MC Simulation of Fluid Phase Equilibria in Square-Well Fluids: From Bulk to Two-Dimensional Layers

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Motivation and aim

- We study the influence of geometric restrictions on vapour/liquid equilibria and critical data of the square-well fluid as a basic potential model involved in realistic molecular models of complex liquids, such as polymers or aqueous liquids.
- Starting with 3-dim bulk we model the confinement by a series of slit-like pores with decreasing slit widths arriving at 2-dim layers.
- We simulate chemical potential isotherms by canonical MC using (virtual) particle insertion and estimate fluid phase equilibria by thermodynamic integration.
- We analyze finite size effects of chemical potentials and estimate the influence of system size on phase equilibrium data.
- We obtain critical data from vapour/liquid coexistence densities by scaling relations.

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Models under consideration and simulation methods

Hard spheres with square-well (SW) attractions:

$$u_{sw}(r) = \begin{cases} \infty & \text{for} \quad r \leq \sigma \\ -\epsilon & \text{for} \quad \sigma < r \leq \lambda\sigma \\ 0 & \text{for} \quad r > \lambda\sigma \end{cases}$$

Chemical potential μ given by Widom's test particle method:

$$\beta\mu = \ln \rho(\vec{r}) + \ln \Lambda^3 - \ln \left(\langle \exp[-\beta \Delta W_{N+1,N}] \rangle_N \right)_{r_{N+1}} \quad (1)$$

Λ is the deBrogli wavelength, and $\rho = N/V$ the particle density.
$W_N(\vec{r}^N) = U_N(\vec{r}^N) + U_N^{ext}(\vec{r}^N)$ is the potential energy in an external potential $U_N^{ext}(\vec{r}^N)$ and $(< ... >_N)_{r_{N+1}}$ MC average over test particles inserted at $\vec{r}_{N+1}$.

Improved Insertion Methods:

- 'Un-bonded' insertion (Tripathi, Chapman 2003; Vörtler, Kettler 2006)
- Scaled particle MC (Labik, Smith 1994)
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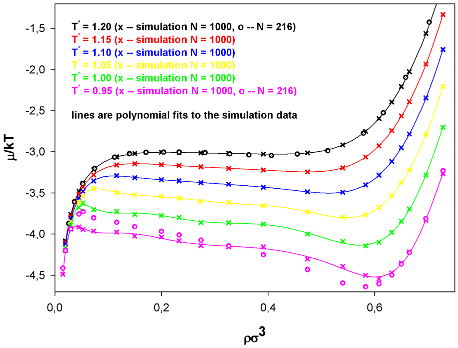
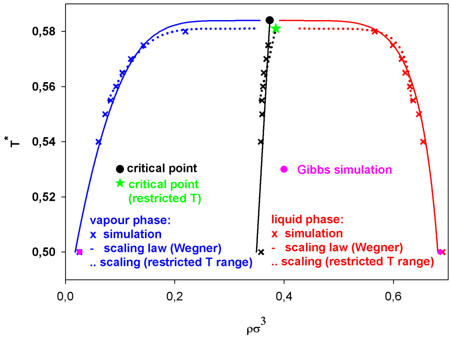
Chemical potential isotherms and phase equilibria

Chemical potential vs. density isotherms
(Comparison of N=1000 and N = 216, SW bulk)



Vapour-liquid equilibrium and critical point
SW monolayer



- Using $\mu(\rho)$ we estimate coexistence data by Gibbs Duhem integration
- Critical T and ρ we obtain from coexistence densities by scaling relations

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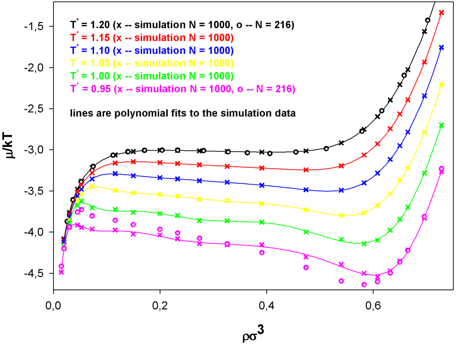

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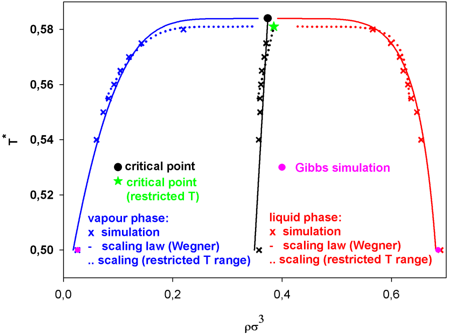

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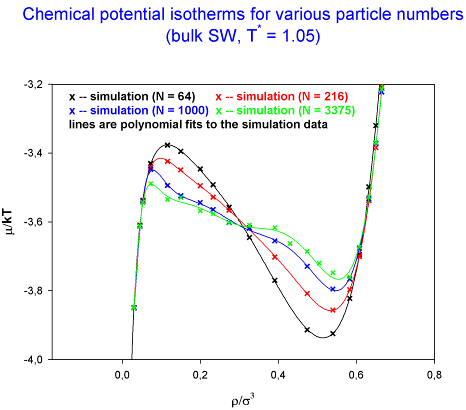
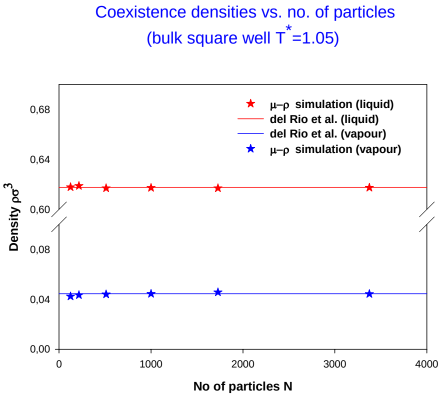
Finite size effects of chemical potential and phase equilibria – Bulk SW





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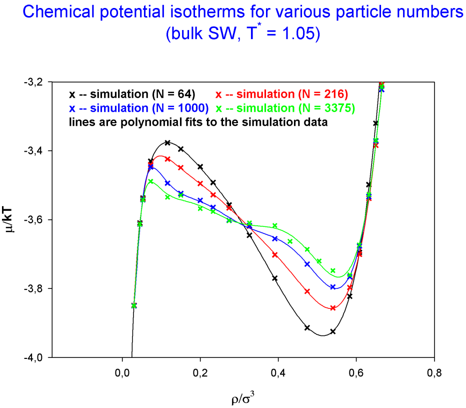

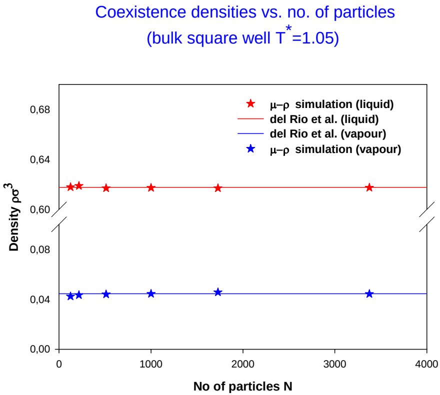

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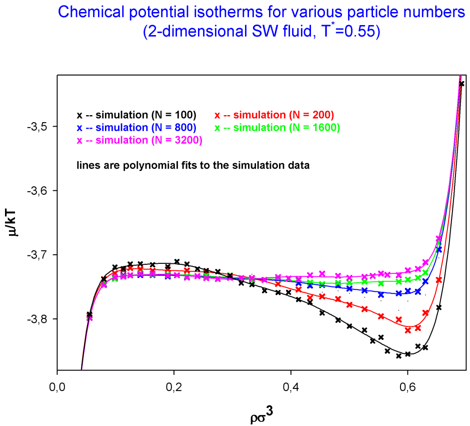
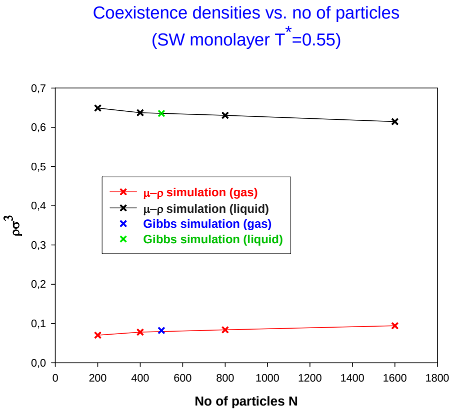


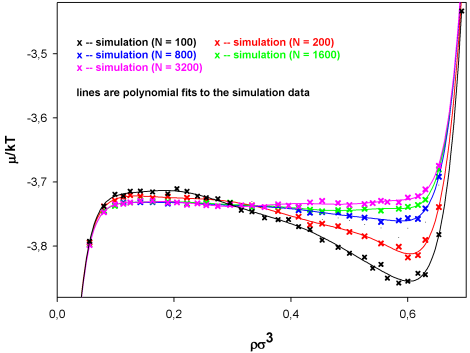


⇒ $\mu(\rho)$ size effects similar to bulk (loops less symmetric and more scattered)

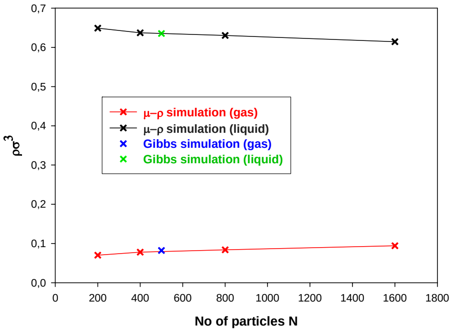
⇒ finite size effects on coexistence properties larger than in the bulk

Finite size effects of chemical potential and phase equilibria – SW monolayer

Chemical potential isotherms for various particle numbers (2-dimensional SW fluid, T^*=0.55)



Coexistence densities vs. no of particles (SW monolayer T^*=0.55)



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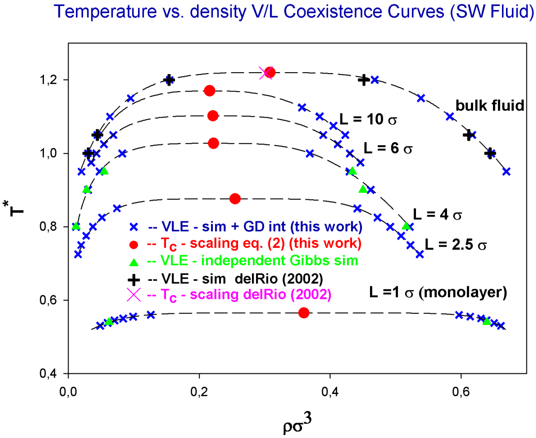
VLE coexistence densities of SW fluid: From bulk to layer



$\Rightarrow$ only weak confinement influence on vapour density
$\Rightarrow$ significant lowering of liquid density
BUT for very narrow slits again increase of ρ_ℓ

Scaling (Wegner expansion) for coexistence densities:

$$\rho_{\ell/v} = \rho_C + C_2(1 - T^*/T^*_C) \pm 0.5 B_0 (1 - T^*/T^*_C)^\beta; \; T < T_C \qquad (2)$$

C_2, B_0 and critical exponent β treated as adjustable parameters

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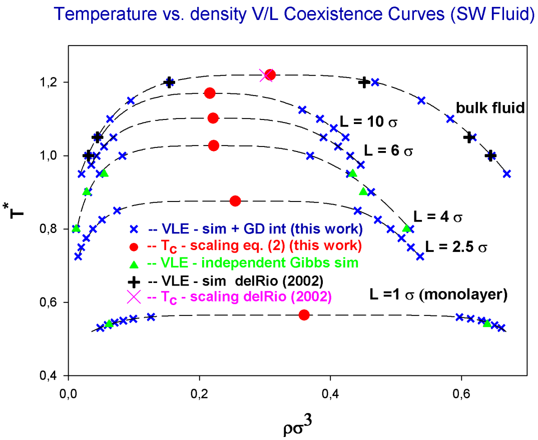

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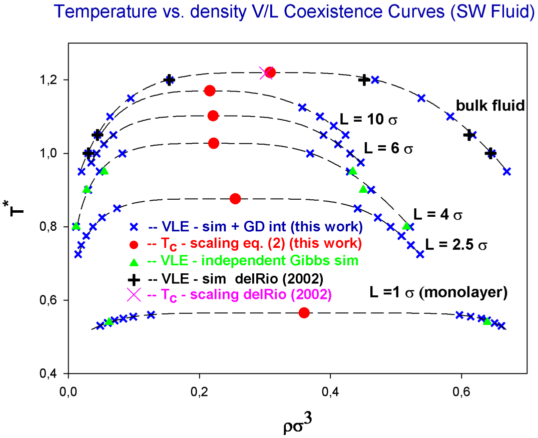

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Shift of critical temperature of SW fluid under confinement

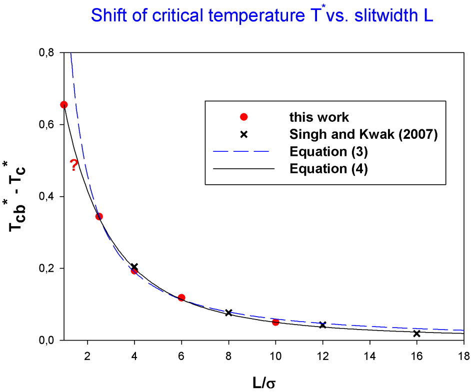
For $2.5\sigma \leq L \leq 10\sigma$ difference between the critical temperature of bulk and confined fluid decays approximately inversely proportional to L

$$\Delta T_c^* \equiv T_{cb}^* - T_c^* \propto 1/L \qquad (3)$$

Exponential decay with exponent reciprocal to linear function in L.

$$\Delta T_c^* = a \exp[1/(bL + c)] \qquad (4)$$

describes accurately all known data. Very narrow slits ($L < 2\sigma$) require further study.



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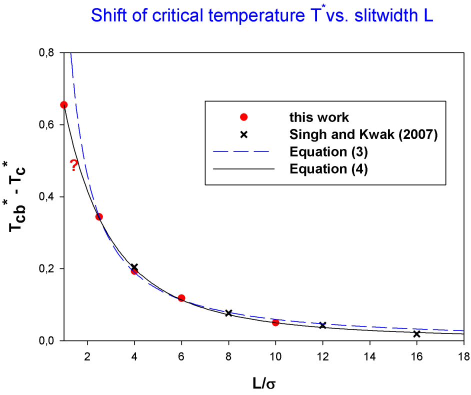

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Summary and conclusions

- Geometrical restrictions from 3-dim to 2-dim system modeled by confining the fluid between two infinitely extended planar walls with decreasing widths.
- VLE under confinement: Coexistence density of vapour does not much change BUT liquid density gets significantly lower.
- Depression of T_c under confinement accurately described by exponential decay with exponent reciprocal to linear function in L.
- Effective critical exponents change from 3-dim bulk-like ($\beta \approx 0.3$) to 2-dim Ising-like (($\beta \approx 0.13$).
- Influence of system size on coexistence properties is moderate ($N \approx 600...1000$ sufficient). Fluid layers show larger effects than bulk fluids.
- Very narrow slits ($L \leq 2\sigma$) are currently under study.

Combination virtual particle insertion MC + thermodynamic integration is found
⇒ conceptionally simple
⇒ easy to implement in existing canonical MC and MD codes
⇒ to provide reliable phase equilibria for bulk and confined fluids.
⇒ interesting alternative to GCMC or GEMC.

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- Horst Vörtler acknowledges financial support by University of Ontario Institute of Technology, Canada

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