(n+1)}(\mathbf{r}_1,\cdots,\mathbf{r}_n,\mathbf{r}) - g_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})\right] \\ &-\rho_{\mathrm{hom}}\int_{\mathbf{r}}\sum_{i=1}^{n}\partial_\lambda\left[\beta v_\lambda(\mathbf{r}-\mathbf{r}_i)\right] g_\lambda^{(n+1)}(\mathbf{r},\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) \\ &-\frac{\rho_{\mathrm{hom}}^2}{2}\int_{\mathbf{r},\mathbf{r}'}\partial_\lambda\left[\beta v_\lambda(\mathbf{r}-\mathbf{r}')\right]\left[g_\lambda^{(n+2)}(\mathbf{r},\mathbf{r}',\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) - g_\lambda^{(2)}(\mathbf{r}-\mathbf{r}')g_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})\right]\end{aligned}$$

Flow eq. for hard core

The divergence is removed when the **cavity distribution functions** are introduced.

$$y_\lambda^{(n)}(\mathbf{r},\cdots,\mathbf{r}_{n-1}) = e^{\beta\sum_{i<j}^{n} v_\lambda(\mathbf{r}_i-\mathbf{r}_j)} g_\lambda^{(n)}(\mathbf{r},\cdots,\mathbf{r}_{n-1})$$

Exact eqs. for cavity distribution functions

0th

$$\partial_\lambda \frac{\beta F_\lambda}{N} = \frac{\rho_{\rm hom}}{2}\int_{\mathbf{r}} \partial_\lambda f_\lambda(\mathbf{r}) y_\lambda^{(2)}(\mathbf{r})$$

1st

$$\partial_\lambda \beta\mu_\lambda = \frac{-\rho_{\rm hom}\int_{\mathbf{r}} \partial_\lambda f_\lambda(\mathbf{r}) y_\lambda^{(2)}(\mathbf{r}) - \frac{\rho_{\rm hom}^2}{2}\int_{\mathbf{r},\mathbf{r}'} \partial_\lambda f_\lambda(\mathbf{r}-\mathbf{r}')\left[e^{-\beta v_\lambda(\mathbf{r})-\beta v_\lambda(\mathbf{r}')} y_\lambda^{(3)}(\mathbf{r},\mathbf{r}') - y_\lambda^{(2)}(\mathbf{r}-\mathbf{r}')\right]}{1+\rho_{\rm hom}\int_{\mathbf{r}}\left[e^{-\beta v_\lambda(\mathbf{r})} y_\lambda^{(2)}(\mathbf{r}) - 1\right]}$$

No divergence!
(Only Mayer function $f_\lambda(\mathbf{r},\mathbf{r}') = e^{-\beta v_\lambda(\mathbf{r},\mathbf{r}')} - 1$ appears)

Method w/o hard-core reference!

nth

$$\partial_\lambda y_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) = \partial_\lambda\beta\mu_\lambda\left(n y_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) + \rho_{\rm hom}\int_{\mathbf{r}}\left[e^{-\beta\sum_i^{n-1} v_\lambda(\mathbf{r}_i-\mathbf{r})-\beta v_\lambda(\mathbf{r})} y_\lambda^{(n+1)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1},\mathbf{r}) - y_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})\right]\right)$$
$$+\rho_{\rm hom}\int_{\mathbf{r}} \partial_\lambda\left[e^{-\beta\sum_i^{n-1} v_\lambda(\mathbf{r}_i-\mathbf{r})-\beta v_\lambda(\mathbf{r})}\right] y_\lambda^{(n+1)}(\mathbf{r},\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})$$
$$+\frac{\rho_{\rm hom}^2}{2}\int_{\mathbf{r},\mathbf{r}'} \partial_\lambda f_\lambda(\mathbf{r}-\mathbf{r}')\left[e^{-\beta\sum_i^{n-1} v_\lambda(\mathbf{r}_i-\mathbf{r})-\beta\sum_i^{n-1} v_\lambda(\mathbf{r}_i-\mathbf{r}')-\beta v_\lambda(\mathbf{r})-\beta v_\lambda(\mathbf{r}')} y_\lambda^{(n+2)}(\mathbf{r},\mathbf{r}',\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) - y_\lambda^{(2)}(\mathbf{r}-\mathbf{r}') y_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})\right]$$

The repulsive reference is unnecessary.

We use the free-gas reference $v_0 = 0$.

$$\beta F_0[\rho] = \int_{\boldsymbol{x}} \rho(\boldsymbol{x})\Big(\ln\left(\Lambda^3\rho(\boldsymbol{x})\right) - 1\Big)$$

Flow eq. for hard core

The divergen
are introduce

We close the hierarchy using
Kirkwood superposition approximation (KSA)

Kirkwood, JCP (1935)

- Ignorance of mean many-body potential
- Exact for low densities

$$y_\lambda^{(3)}(\mathbf{r},\mathbf{r}_1) \approx y_\lambda^{(2)}(\mathbf{r}_1)y_\lambda^{(2)}(\mathbf{r})y_\lambda^{(2)}(\mathbf{r}-\mathbf{r}_1)$$

$$y_\lambda^{(4)}(\mathbf{r},\mathbf{r}',\mathbf{r}_1) \approx y_\lambda^{(2)}(\mathbf{r})y_\lambda^{(2)}(\mathbf{r}')y_\lambda^{(2)}(\mathbf{r}_1)y_\lambda^{(2)}(\mathbf{r}-\mathbf{r}')y_\lambda^{(2)}(\mathbf{r}'-\mathbf{r}_1)y_\lambda^{(2)}(\mathbf{r}_1-\mathbf{r})$$

Exact eqs. for

0th

$$\partial_\lambda \frac{\beta F_\lambda}{N} = \frac{\rho_{\mathrm{hom}}}{2} \int_{\mathbf{r}}$$

1st

$$\partial_\lambda \beta\mu_\lambda = \frac{-\rho_{\mathrm{hom}}\int_{\mathbf{r}} \partial_\lambda f_\lambda(\mathbf{r}) y_\lambda^{(2)}(\mathbf{r}) - \frac{\rho_{\mathrm{hom}}^2}{2}\int_{\mathbf{r},\mathbf{r}'} \partial_\lambda f_\lambda(\mathbf{r}-\mathbf{r}')\left[e^{-\beta v_\lambda(\mathbf{r})-\beta v_\lambda(\mathbf{r}')} y_\lambda^{(3)}(\mathbf{r},\mathbf{r}') - y_\lambda^{(2)}(\mathbf{r}-\mathbf{r}')\right]}{1+\rho_{\mathrm{hom}}\int_{\mathbf{r}}\left[e^{-\beta v_\lambda(\mathbf{r})} y_\lambda^{(2)}(\mathbf{r}) - 1\right]}$$

nth

$$\partial_\lambda y_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) = \partial_\lambda\beta\mu_\lambda \left(n y_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) + \rho_{\mathrm{hom}}\int_{\mathbf{r}} \left[e^{-\beta\sum_i^{n-1} v_\lambda(\mathbf{r}_i-\mathbf{r})-\beta v_\lambda(\mathbf{r})} y_\lambda^{(n+1)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1},\mathbf{r}) - y_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})\right]\right)$$

$$+\rho_{\mathrm{hom}}\int_{\mathbf{r}} \partial_\lambda \left[e^{-\beta\sum_i^{n-1} v_\lambda(\mathbf{r}_i-\mathbf{r})-\beta v_\lambda(\mathbf{r})}\right] y_\lambda^{(n+1)}(\mathbf{r},\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})$$

$$+\frac{\rho_{\mathrm{hom}}^2}{2}\int_{\mathbf{r},\mathbf{r}'} \partial_\lambda f_\lambda(\mathbf{r}-\mathbf{r}')\left[e^{-\beta\sum_i^{n-1} v_\lambda(\mathbf{r}_i-\mathbf{r})-\beta\sum_i^{n-1} v_\lambda(\mathbf{r}_i-\mathbf{r}')-\beta v_\lambda(\mathbf{r})-\beta v_\lambda(\mathbf{r}')} y_\lambda^{(n+2)}(\mathbf{r},\mathbf{r}',\mathbf{r}_1,\cdots,\mathbf{r}_{n-1}) - y_\lambda^{(2)}(\mathbf{r}-\mathbf{r}')y_\lambda^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n-1})\right]$$

The repulsive reference is unnecessary.

We use the free-gas reference $v_0 = 0$.

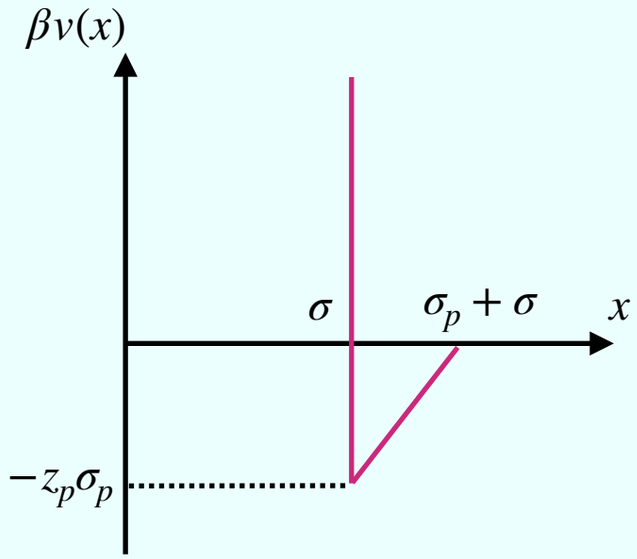
$$\beta F_0[\rho] = \int_{\boldsymbol{x}} \rho(\boldsymbol{x})\Big(\ln\left(\Lambda^3\rho(\boldsymbol{x})\right) - 1\Big)$$

Demonstration w/ 1D exactly solvable model (previous work)

TY, Haruyama, Sugino, PRE (2021)

Better results compared to integral-equation methods are obtained in 1D demonstrations.

Model (hard rod w/ attraction)



Integral-equation method

Ornstein-Zernike eq. $g(\mathbf{x}) = 1 + c(\mathbf{x})$ Direct cor. func. $(\delta^2\beta F/\delta\rho^2 + \cdots)$

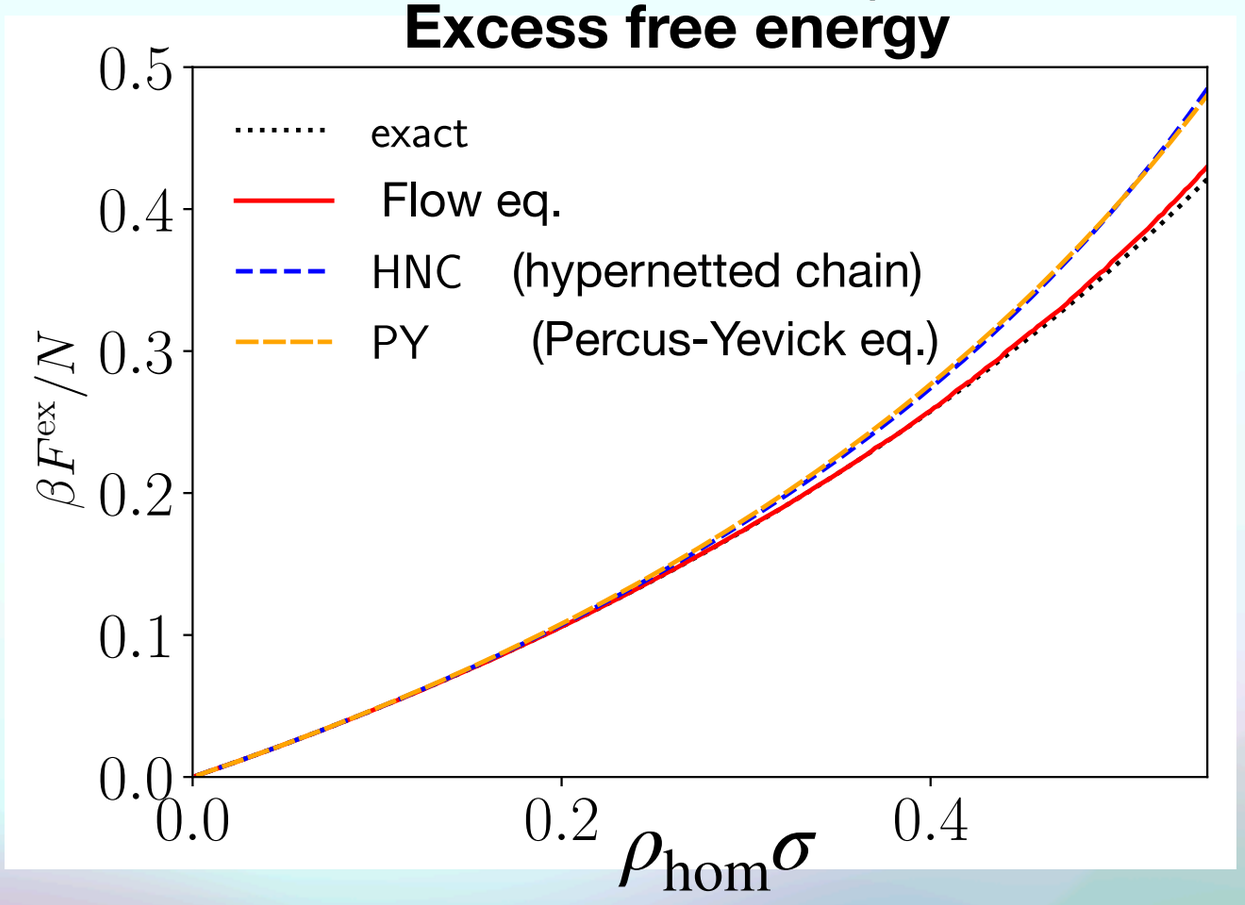
(Schwinger-Dyson eq.)

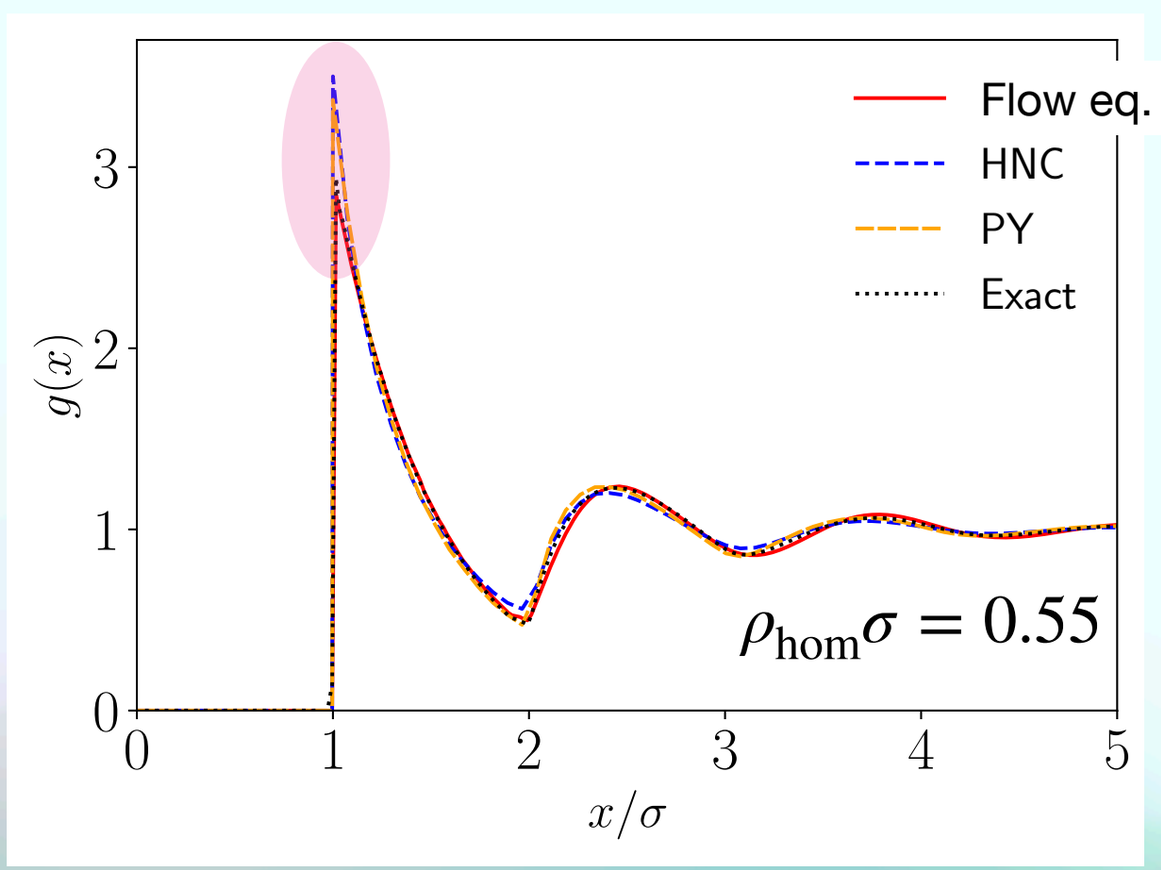
$$+\int d\mathbf{x}' c(|\mathbf{x}-\mathbf{x}'|)\left[g(\mathbf{x}')-1\right]$$

+

Closure (approx.)

- Hypernetted chain (HNC) $g(\mathbf{x}) = e^{-\beta v(\mathbf{x})+g(\mathbf{x})-c(\mathbf{x})-1}$
- Percus-Yevick eq. (PY) $g(\mathbf{x}) = e^{-\beta v(\mathbf{x})}\left[g(\mathbf{x})-c(\mathbf{x})\right]$





Extension to 3D case?

Spatial integrals in 3D cases

Flow eq. w/ KSA

$$h_\lambda^{(2)}(\boldsymbol{r}) = e^{-\beta v(\boldsymbol{r})} y^{(2)}(\boldsymbol{r}) - 1$$

$$\partial_\lambda \ln y_\lambda^{(2)}(\mathbf{r}_1) = \frac{\rho^2}{2} \int d\boldsymbol{r} \int d\boldsymbol{r}' \partial_\lambda f_\lambda(\mathbf{r}-\mathbf{r}') y_\lambda^{(2)}(\mathbf{r}-\mathbf{r}') h_\lambda^{(2)}(\mathbf{r}) h_\lambda^{(2)}(\mathbf{r}-\mathbf{r}_1) h_\lambda^{(2)}(\mathbf{r}') h_\lambda^{(2)}(\mathbf{r}'-\mathbf{r}_1) + \cdots$$

Time consuming spatial integral…

Technique to reduce cost: Legendre expansion!

Baker, Monaghan, JCP (1962)

$$\hat{h}_l(r_1, r_2) = \frac{2l+1}{2} \int_{-1}^{1} dt\, h\left(\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 t}\right) P_l(t)$$

Angular integrals are analytically performed.

Cutoff L for computation

$$\partial_\lambda \ln y_\lambda^{(2)}(r_1) = 8\pi^2\rho^2 \int_0^\infty dr\, r^2 g_\lambda^{(2)}(r) \sum_{l=0}^{\infty} \frac{1}{(2l+1)^2} \int_0^\infty dr'\, r'^2 g_\lambda^{(2)}(r') \hat{R}_l(r, r') \hat{Q}_l(r', r_1) \hat{Q}_l(r, r_1) + \cdots$$

$$\hat{Q}_l(r, r') = \frac{2l+1}{2} \int_{-1}^{1} dt\, g_\lambda\left(\sqrt{r^2 + r'^2 - 2rr't}\right) P_l(t)$$

$$\hat{R}_l(r, r') = \frac{2l+1}{2} \int_{-1}^{1} dt\, \partial_\lambda f_\lambda\left(\sqrt{r^2 + r'^2 - 2rr't}\right) y_\lambda^{(2)}\left(\sqrt{r^2 + r'^2 - 2rr't}\right) P_l(t)$$

- **Dimensions of integral:** $6 \to 2$
- **Summation w.r.t. l is evaluated w/ a cutoff.**

Model

- **Lennard-Jones potential**

$$v(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

- **So far, numerical results have been obtained for $\rho^* \lesssim 0.5$**
  - Our calculation becomes unstable for higher densities.
    - It may not be an issue with the algorithms (such as the discretization of derivatives), but rather a problem with truncation (currently under investigation).

- The setting of flow:

$$f_\lambda(r) = f(r)\theta(\lambda\sigma - r)$$

$$f(r) = e^{-\beta v(r)} - 1$$

MD simulation, Lin, Blanco, Goddard, JCP 119 (2003)

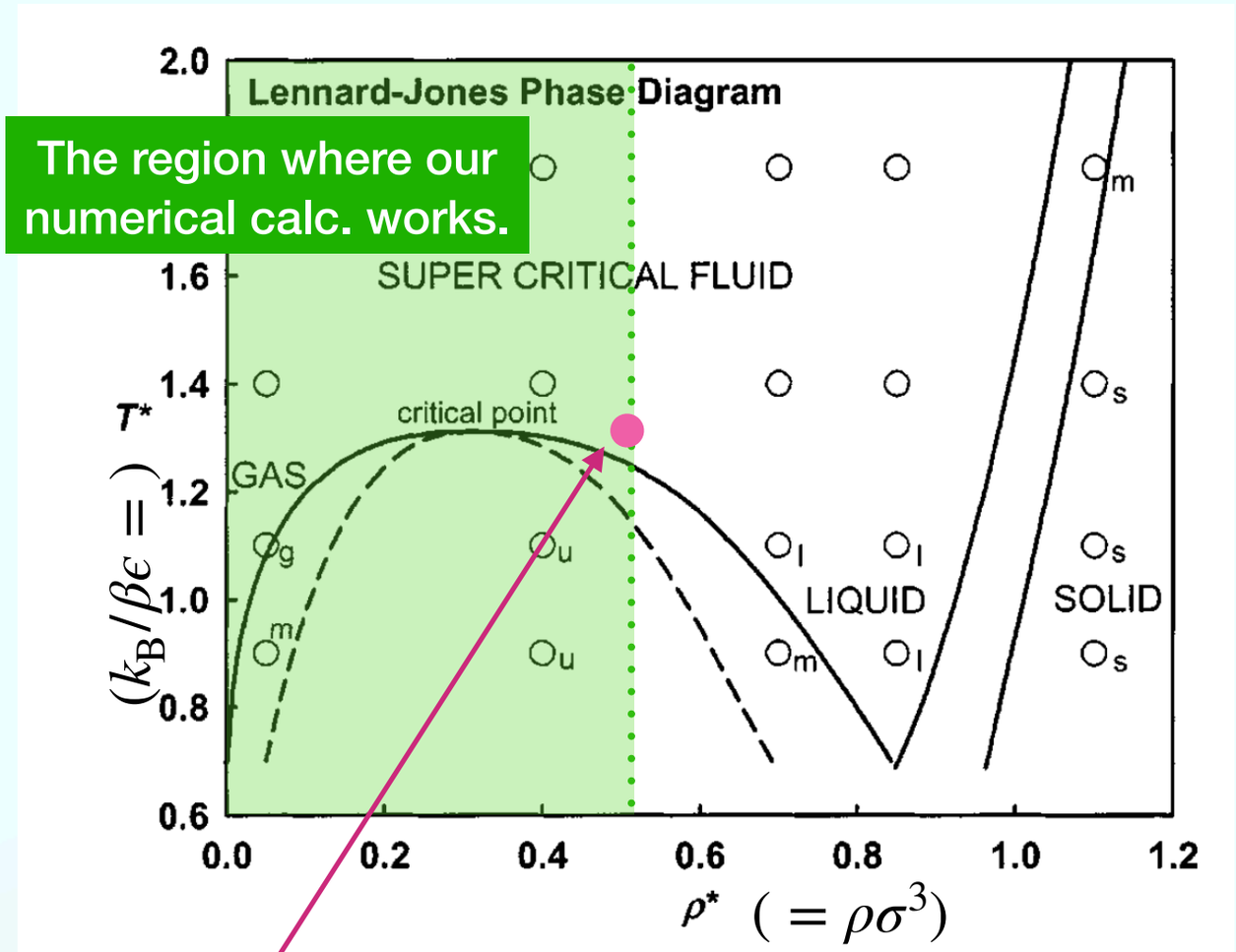


FIG. 3. Phase diagram of Lennard-Jones systems. The open circles represent the states studied in this work. The solid curves indicate the phase boundary (bimodal lines) and the dashed curves are the stability limits (spinodal lines) for liquid–gas equilibrium. Labels are added next to the open circles to help identify the thermodynamic state of each point (*s* for solid, *l* for liquid, *g* for gas, *m* for metastable, and *u* for unstable). For clarity, points in the super- abeled.

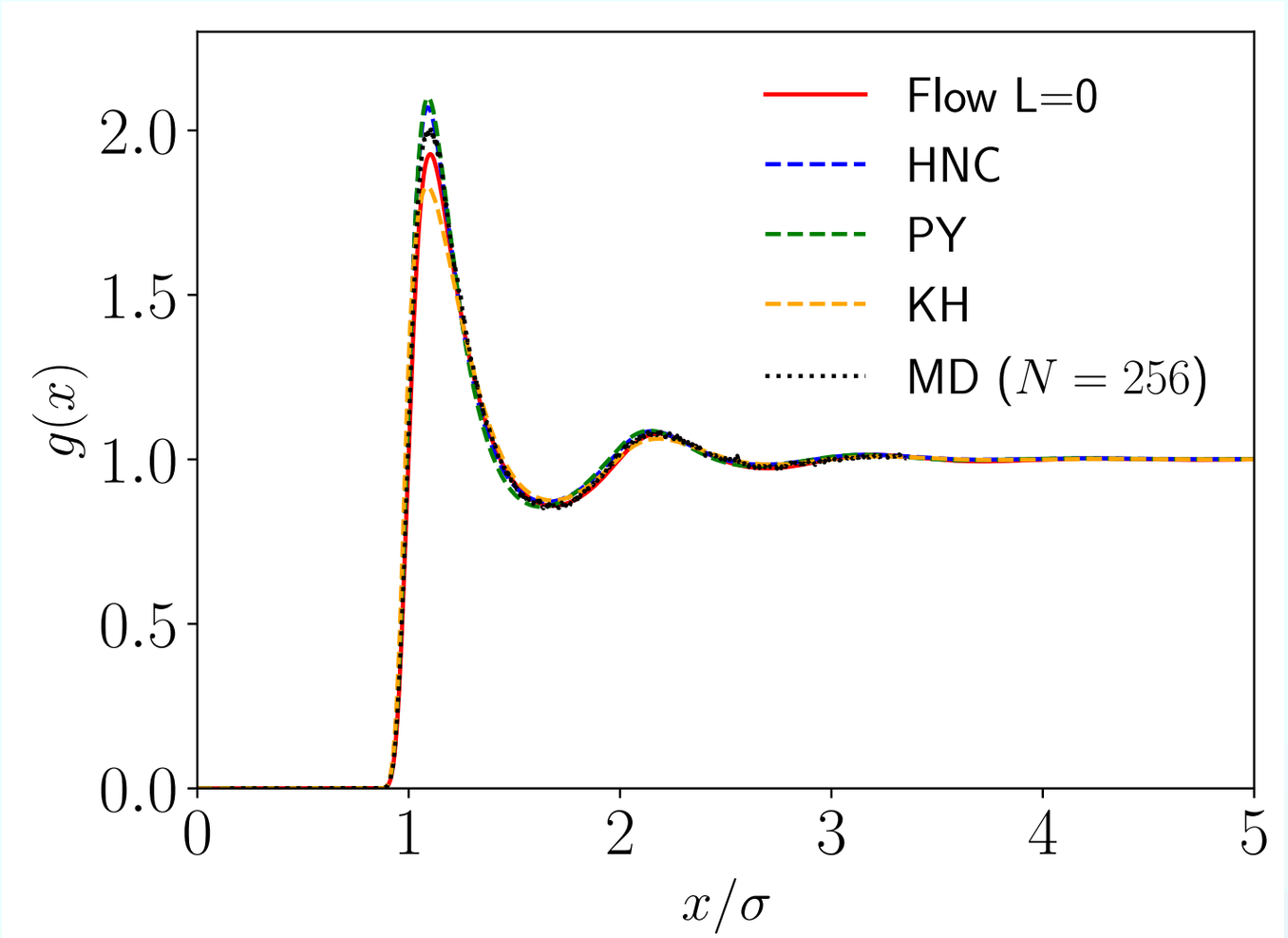
Parameters for calculation

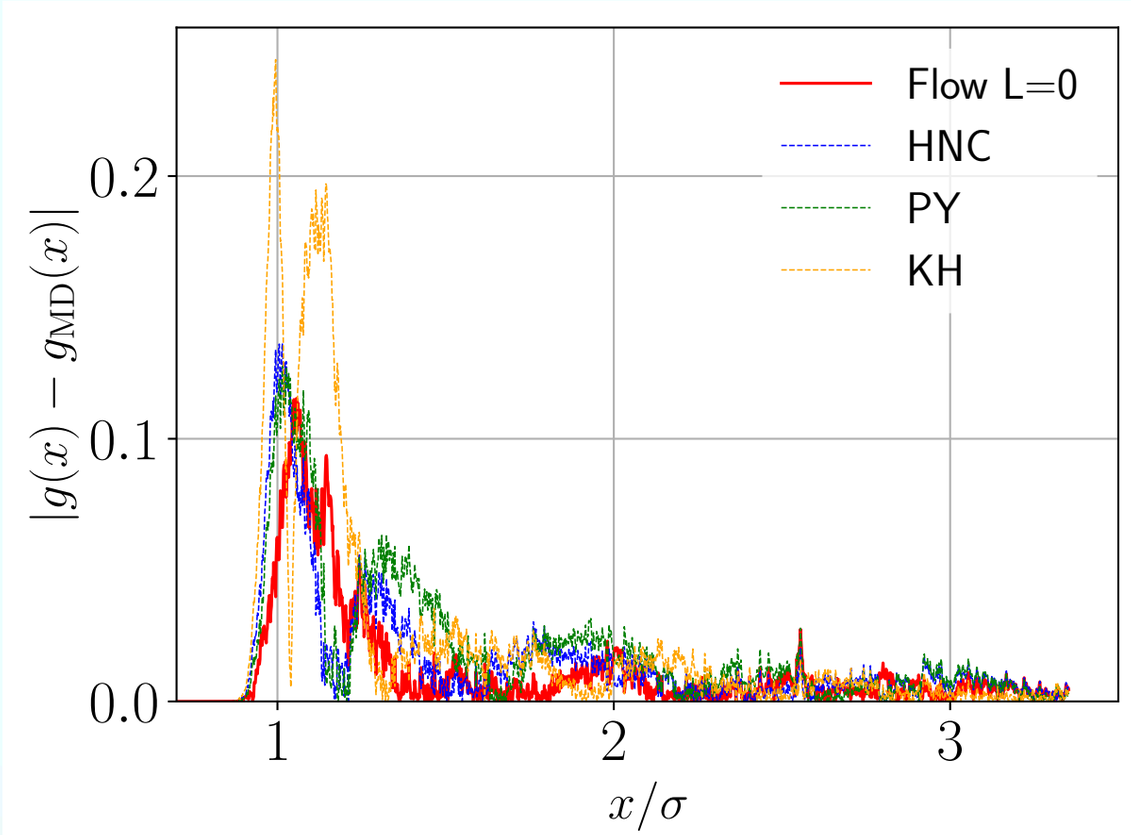
$T^* = 1.3, \rho^* = 0.5$

Result

Comparison of the pair distribution function w/ HNC, PY, KH (Kovalenko-Hirata), and molecule dynamics (MD)

$T^* = 1.3, \rho^* = 0.5$





- Even with $L = 0$ (the cutoff for the series sum), the flow equation method reproduces the MD result.
- The flow equation shows more minor deviations from the MD results than the integral-equation methods.

Summary

- **The classical version of the density functional framework is a fundamental framework in classical liquid theory.**
- **Previous work: Density functional flow equation without hard-core references**

TY, Haruyama, Sugino, PRE (2021)

- **In this talk, I presented an extension to 3D cases.**
  - Lennard-Jones potential
  - Reduction of numerical cost by use of Legendre expansion

Outlook

- Is it possible to achieve stable calculations in a higher-density regime?
- Extension to non-simple liquids (water)