Awakening a Sleeping Beauty. The Chemical-Potential Route to the Equation of State

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Helmholtz free energy

- $F(T,V,N) = E - TS$ (Legendre transformation)

$$= pV + \mu N.$$

- $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$

$$= \frac{S}{k_B\beta^2}\mathrm{d}\beta - p\mathrm{d}V + \mu\mathrm{d}N, \quad \beta \equiv \frac{1}{k_B T}.$$

- Derived thermodynamic quantities:

$$E = \left(\frac{\partial \beta F}{\partial \beta}\right)_{V,N}, \; p = -\left(\frac{\partial F}{\partial V}\right)_{\beta,N}, \; \mu = \left(\frac{\partial F}{\partial N}\right)_{\beta,V}.$$

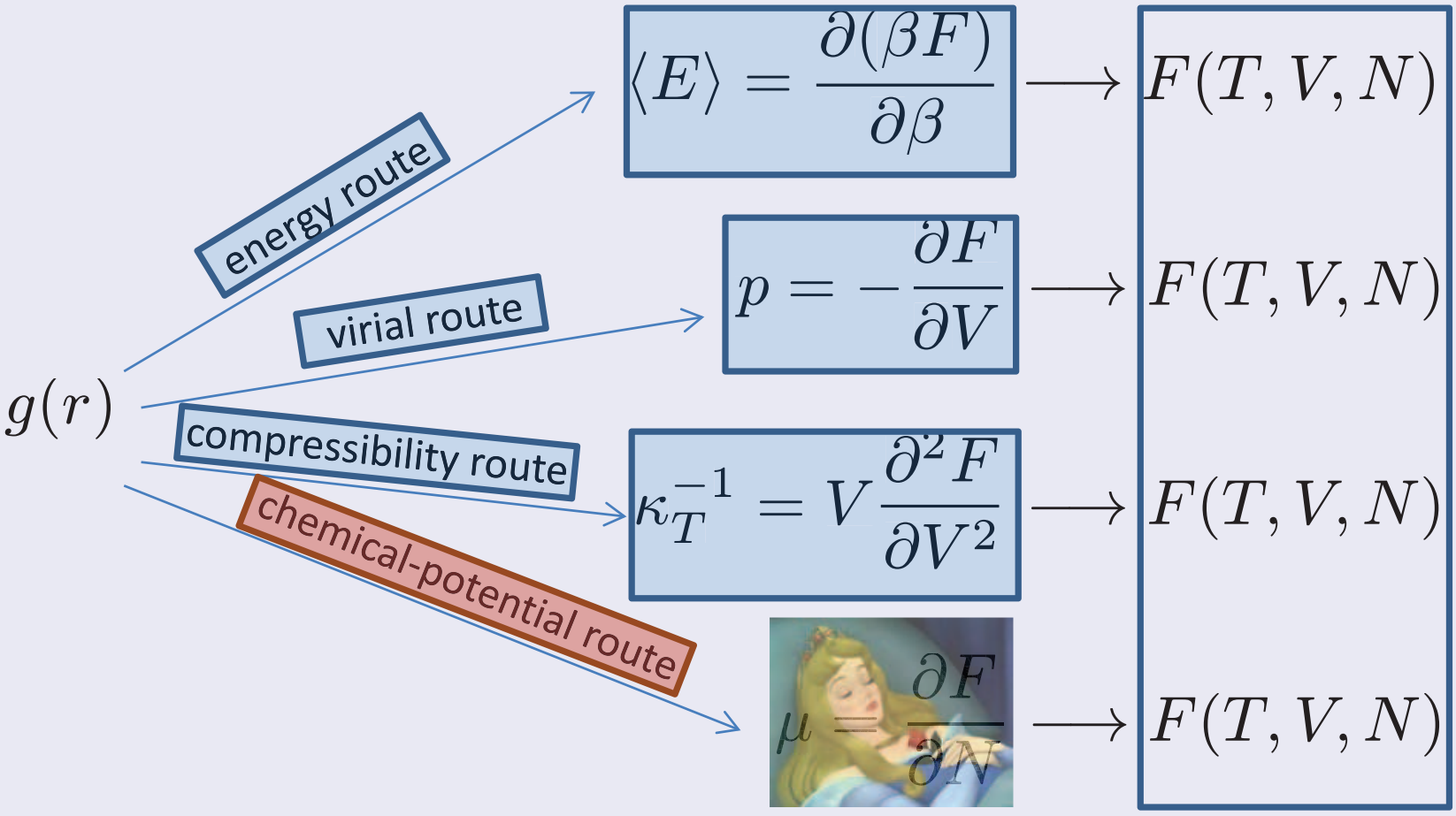
(Equilibrium) Statistical-mechanical roadmaps

1. Partition function:
   $\mathcal{Z}_N(\beta, V) \Rightarrow F(T, V, N) = -k_B T \ln \mathcal{Z}_N(\beta, V)$.
2. Radial distribution function:
   $g(r) \Rightarrow$ thermodynamic quantities $\Rightarrow F(T, V, N)$.

Formally,
Roadmap #1 $\equiv$ Roadmap #2,
but ...
Roadmap #2 is more useful from a practical point of view because

- it is more intuitive,
- the most successful theoretical approximations are based on it,
- and $g(r)$ is an important physical quantity by itself.

Roadmap #2. Thermodynamic routes



Same result?

Our aim

To “awake” the (sleeping) chemical-potential route

Collaborators

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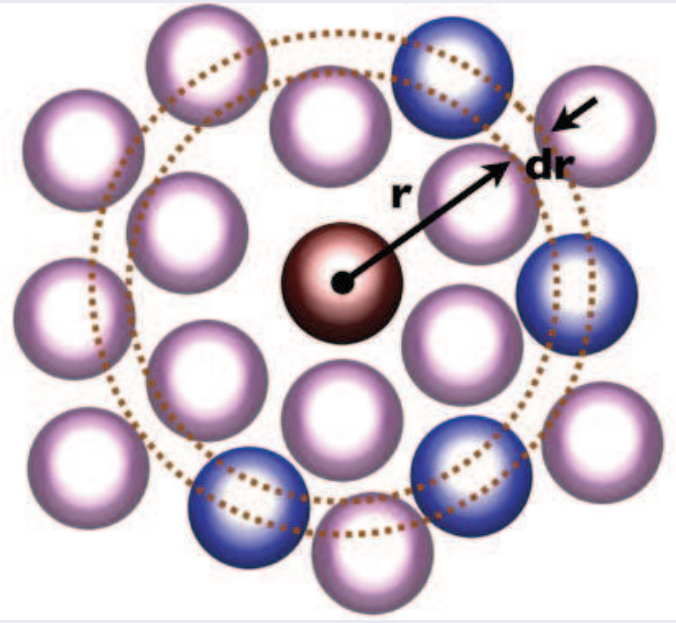
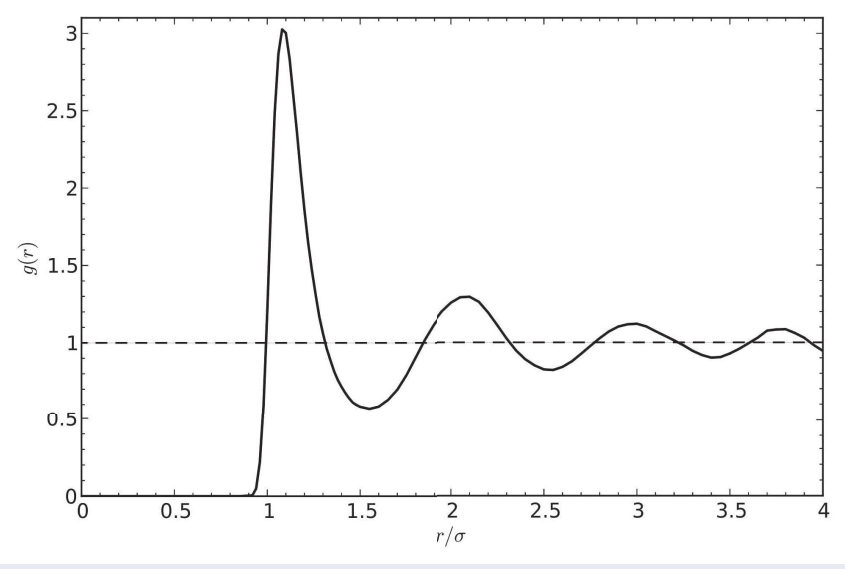
Contents

Physical interpretation of $g(r)$

If a given particle is taken to be at the origin, then the *local* average density at a distance r from that particle is $\rho g(r)$ (where $\rho = N/V$ is the *global* density)





Radial distribution function for a Lennard–Jones fluid at $T^* = 0.71$, $\rho^* = 0.844$.

- Formal definition (identical particles):

$$g(r_{12}) = \frac{V^{-(N-2)}}{Q_N} \int \mathrm{d}\mathbf{r}_3 \cdots \int \mathrm{d}\mathbf{r}_N \, e^{-\beta \Phi_N(\mathbf{r}^N)}.$$

- Configuration integral:

$$Q_N(\beta, V) = V^{-N} \int \mathrm{d}\mathbf{r}^N \, e^{-\beta \Phi_N(\mathbf{r}^N)}.$$

- Total potential energy:

$$\Phi_N(\mathbf{r}^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(r_{ij}) = \frac{1}{2} \sum_{i \neq j} \phi(r_{ij}).$$

- $\rho = N/V =$ number density, $\quad d =$ dimensionality of the system.

Energy, pressure, and isothermal compressibility

- Energy route:

$$\langle E \rangle = \frac{\partial(\beta F)}{\partial \beta} = N \left[\frac{d}{2} k_B T + \frac{\rho}{2} \int \mathbf{dr}\, \phi(r) g(r) \right].$$

- Virial (or pressure) route:

$$p = -\frac{\partial F}{\partial V} = \rho k_B T \left[1 - \frac{\rho \beta}{2d} \int \mathbf{dr}\, r \frac{\mathrm{d}\phi(r)}{\mathrm{d}r} g(r) \right].$$

- Compressibility route:

$$\kappa_T^{-1} = V \frac{\partial^2 F}{\partial V^2} = \frac{\rho k_B T}{1 + \rho \int \mathbf{dr}\, [g(r) - 1]}.$$

Chemical potential

$$\beta\mu^{\text{ex}} = -\frac{\partial \ln Q_N}{\partial N} \to \ln \frac{Q_N(\beta, V)}{Q_{N+1}(\beta, V)}.$$

- N-particle system: $i = 1, 2, \ldots, N$.

$$\Phi_N(\mathbf{r}^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(r_{ij}).$$

- $(N+1)$-particle system: $i = 0, 1, 2, \ldots, N$.

$$\Phi_{N+1}(\mathbf{r}^{N+1}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(r_{ij}) + \sum_{j=1}^{N} \phi(r_{0j}).$$

"Charging" process

- We introduce a *coupling parameter* ξ such that its value $0 \leq \xi \leq 1$ controls the strength of the interaction of particle $i = 0$ to the rest of particles:

$$\phi^{(\xi)}(r_{0j}) = \begin{cases} 0, & \xi = 0, \\ \phi(r_{0j}), & \xi = 1. \end{cases}$$

- The associated total potential energy and configuration integral are

$$\Phi_{N+1}^{(\xi)}(\mathbf{r}^{N+1}) = \Phi_N(\mathbf{r}^N) + \sum_{j=1}^{N} \phi^{(\xi)}(r_{0j}),$$

$$Q_{N+1}^{(\xi)}(\beta, V) = V^{-(N+1)} \int \mathrm{d}\mathbf{r}^{N+1}\, e^{-\beta \Phi_{N+1}^{(\xi)}(\mathbf{r}^{N+1})}.$$

- Thus,

$$\beta\mu^{\text{ex}} = \ln \frac{Q_N(\beta, V)}{Q_{N+1}(\beta, V)} = -\int_0^1 \mathrm{d}\xi \, \frac{\partial \ln Q_{N+1}^{(\xi)}(\beta, V)}{\partial \xi}.$$

- Taking into account that

$$\frac{\partial \ln Q_{N+1}^{(\xi)}}{\partial \xi} = -\frac{\rho\beta V^{-N}}{Q_{N+1}^{(\xi)}} \int \mathrm{d}\mathbf{r}^{N+1} \, e^{-\beta\Phi_{N+1}^{(\xi)}(\mathbf{r}^{N+1})} \frac{\partial \phi^{(\xi)}(r_{01})}{\partial \xi},$$

$$g^{(\xi)}(r_{01}) = \frac{V^{-(N-1)}}{Q_{N+1}^{(\xi)}} \int \mathrm{d}\mathbf{r}_2 \cdots \int \mathrm{d}\mathbf{r}_N \, e^{-\beta\Phi_{N+1}^{(\xi)}(\mathbf{r}^{N+1})},$$

- we get

$$\frac{\partial \ln Q_{N+1}^{(\xi)}}{\partial \xi} = -\frac{\rho\beta}{V} \int \mathrm{d}\mathbf{r}_0 \int \mathrm{d}\mathbf{r}_1 \, g^{(\xi)}(r_{01}) \frac{\partial \phi^{(\xi)}(r_{01})}{\partial \xi}.$$

- Finally [A.S., Phys. Rev. Lett. **109**, 120601 (2012)],

$$\boxed{\mu = k_B T \ln\left(\rho \Lambda^d\right) + \rho \int_0^1 \mathrm{d}\xi \int \mathbf{dr}\, g^{(\xi)}(r) \frac{\partial \phi^{(\xi)}(r)}{\partial \xi}}.$$

- where

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \text{ (thermal de Broglie wavelength).}$$

- The μ-route requires the pair correlation function of an *impurity* (or "solute") coupled to the rest of the particles (the "solvent") via a potential $\phi^{(\xi)}(r)$.
- The final result *should* be independent of the *protocol*

$$0 \to \phi^{(\xi)}(r) \to \phi(r)$$

followed in the charging process.

Extension to mixtures

- Number of particles of species α: N_α.
- Total number of particles: $N = \sum_\alpha N_\alpha$.
- Mole fraction of species α: $x_\alpha = N_\alpha/N$, $\sum_\alpha x_\alpha = 1$.
- Interaction potential between a particle of species α and a particle of species γ: $\phi_{\alpha\gamma}(r)$.
- Radial distribution function for the pair $\alpha\gamma$: $g_{\alpha\gamma}(r)$

- Chemical-potential route [A.S. & R.D. Rohrmann, Phys. Rev. E **87**, 052138, (2013)] :

$$\mu_\nu = k_B T \ln\left(\rho x_\nu \Lambda_\nu^d\right) + \rho \sum_\alpha x_\alpha \int_0^1 \mathrm{d}\xi \int \mathbf{dr}\, g_{\nu\alpha}^{(\xi)}(r) \frac{\partial \phi_{\nu\alpha}^{(\xi)}(r)}{\partial \xi}.$$

- Here, particle $i = 0$ is coupled to a particle of species α via an interaction potential $\phi_{\nu\alpha}^{(\xi)}(r)$ such that

$$\phi_{\nu\alpha}^{(\xi)}(r) = \begin{cases} 0, & \xi = 0, \\ \phi_{\nu\alpha}(r), & \xi = 1. \end{cases}$$

PY equation

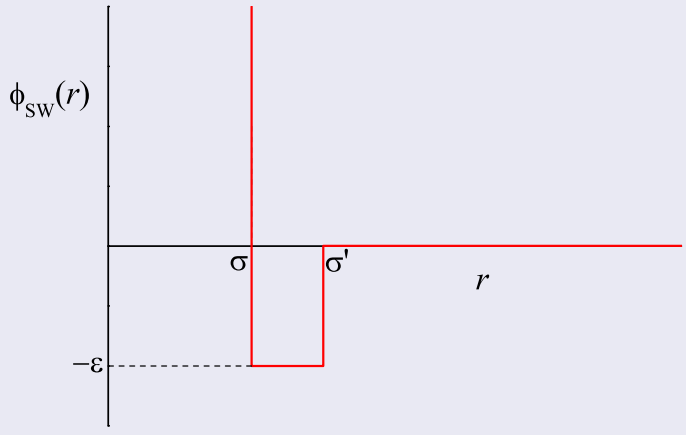
$$y(r) = 1 + \rho \int \mathrm{d}\mathbf{r}' \, \left[g(r') - y(r') \right] \left[g(|\mathbf{r} - \mathbf{r}'|) - 1 \right],$$

where

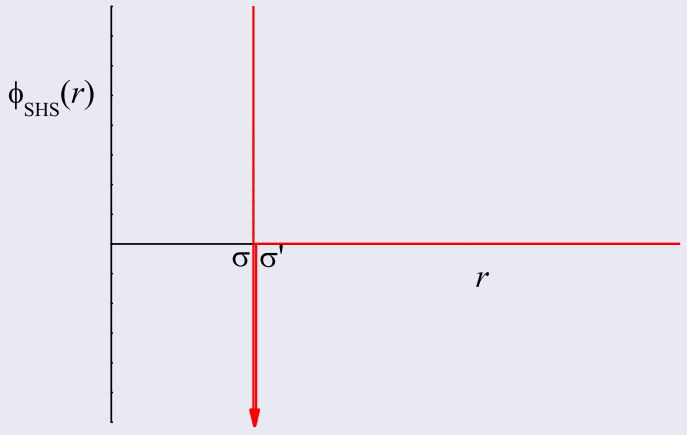
$$y(r) \equiv g(r) e^{\beta \phi(r)} \; : \; \text{cavity function.}$$

- The PY equation admits an *exact* solution for
  - Sticky hard spheres.
  - Additive hard-sphere mixtures.

Square-well potential → "Sticky" hard spheres (Baxter, 1968)



Square-well (SW) potential



Sticky-hard-sphere (SHS) potential

$$\sigma' \to \sigma, \quad \epsilon \to \infty,$$

$$\alpha \equiv \frac{\sigma' - \sigma}{\sigma} e^{\beta\epsilon} = \text{finite ("stickiness" parameter)}.$$

$$e^{-\beta\phi_{SW}(r)} \to e^{-\beta\phi_{SHS}(r)} = \Theta(r-\sigma) + \alpha\sigma\delta(r-\sigma).$$

The μ-route at work

- Coupling of the *impurity* to the solvent:

$$e^{-\beta\phi^{(\xi)}(r)} = \Theta(r-\xi\sigma) + \alpha^{(\xi)}\xi\sigma\delta(r-\xi\sigma), \quad 0 \le \alpha^{(\xi)} \le \alpha.$$

- The function $\alpha^{(\xi)}$ *defines* the coupling protocol.

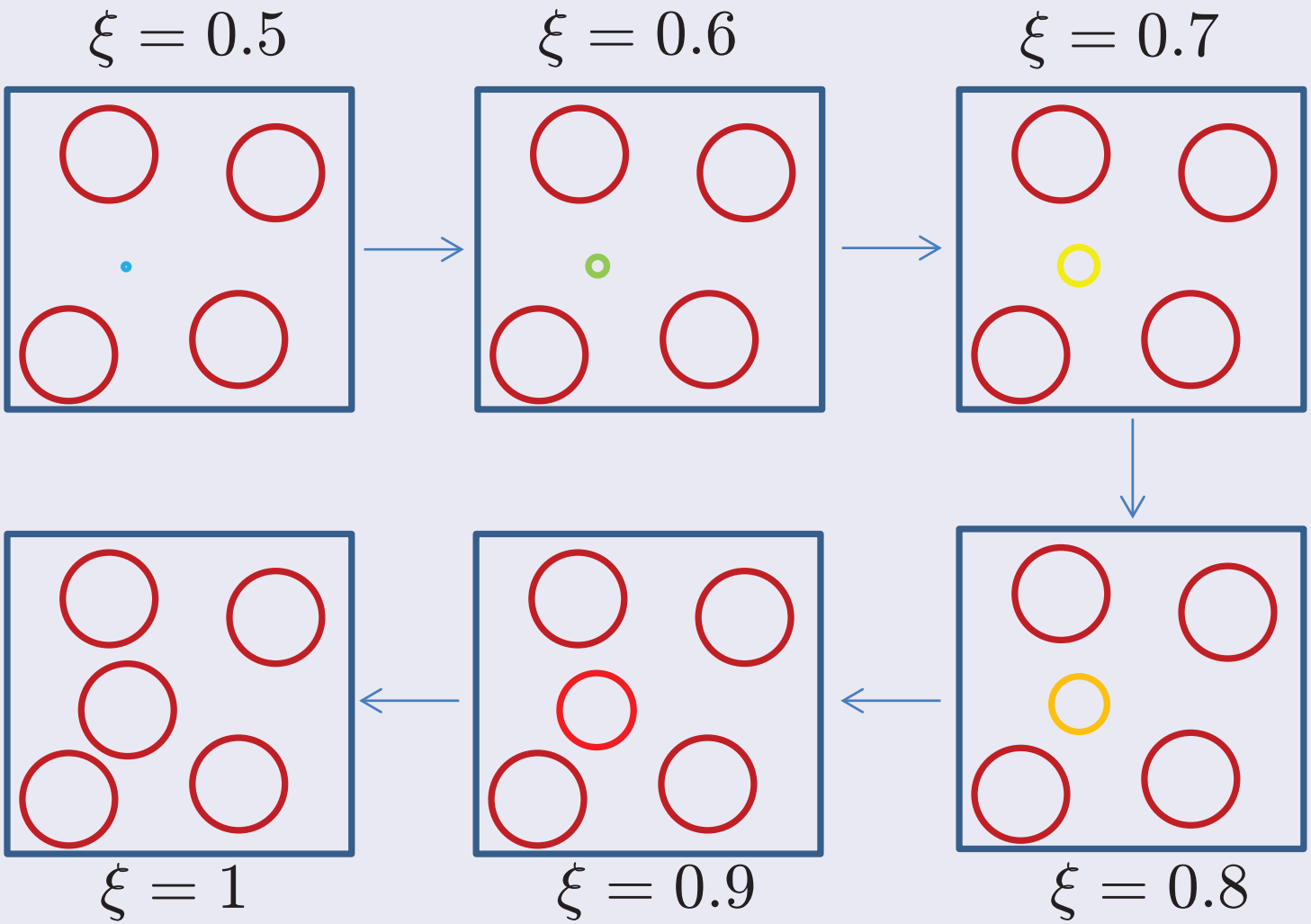
μ-route [R.D. Rohrmann & A.S., unpublished (2014)]

$$\beta\mu^{\text{ex}}(\eta,\alpha) = \underbrace{-\ln(1-\eta)}_{0\le\xi\le\frac{1}{2}} - d2^d\eta \int_{\frac{1}{2}}^{1} \mathrm{d}\xi\, M^{(\xi)}(\eta,\alpha),$$

where

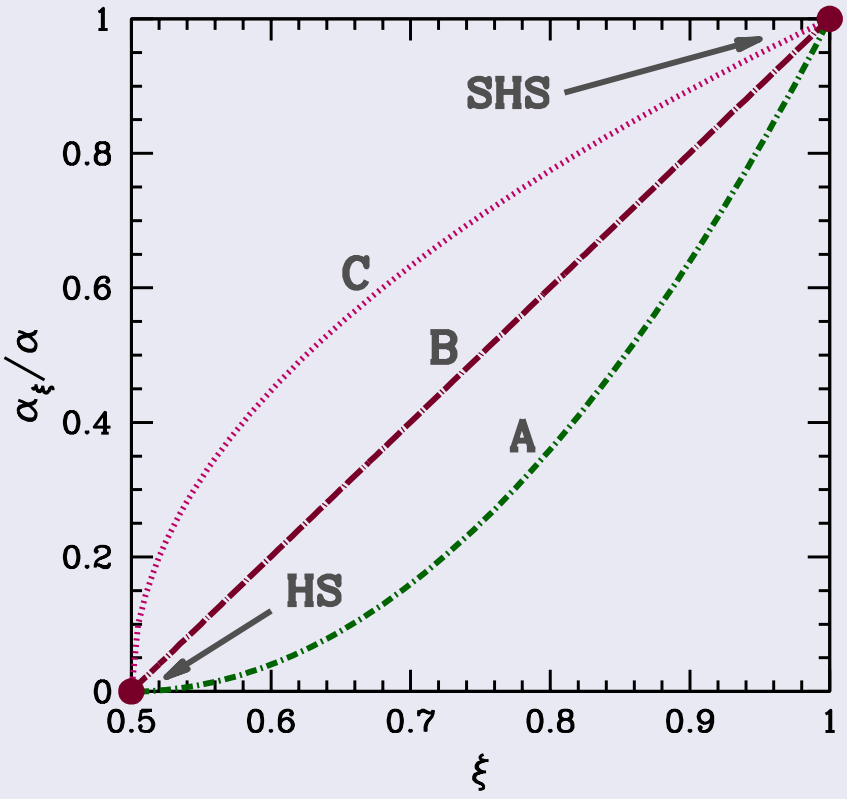
- $\eta =$ packing fraction,
- $M^{(\xi)}(\eta,\alpha) \equiv \frac{\partial\left(\alpha^{(\xi)}-1\right)\xi}{\partial\xi}\xi^{d-1}y^{(\xi)}(\xi\sigma) + \frac{\alpha^{(\xi)}\xi}{\sigma^{d-2}}\left.\frac{\partial\left[r^{d-1}y^{(\xi)}(r)\right]}{\partial r}\right|_{r=\xi\sigma}$.

Sketch of the *charging* process



Three different protocols

$$\alpha^{(\xi)} = \begin{cases} (2\xi-1)^2\alpha, & \text{(A)}, \\ (2\xi-1)\alpha, & \text{(B)}, \\ \sqrt{2\xi-1}\alpha, & \text{(C)}. \end{cases}$$



- If the *exact* $y^{(\xi)}(r)$ were used, the result for μ would be *independent* of the protocol and, of course, would be exact.

PY approximation

- The known exact solution of the PY *approximation* for SHS mixtures ($d = 3$) [J.W. Perram & E.R. Smith, Chem. Phys. Lett. **35**, 138 (1975)] allows one to obtain analytical expressions for
  - $y^{(\xi)}(\xi\sigma)$,
  - $\partial y^{(\xi)}(r)/\partial r\big|_{r=\xi\sigma}$.
- From there, application of the μ-route yields

$$\mu \Rightarrow F \Rightarrow Z \equiv \frac{p}{\rho k_B T} \text{ (equation of state).}$$

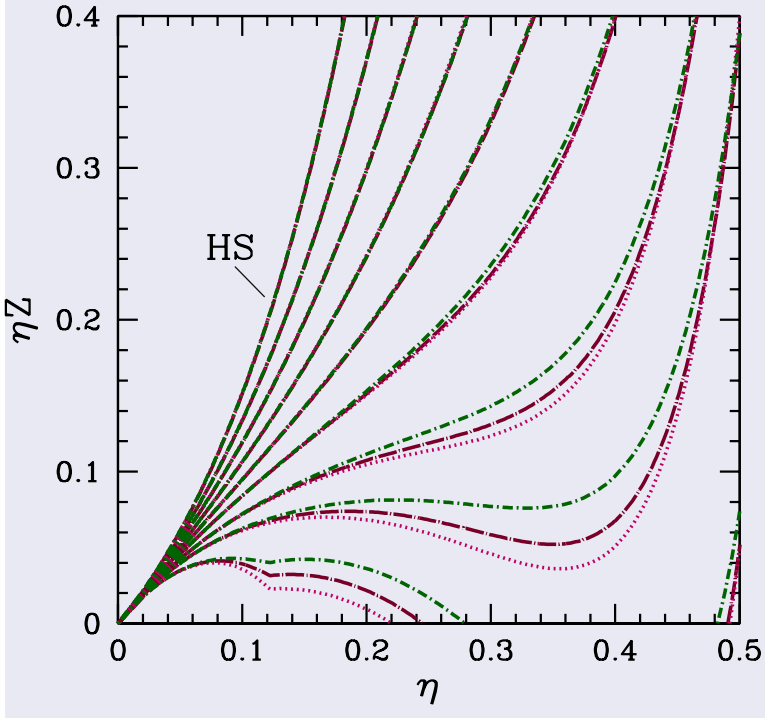
- Not surprisingly, the outcome depends on the protocol (and is different from that of the other three routes).

Results. Weak stickiness limit [R.D. Rohrmann & A.S., unpublished (2014)]

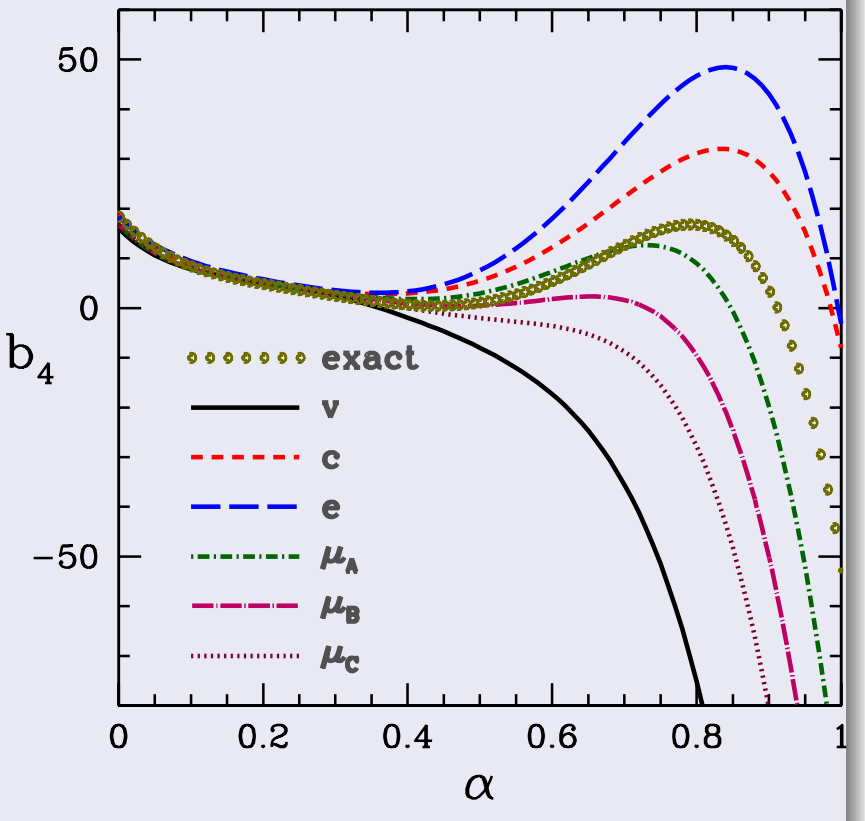
$$Z(\eta,\alpha) = Z_{\mathsf{HS}}(\eta) + Z_1(\eta)\alpha + Z_2(\eta)\alpha^2 + \cdots .$$

	$Z_{\mathsf{HS}}(\eta)$	$Z_1(\eta)$
PY-v	$\frac{1+2\eta+3\eta^2}{(1-\eta)^2}$	$-\frac{12\eta(1+2\eta)}{(1-\eta)^3}$
PY-e	Undetermined	$-\frac{12\eta(1+2\eta)}{(1-\eta)^3}$
PY-c	$\frac{1+\eta+\eta^2}{(1-\eta)^3}$	$-\frac{3\eta(2+\eta)^2}{(1-\eta)^4}$
PY-μ	$-9\frac{\ln(1-\eta)}{\eta} - \frac{16-31\eta}{2(1-\eta)^2}$	$-27\frac{\ln(1-\eta)}{\eta} - \frac{3(18-37\eta+49\eta^2)}{2(1-\eta)^3}$

Results. Finite stickiness [R.D. Rohrmann & A.S., unpublished (2014)]

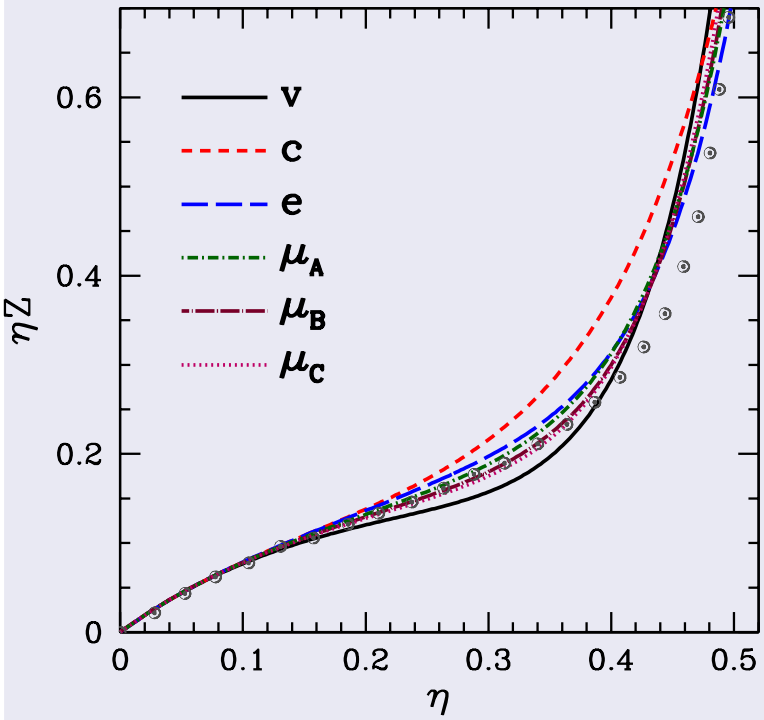


Reduced pressure for increasing stickiness: $\alpha = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.612, 0.703, 0.854.
A: -·-·; B: —·—·; C: · · · .

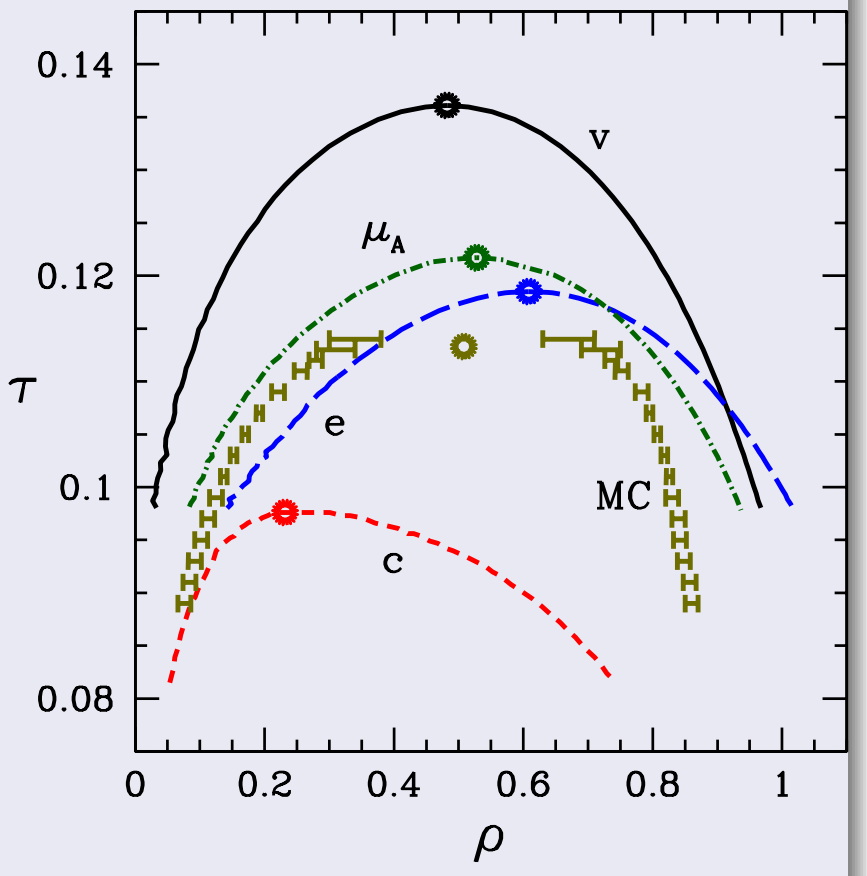


Fourth virial coefficient.

Results. Comparison with simulations [R.D. Rohrmann & A.S., unpublished (2014)]

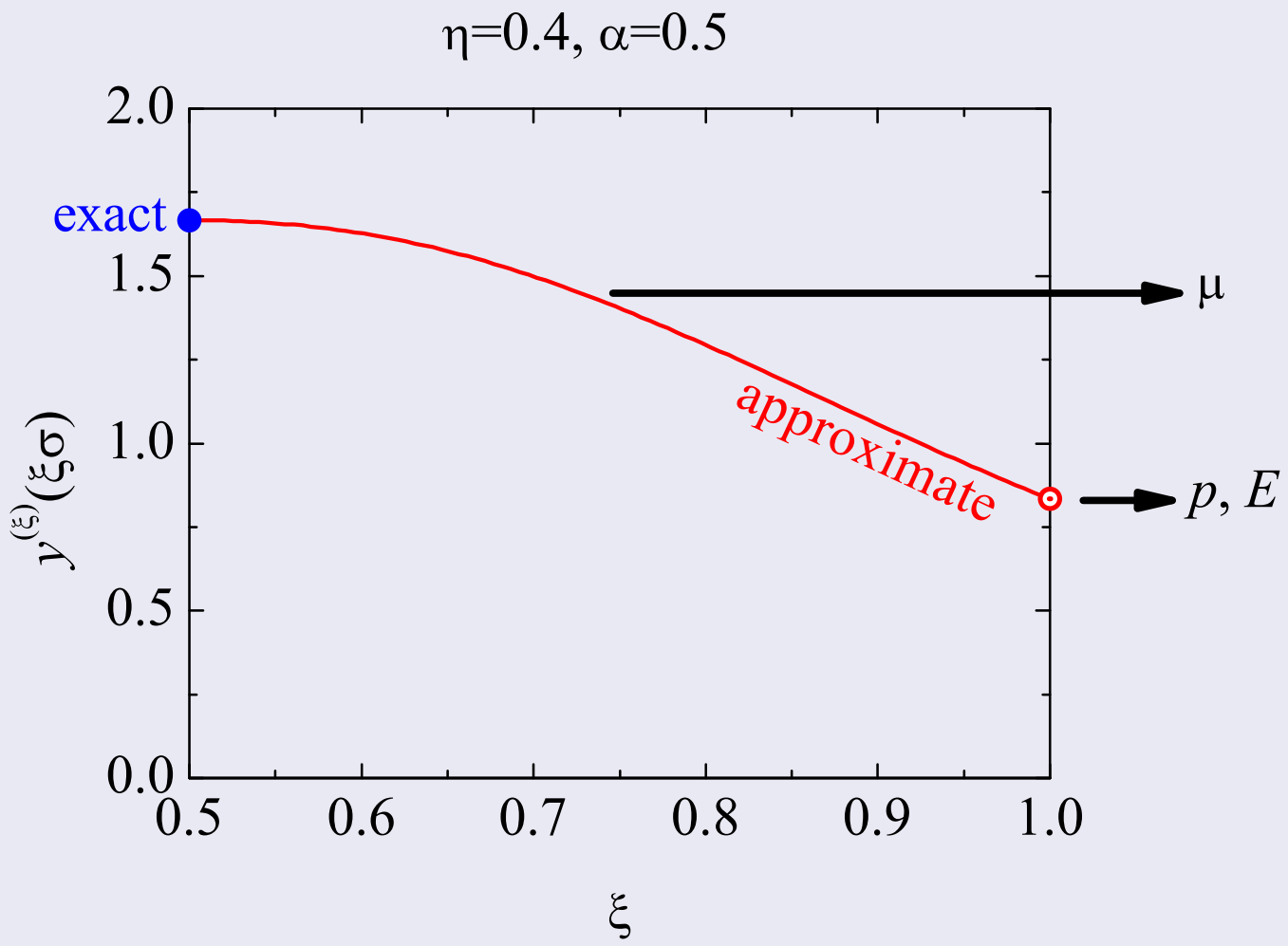


Comparison of PY theoretical curves with Monte Carlo simulations [M.A. Miller & D. Frenkel, J. Chem. Phys. **121**, 535 (2004)] at $\alpha = 0.555$.



Vapor-liquid coexistence curves. Here, $\tau = 1/12\alpha$.

Why the μ-route is more accurate than the virial and energy routes?



Hard spheres

Hard-sphere potential.

$$\phi_{\alpha\gamma}(r) = \begin{cases} \infty, & r < \sigma_{\alpha\gamma}, \\ 0, & r > \sigma_{\alpha\gamma}. \end{cases}$$

$$\frac{\partial e^{-\beta\phi_{\alpha\gamma}(r)}}{\partial r} = \delta\left(r - \sigma_{\alpha\gamma}\right).$$

Additivity condition:

$$\sigma_{\alpha\gamma} = \frac{\sigma_\alpha + \sigma_\gamma}{2}.$$

The μ-route at work

- Coupling of the *impurity* to the solvent:

$$e^{-\beta\phi_{\nu\alpha}^{(\xi)}(r)} = \Theta(r - \sigma_{\nu\alpha}^{(\xi)}), \quad 0 \leq \sigma_{\nu\alpha}^{(\xi)} \leq \sigma_{\nu\alpha}.$$

- Change of variable:

$$\sigma_{\nu\alpha}^{(\xi)} \to \sigma_{0\alpha} \Rightarrow \frac{\partial e^{-\beta\phi_{\nu\alpha}^{(\xi)}(\mathbf{r})}}{\partial\xi}\mathrm{d}\xi = -\delta(r - \sigma_{0\alpha})\mathrm{d}\sigma_{0\alpha}.$$

Chemical potential [A.S. & R.D. Rohrmann, Phys. Rev. E **87**, 052138 (2013)]

$$\beta\mu_\nu = \ln\left(\rho x_\nu \Lambda_\nu^d\right) + d2^d \rho v_d \sum_\alpha x_\alpha \int_0^{\sigma_{\nu\alpha}} \mathrm{d}\sigma_{0\alpha}\, \sigma_{0\alpha}^{d-1} y_{0\alpha}(\sigma_{0\alpha}).$$

PY approximation

- The known exact solution of the PY *approximation* for AHS mixtures $(d = 3)$ [J.L. Lebowitz, Phys. Rev. **133**, A895 (1964)] allows one to obtain

$$y_{\alpha\gamma}(\sigma_{\alpha\gamma}) = \frac{1}{1-\eta} + \frac{3}{2}\frac{\eta}{(1-\eta)^2}\frac{\sigma_\alpha\sigma_\gamma M_2}{\sigma_{\alpha\gamma} M_3}, \qquad M_n \equiv \sum_\alpha x_\alpha \sigma_\alpha^n.$$

- From here, [A.S. & R.D. Rohrmann, Phys. Rev. E **87**, 052138 (2013)]

$$\beta\mu_\nu^{\text{ex}} = -\ln(1-\eta) + \frac{3\eta}{1-\eta}\frac{M_2}{M_3}\left\{\sigma_\nu + \left[\frac{M_1}{M_2} + \frac{3\eta}{2(1-\eta)}\frac{M_2}{M_3}\right]\sigma_\nu^2 + \left[\frac{1}{3M_2} + \frac{\eta}{1-\eta}\frac{M_1}{M_3}\right]\sigma_\nu^3\right\}.$$

An extra source of thermodynamic inconsistency

- From thermodynamics,

$$\mu_\nu = \left(\frac{\partial F}{\partial N_\nu}\right)_{T,V,\{N_{\gamma\neq\nu}\}} \Rightarrow \frac{\partial \mu_\nu}{\partial N_\alpha} = \frac{\partial \mu_\alpha}{\partial N_\nu}.$$

- However, in the PY approximation,

$$\frac{\partial \mu_\nu}{\partial N_\alpha} \neq \frac{\partial \mu_\alpha}{\partial N_\nu}.$$

- How, then, can we obtain F from the μ-route?
  Answer: Use the Gibbs free energy G instead!

$$\sum_\nu N_\nu \mu_\nu = G = -V^2 \frac{\partial (F/V)}{\partial V} \Rightarrow F \Rightarrow Z = \frac{p}{\rho k_B T}.$$

Results

$$Z = \frac{1}{1-\eta} + \frac{3\eta}{(1-\eta)^2}\frac{M_1 M_2}{M_3} + \frac{3\eta^2}{(1-\eta)^3}\frac{M_2^3}{M_3^2} - \frac{3M_2^3}{2M_3^2}\left[\frac{6-15\eta+11\eta^2}{(1-\eta)^3} + 6\frac{\ln(1-\eta)}{\eta}\right].$$

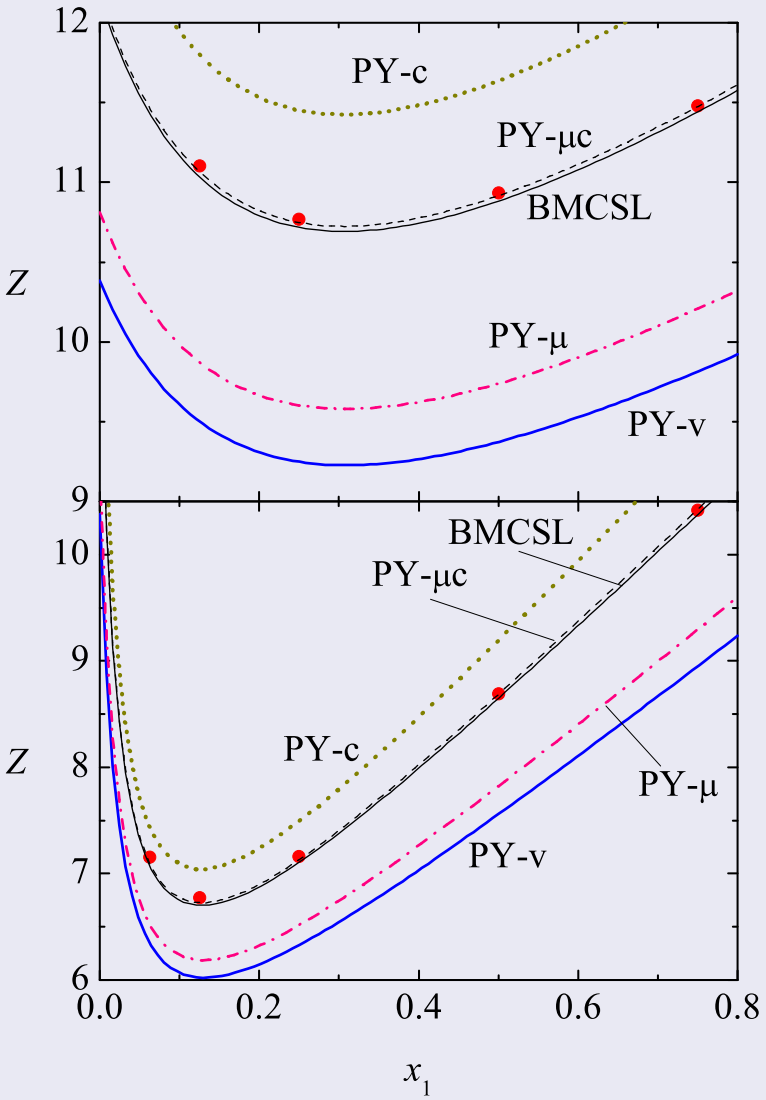
- The μ-route turns out to be more accurate than the virial route (as expected) but less than the compressibility route.
- Standard semi-empirical equation of state:

$$Z_{\text{BMCSL}} = \frac{1}{3}Z_{\text{PY-}v} + \frac{2}{3}Z_{\text{PY-}c}.$$

- In the same spirit we can propose

$$Z_{\text{PY-}\mu c} = \lambda Z_{\text{PY-}\mu} + (1-\lambda)Z_{\text{PY-}c}, \quad \lambda \simeq 0.4.$$

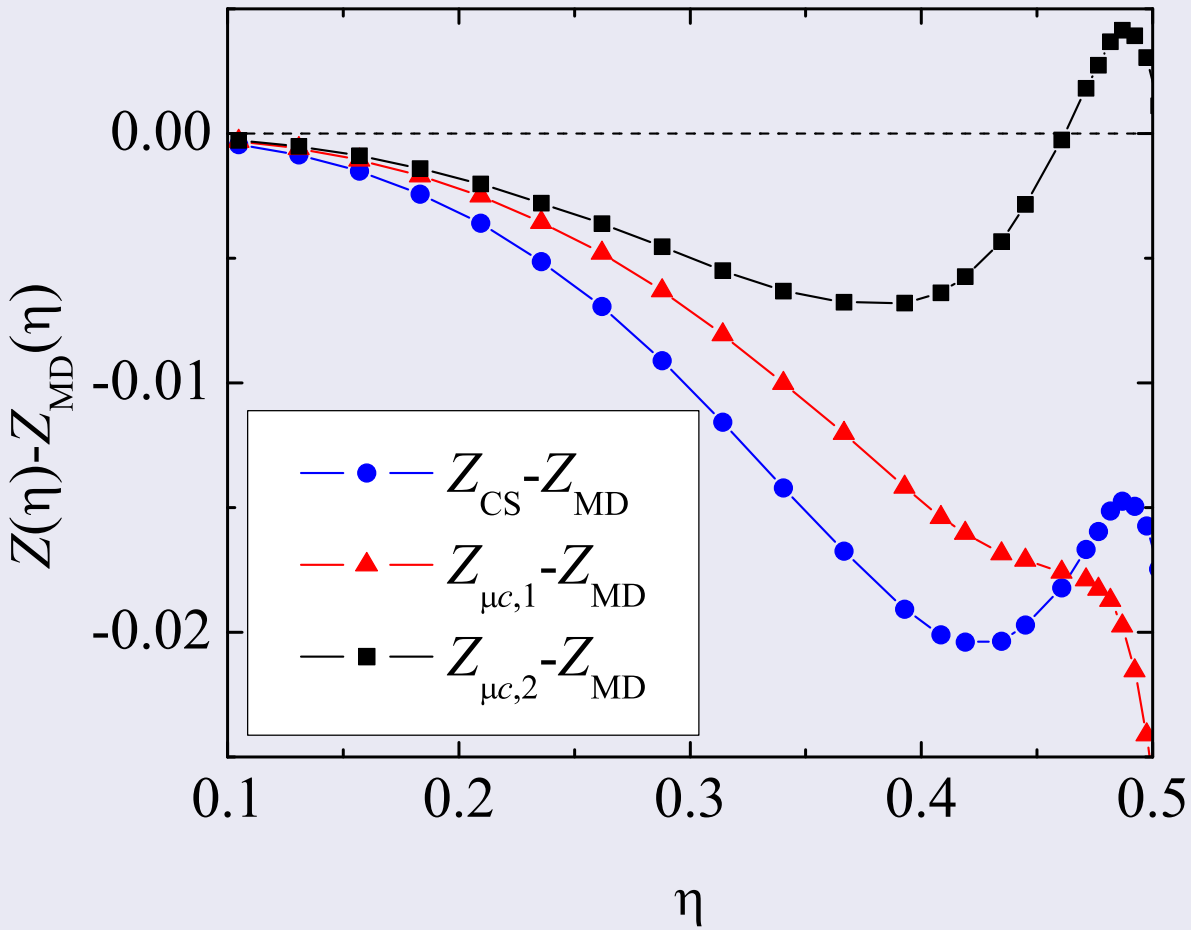
Comparison with computer simulations (binary mixtures)



Compressibility factor Z as a function of the mole fraction x_1 for an AHS binary mixture with a packing fraction $\eta = 0.49$ and a size ratio $\sigma_2/\sigma_1 = 0.6$ (top panel) or $\sigma_2/\sigma_1 = 0.3$ (bottom panel).

The symbols are computer simulation values, while the lines stand for theoretical predictions. Here, $\lambda = \frac{37}{100}$ in $Z_{\text{PY-}\mu c}$.

Comparison with computer simulations (one-component system)



Deviations of theoretical compressibility factors from molecular dynamics results for a one-component HS fluid. The symbols are computer simulation values, while the lines stand for theoretical predictions. Here, $\lambda = \frac{2}{5}$ and $\lambda = \frac{7}{18}$ in $Z_{\text{PY-}\mu c,1}$ and $Z_{\text{PY-}\mu c,2}$, respectively.

Virial expansion

$$Z \equiv \frac{p}{\rho k_B T} = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + \cdots .$$

- Exact results:

$$B_2 = \frac{\pi}{6}\left(3M_1M_2 + M_3\right),$$

$$B_3 = \left(\frac{\pi}{6}\right)^2\left(6M_1M_2M_3 + 3M_2^3 + M_3^2\right).$$

- B_4: Numerical results for *binary* mixtures

  [S. Labík and J. Kolafa, Phys. Rev. E **80**, 051122 (2009)].

PY equation

$$y(r) = 1 + \rho \int \mathbf{dr}' \, \left[g(r') - y(r') \right] \left[g(|\mathbf{r} - \mathbf{r}'|) - 1 \right] .$$

HNC equation

$$\ln y(r) = \rho \int \mathbf{dr}' \, \left[g(r') - 1 - \ln y(r') \right] \left[g(|\mathbf{r} - \mathbf{r}'|) - 1 \right] .$$

- Interestingly,

$$\ln y(r) \to y(r) - 1 \Rightarrow \text{HNC} \to \text{PY}.$$

Results [E. Beltrán-Heredia & A.S., unpublished (2014)]

PY-v
PY-c
PY-μ
HNC-v
HNC-μ

$$\Rightarrow B_4 = \left(\frac{\pi}{6}\right)^3 \left[C_4^{(1)} M_1 M_2 M_3^2 + C_4^{(2)} M_2^3 M_3 + C_4^{(3)} M_3^3\right].$$

Approximation-route	$C_4^{(1)}$	$C_4^{(2)}$	$C_4^{(3)}$	b_4
PY-v	9	6	1	16
PY-μ	9	$\frac{27}{4}$	1	$\frac{57}{4} = 16.75$
PY-c	9	9	1	19
HNC-v	$\frac{27}{2}$	$\frac{27}{2}$	$\frac{3}{2}$	$\frac{57}{2} = 28.5$
HNC-μ	$\frac{27}{2}$	$\frac{27}{2}$	$\frac{11}{8}$	$\frac{227}{8} = 28.375$
HNC-c	–	–	–	$\frac{5623}{420} \simeq 13.388$

- $B_4^{\text{HNC-}c} \neq$ Function of $\{x_i\}$ and $\{\sigma_i\}$ *only* through the size moments $\{M_n\}$.

$$\left(\frac{\pi}{6}\right)^{-3} B_4^{\text{HNC-}c} = \left(\frac{\pi}{6}\right)^{-3} B_4^{\text{PY-}c} + M_1\left(\frac{27}{40}M_1^2M_6 + \frac{63}{40}M_1M_2M_5 - \frac{9}{8}M_1M_3M_4 - \frac{9}{280}M_1M_7 - \frac{9}{8}M_2^2M_4 - \frac{3}{2}M_2M_3^2 + \frac{3}{20}M_2M_6 - \frac{3}{4}M_3M_5 - \frac{3}{28}M_8\right) - M_2\left(\frac{9}{4}M_2^2M_3 + \frac{9}{40}M_2M_5 + \frac{3}{4}M_3M_4 + \frac{3}{280}M_7\right) - \frac{1}{8}M_3M_6 - \frac{1}{84}M_9 + \Delta,$$

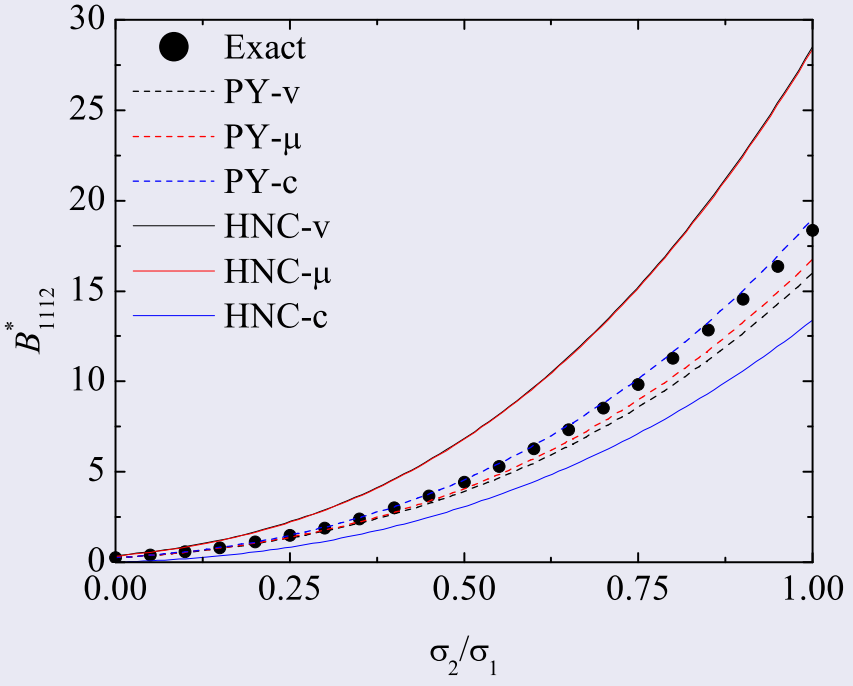
where, for a *binary* mixture (assuming $\sigma_2 \leq \sigma_1$),

$$\Delta = x_1x_2\frac{(\sigma_1-\sigma_2)^5}{105}\left(179M_1M_3 + 174M_2^2 + 25M_4\right) - x_1x_2\frac{(\sigma_1-\sigma_2)^6}{420} \times \left[x_1^2(1039\sigma_1^3 + 393\sigma_1^2\sigma_2 + 75\sigma_1\sigma_2^2 + 5\sigma_2^3) - x_2^2(1039\sigma_2^3 + 393\sigma_2^2\sigma_1 + 75\sigma_2\sigma_1^2 + 5\sigma_1^3)\right].$$

Composition-independent virial coefficients

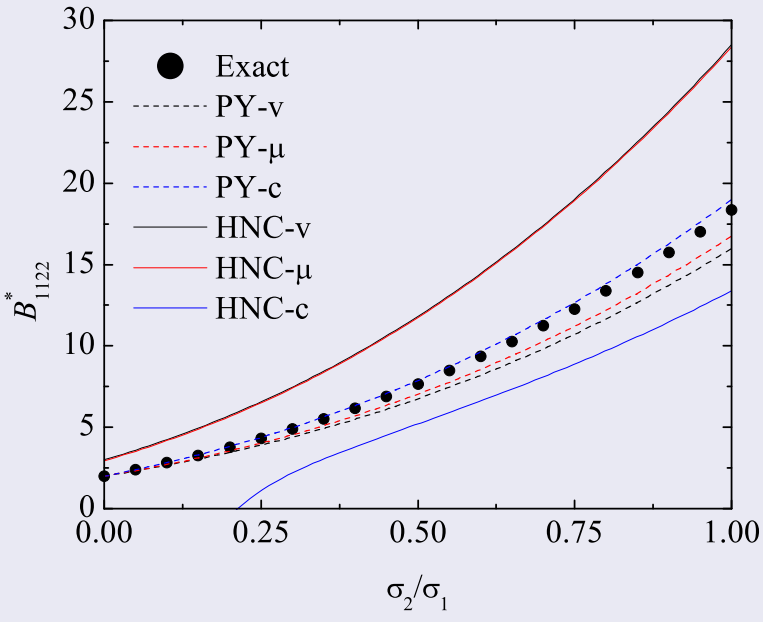
Comparison with (exact) numerical results

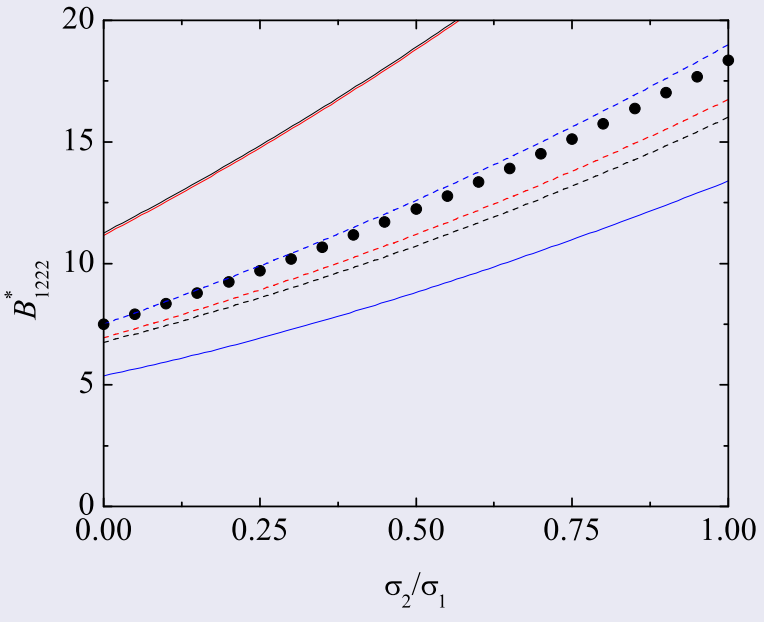
$$B_4 = \sum_{i,j,k,\ell} x_i x_j x_k x_\ell B_{ijk\ell}$$



$$B_{1112} = \left(\tfrac{\pi}{6}\right)^{-3} \sigma_1^{-9} B_{1112}$$

Comparison with (exact) numerical results





$$B_{1122} = \left(\frac{\pi}{6}\right)^{-3} \sigma_1^{-6} \sigma_2^{-3} B_{1122}$$

$$B_{1222} = \left(\frac{\pi}{6}\right)^{-3} \sigma_1^{-3} \sigma_2^{-6} B_{1222}$$

Messages to take home

- The chemical-potential route deserves to be treated on the same footing as the other three standard routes.
- Even in one-component systems, the μ-route requires the impurity-solvent correlation function.
- In approximate theories, the μ-route may yield protocol-dependent results and (in the case of mixtures) may violate the symmetry condition $\partial\mu_\nu/\partial N_\gamma = \partial\mu_\gamma/\partial N_\nu$.
- The μ-route can be useful as a test of the internal consistency of approximate theories and as a guide to construct improved theories.
- Within the PY approximation, the μ-route is typically the most accurate one for attractive interactions (SHS) but is less accurate than the compressibility route for repulsive interactions (HS).
- Future (not yet foreseen) applications can be expected.

Thanks for your attention!