

Using Effective Potentials for Complex Fluids

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Topics

- Entropic Phase Transitions
- Colloids as model atoms?
- Exactly solvable model of depletion
- van der Waals picture of fluids
- Energetic v.s. Entropic fluids
- Isosbestic points

Entropic Phase Transitions

$$A = U - TS$$

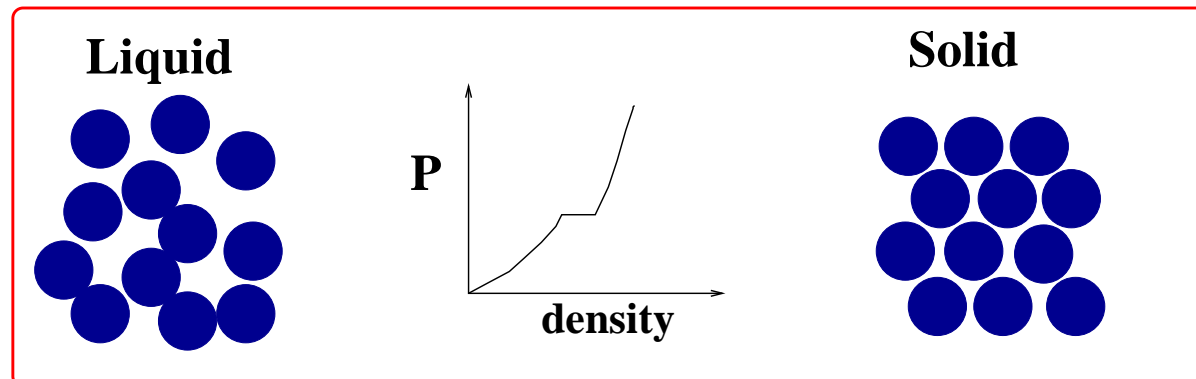
Intuitively: *Energy* favours *order*

Entropy favours *disorder*

$$S = k_B \ln \Omega$$

Freezing of Hard-Spheres:

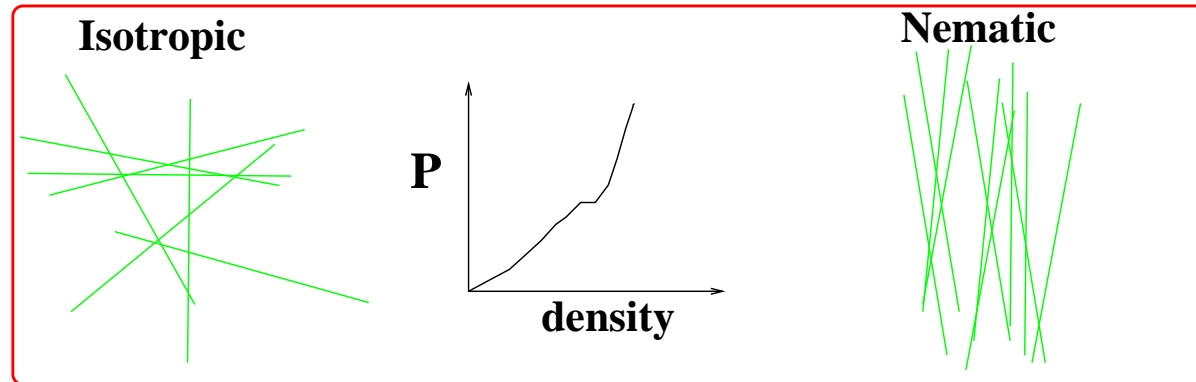
J. E. Kirkwood (1951); B. Alder & T.E. Wainwright (1957)



New Concept is **Entropy Competition**

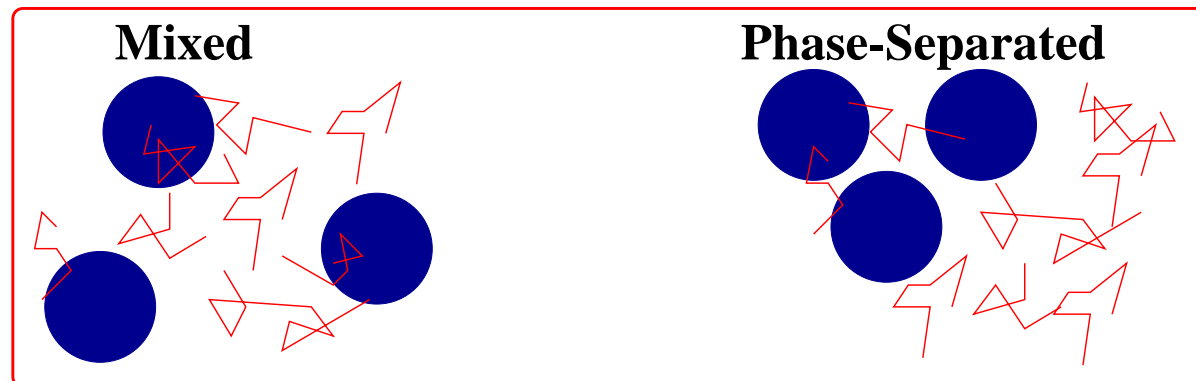
Isotropic-Nematic Transition of Liquid Crystals:

L. Onsager (1942)



De-mixing Polymer-Colloid Mixtures:

S. Asakura & F. Oosawa (1954); A. Vrij (1976)



Topics

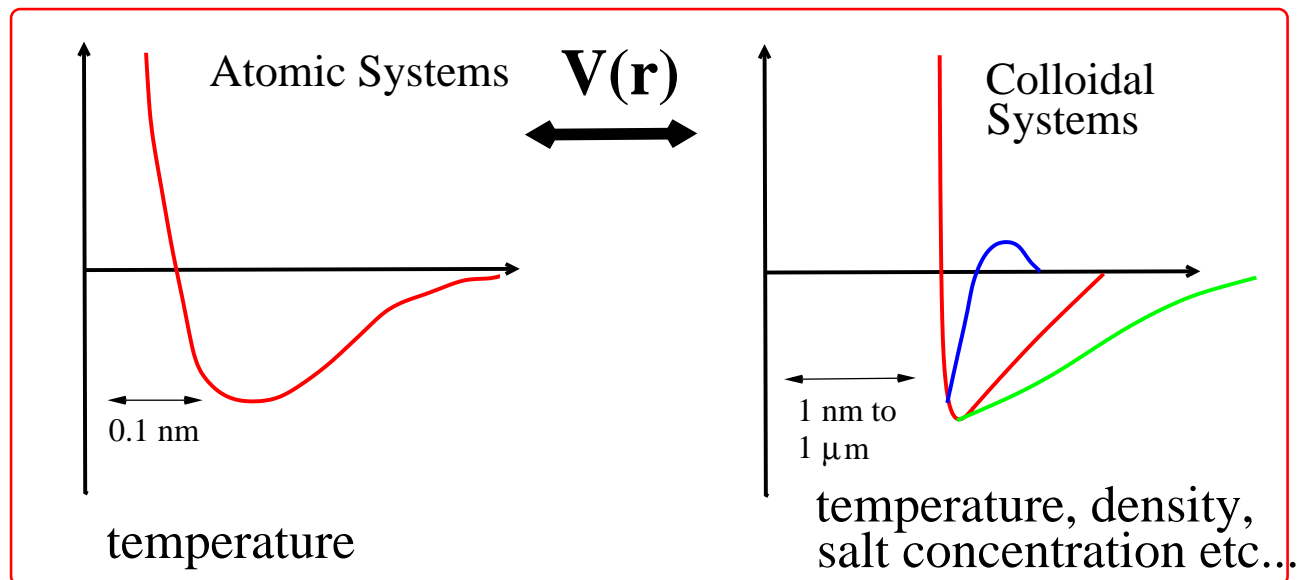
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Colloids as Model Atoms?

Colloids “κολλα”

To some the word 'colloidal' conjures up visions of things indefinite in shape, indefinite in chemical composition and physical properties, fickle in chemical deportment, things infiltrable and generally unmanageable.

– E.S. Hedges, 'Colloids' (1931)



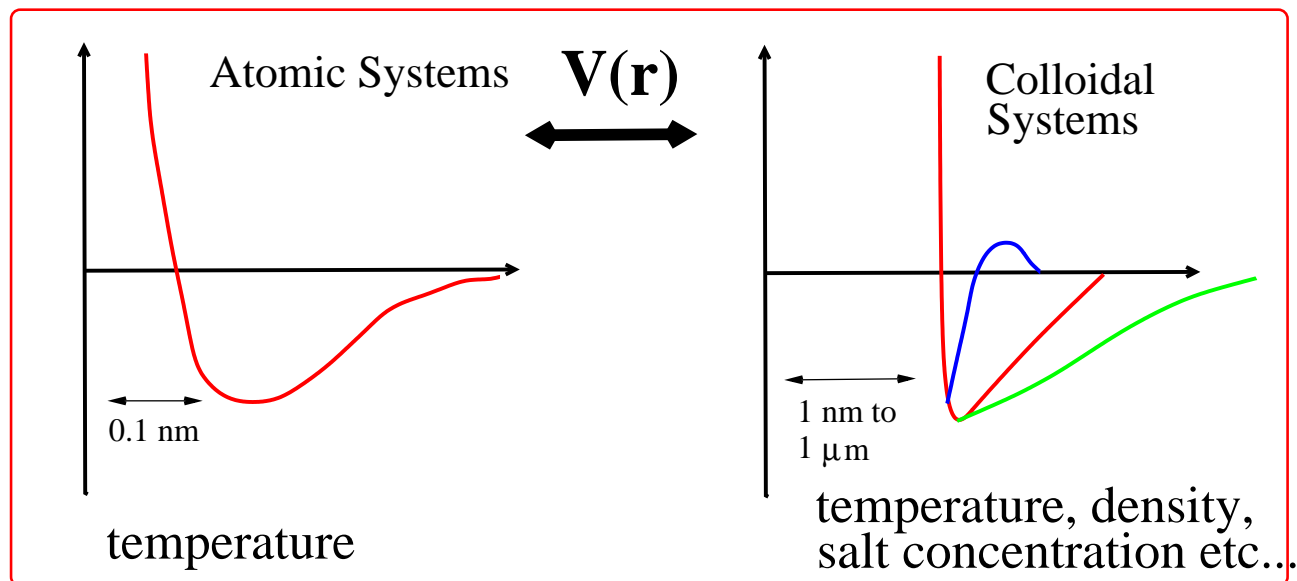
Colloidi come atomi di modello?

Colloids “κολλα”

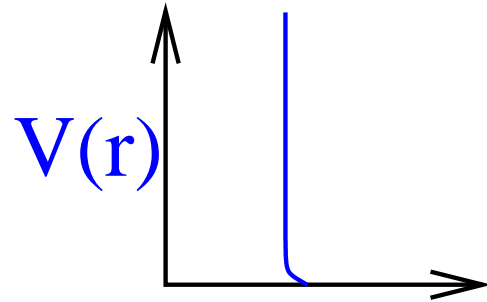
Ad alcuno la parola 'colloidale' in evoca le visioni delle cose indefinite nella figura, indefinite la composizione chimica e proprietà fisiche, fickle nel comportamento chimico, cose infiltrable e generalmente unmanageable

– E.S. Hedges, 'Colloids' (1931)

– translation thanks to babelfish.altavista.com

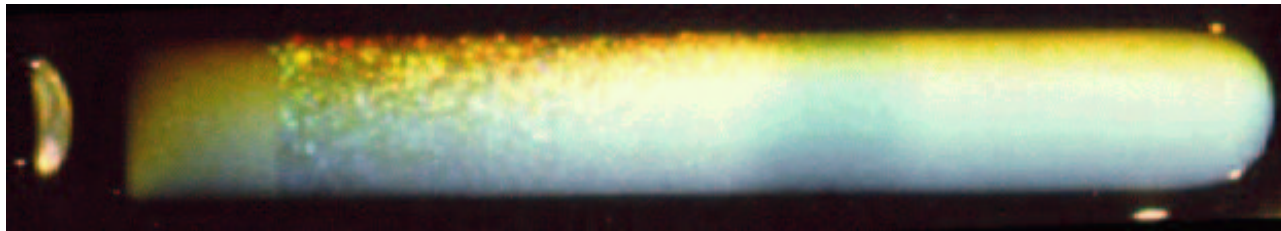


“Hard Sphere Colloids” : tailoring an effective potential



$\phi=0.494$ $\phi=0.545$ $\phi=0.64$

Fluid || Solid  Glass



picture courtesy of Dr. A. Moussaid

Why Effective Potentials?

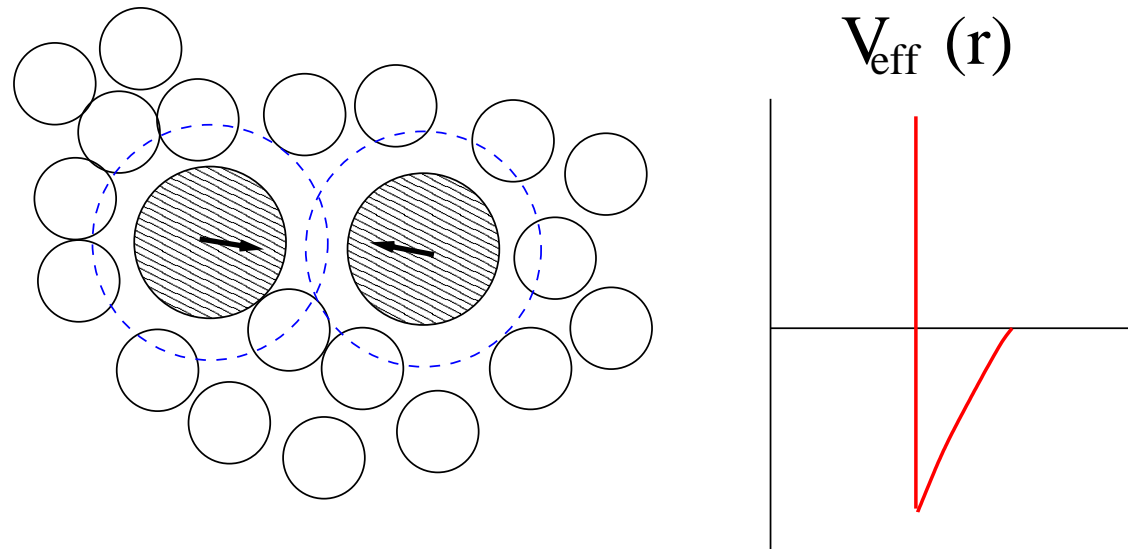


MAIN IDEAS

- 1) First do some hard work to derive an **effective potential**
- 2) Then you can unleash all the well-oiled statistical mechanics of **liquid state theory** to calculate phase behaviour & correlations.

Similar approach holds for many problems in other materials (where you often need to worry about Quantum Mechanics)

Asakura-Oosawa Depletion Potential



Be careful! The fluids can be very different

AAL Phil. Trans. R. Soc. A. **359**, 939 (2001).

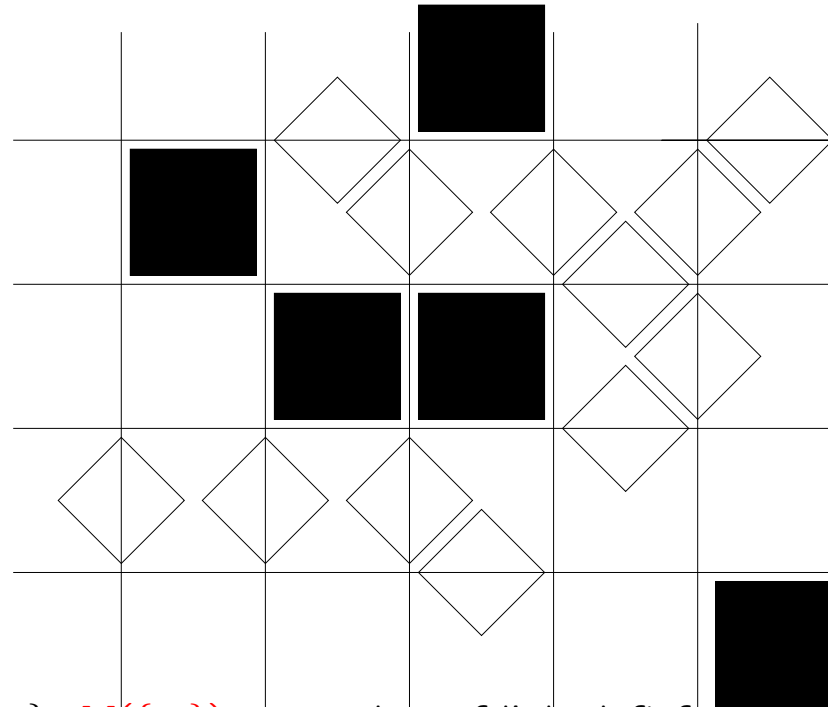
- short range attractions → **energetic fluids** (energetic freezing!)
- soft repulsions → **mean-field fluids**
- Normal liquid state theories may break down.

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Exactly Solvable Lattice Model

(D. Frenkel & AAL PRL. 68, 3363 (1992))



fix the large particles $\{n_i\}$, $M(\{n_i\})$ = number of links left for small particles

$$\Xi_{small}(\{m_i\}) = \sum_{l=0}^M \frac{M! z_s^l}{l!(M-l)!} = (1 + z_s)^{M(\{n_i\})}$$

$$\Xi_{mixture} = \sum_{\{n_i\}} \sum_{\{m_i\}} \exp \left(\beta \mu_l \sum_i n_i + \beta \mu_s \sum_i m_i \right) = \sum_{\{n_i\}} \exp \left(\beta \mu_l \sum_i n_i + M(\{n_i\}) \ln(1 + z_s) \right)$$

$$M(\{n_i\}) = 2N - 4 \sum_i n_i + \sum_{\langle ij \rangle} n_i n_j$$

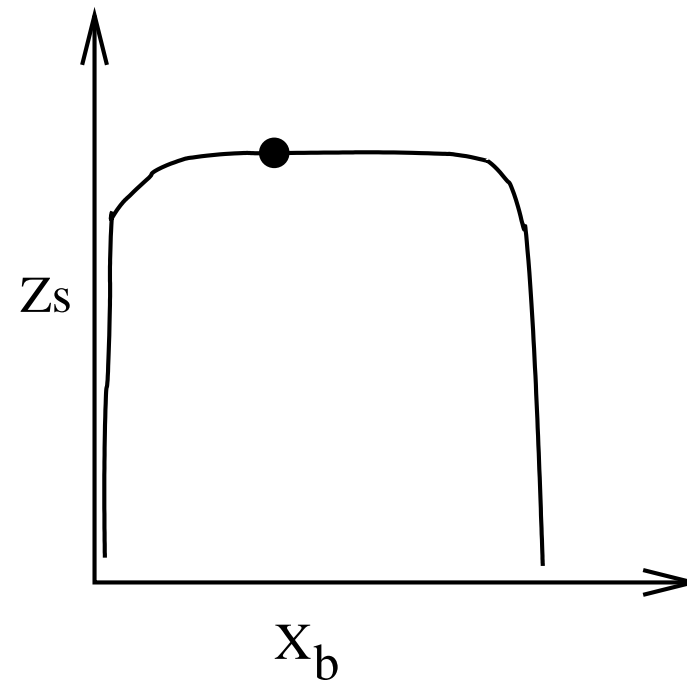
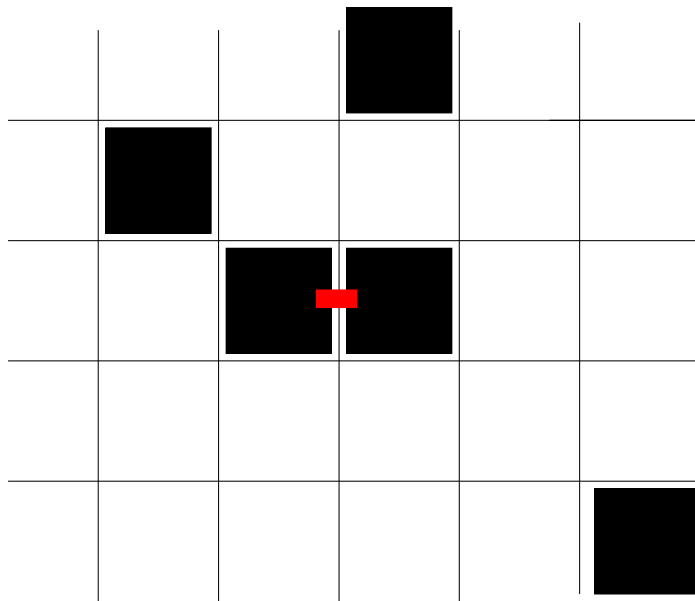
Reduction to an Effective One-Component Model

$$\Xi_{mixture} = \sum_{\{n_i\}} \exp \left(\beta\mu^* \sum_i n_i + \beta\epsilon^* \sum_{\langle ij \rangle} n_i n_j \right)$$

$$\begin{aligned} \beta\mu^* &= \beta\mu_l - 4 \ln(1 + z_s) \\ \beta\epsilon^* &= \ln(1 + z_s) \end{aligned}$$

(1)

Maps onto **exactly solvable** Ising Model



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van der Waals picture of fluids

Structure and correlations are dominated by steric effects:

Attractive interactions can be treated as a perturbation.

freezing

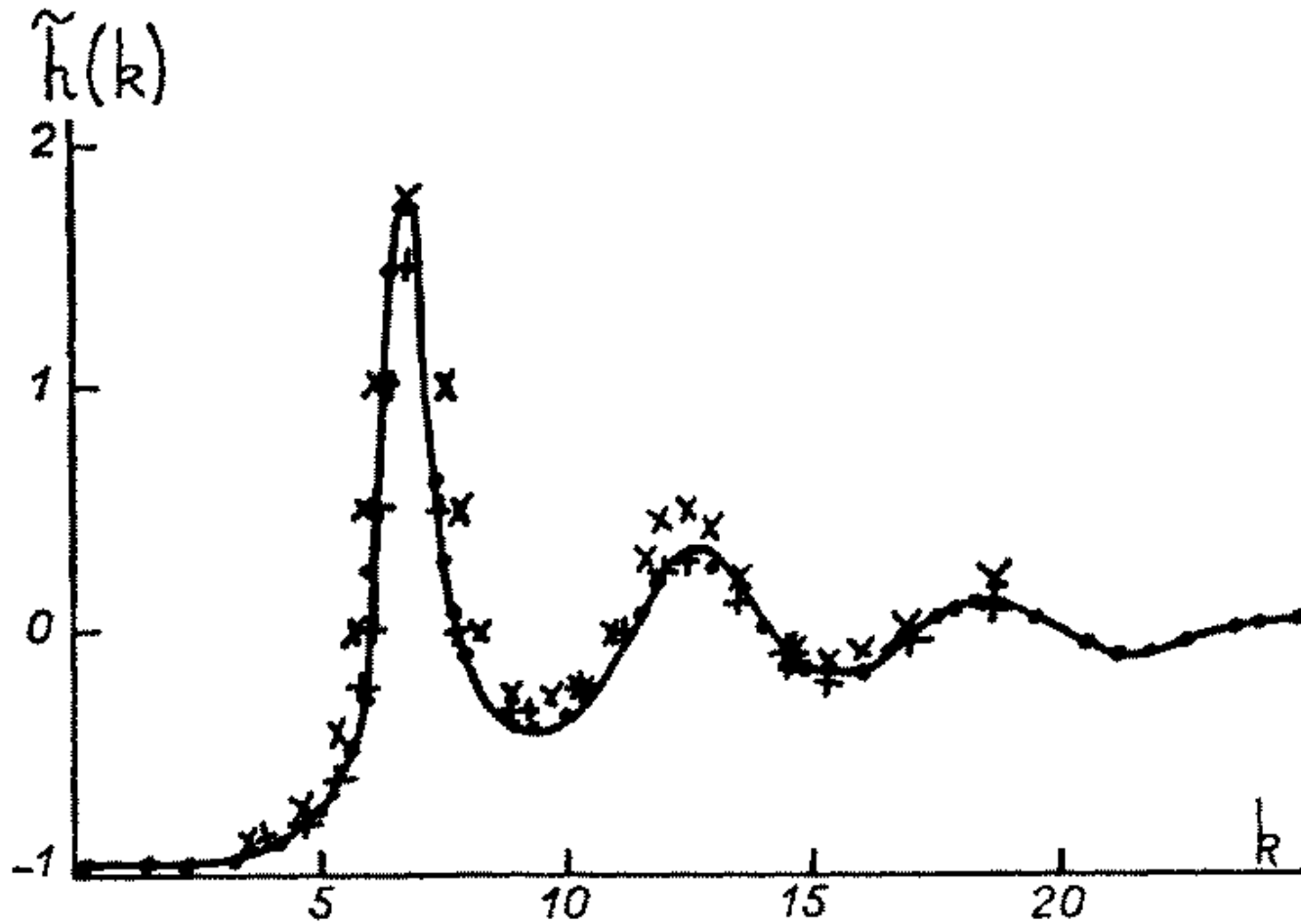
- Alder – HS freezing (1957)
- Longuet-Higgins and Widom (1964) and Widom (1967)– Attractive potentials only *qualitatively* affect the freezing transition.

structure

- Ashcroft and Lekner (1966) and Verlet (1968) – HS $S(k)$ is a good approximation for many atomic fluids, even for liquid metals.
- Hansen and Verlet (1969)– $S(k) \approx 2.85$ at freezing.

Potentials can be split into a **repulsive** and an **attractive** part through e.g. WCA. The **attractions** have a **quantitative** but not a **qualitative** effect.

L. Verlet, Phys. Rev. 165, 201 (1968)



Cheerios & blueberries

Marx and Napoleon

Does the **colloid** \leftrightarrow **atom analogy** imply a van der Waals picture for colloids, or does this picture break down?

Cheerios & blueberries

Similarly the arrangements of molecules in liquid benzene are similar to the average arrangements of neighboring Cheerios in a bowl of breakfast cereal, and a solution of argon in benzene should be similar to the structure achieved when blueberries are mixed with Cheerios.

Chandler, Weeks & Anderson, Science **220**, 787
(1983)

Marx & Napoleon

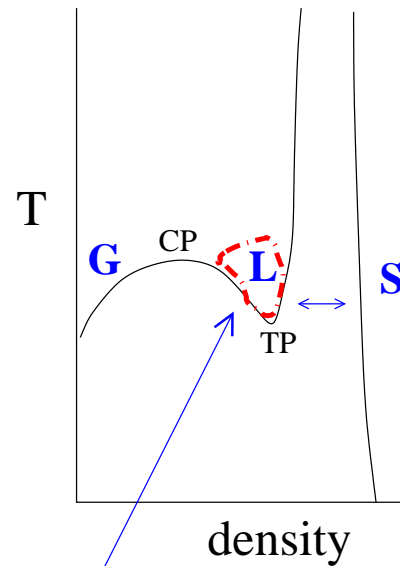
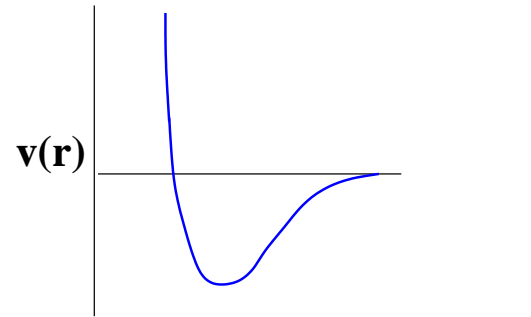
Karl Marx has said that, in history, things always happen twice: the first time as a tragedy; the second time as a farce. This comment of Marx applied to Napoleon I and III. . . . in physics, analogies are very useful in formulating an approximate description of a phenomenon – but even more interesting than the analogy itself, is its breakdown.

Daan Frenkel, in Soft and Fragile Matter (ed. M.E. Cates and M.R. Evans) (1999)

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Energetic Fluids as a new paradigm?

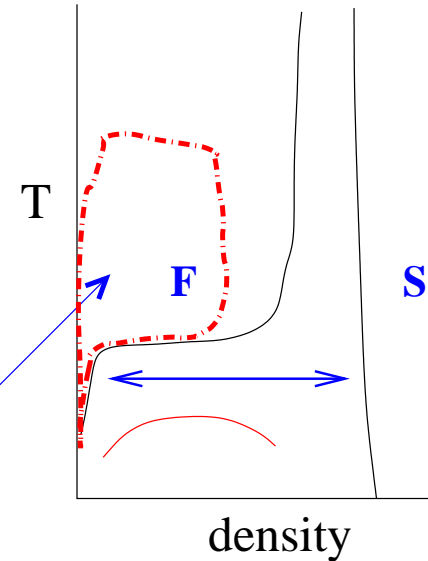
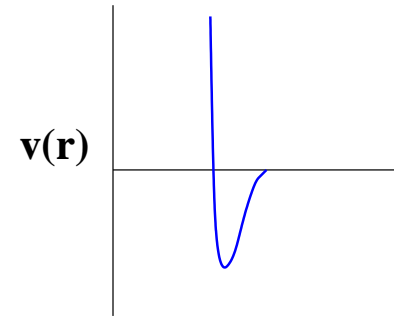


Entropic Liquids

Entropic effects dominate:
structure and crystallization
attractive interactions
are a perturbation

Examples:

atomic and molecular fluids
simple liquids

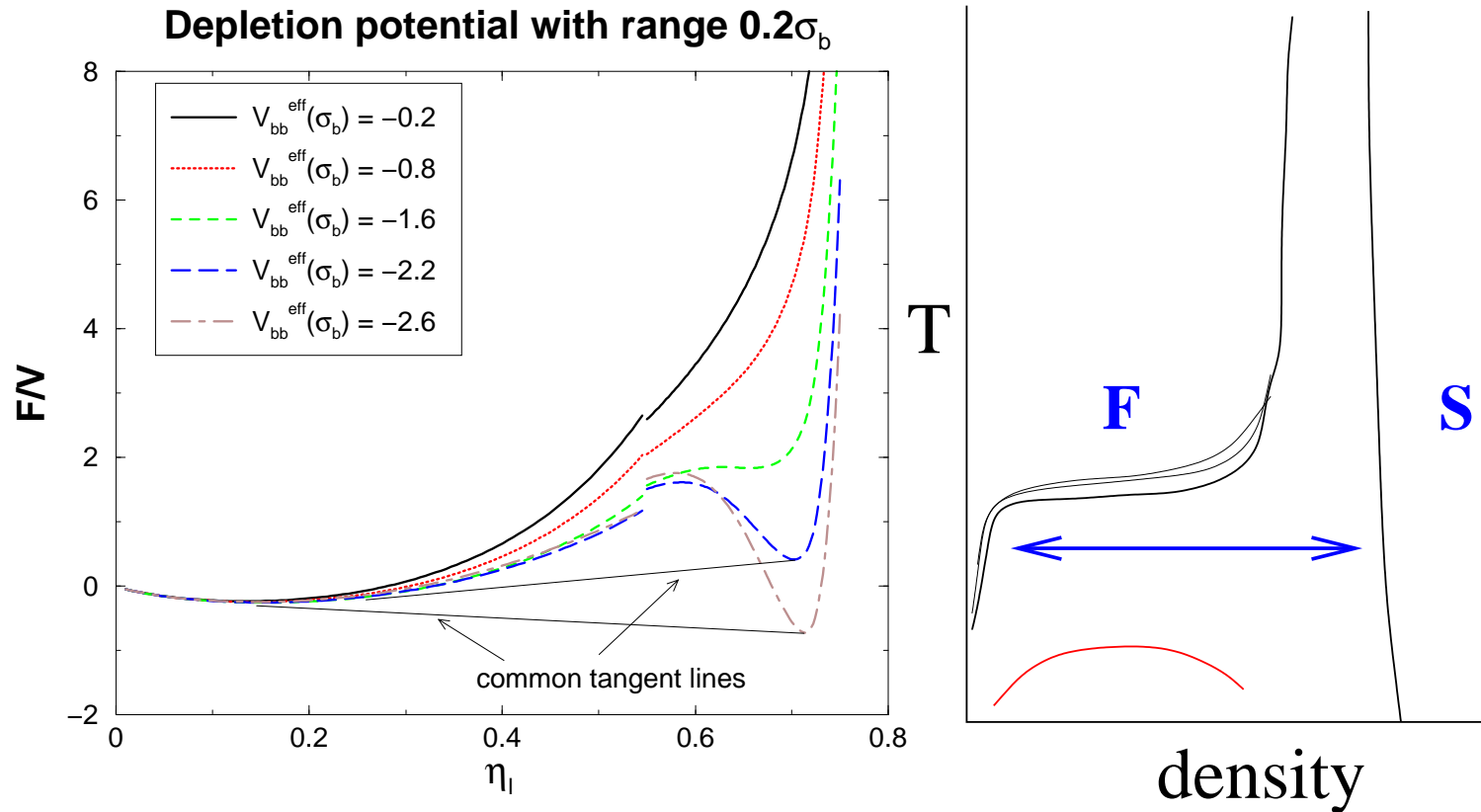


Energetic Fluids

Energetic effects dominate
structure and crystallization
attractive interactions
determine behaviour

Examples:

colloids in solution
globular proteins



crystallization line broadens at $\beta V_{eff}(contact) \approx 2.5$

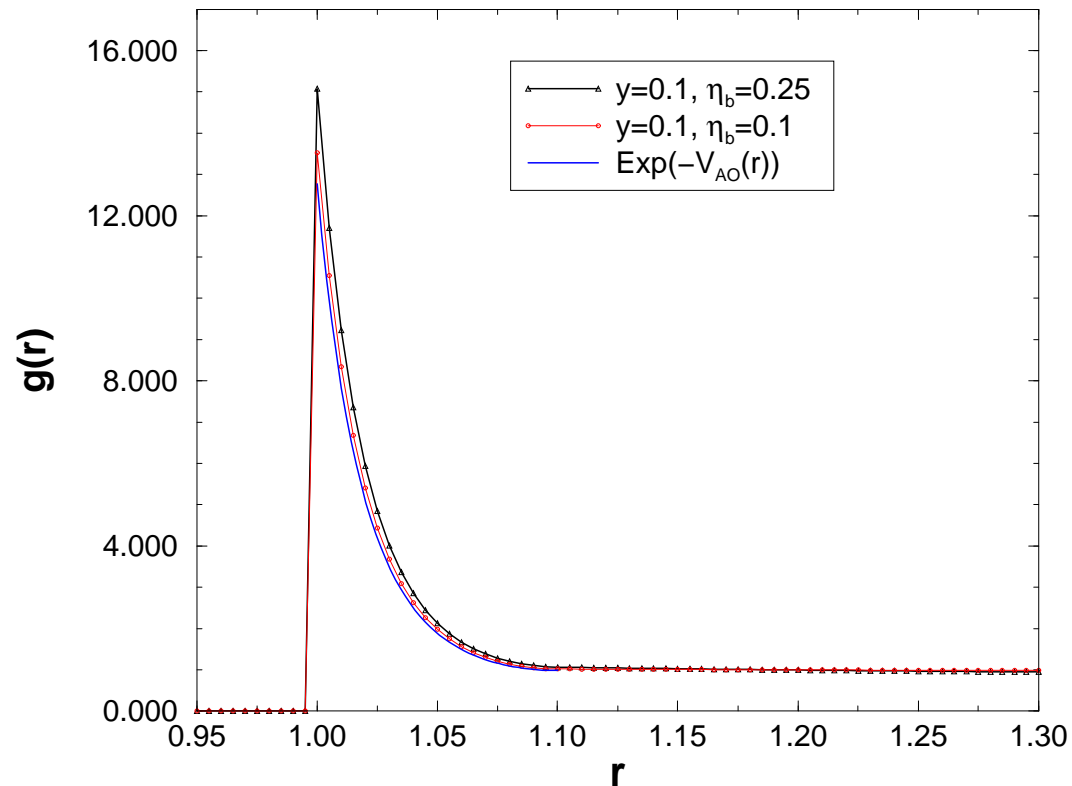
– **energetic/enthalpic crystallization** driven by potential depth, **not** steric effects! Opposite of van der Waals picture

Relevant for the crystallization of globular proteins and other particles in solution. (See work of Messina group, Caccamo, Costa, Pellicane ..)

Structure of Energetic/Enthalpic Fluids

$g(r)$ compared to $\text{Exp}(-V_{AO}(r))$

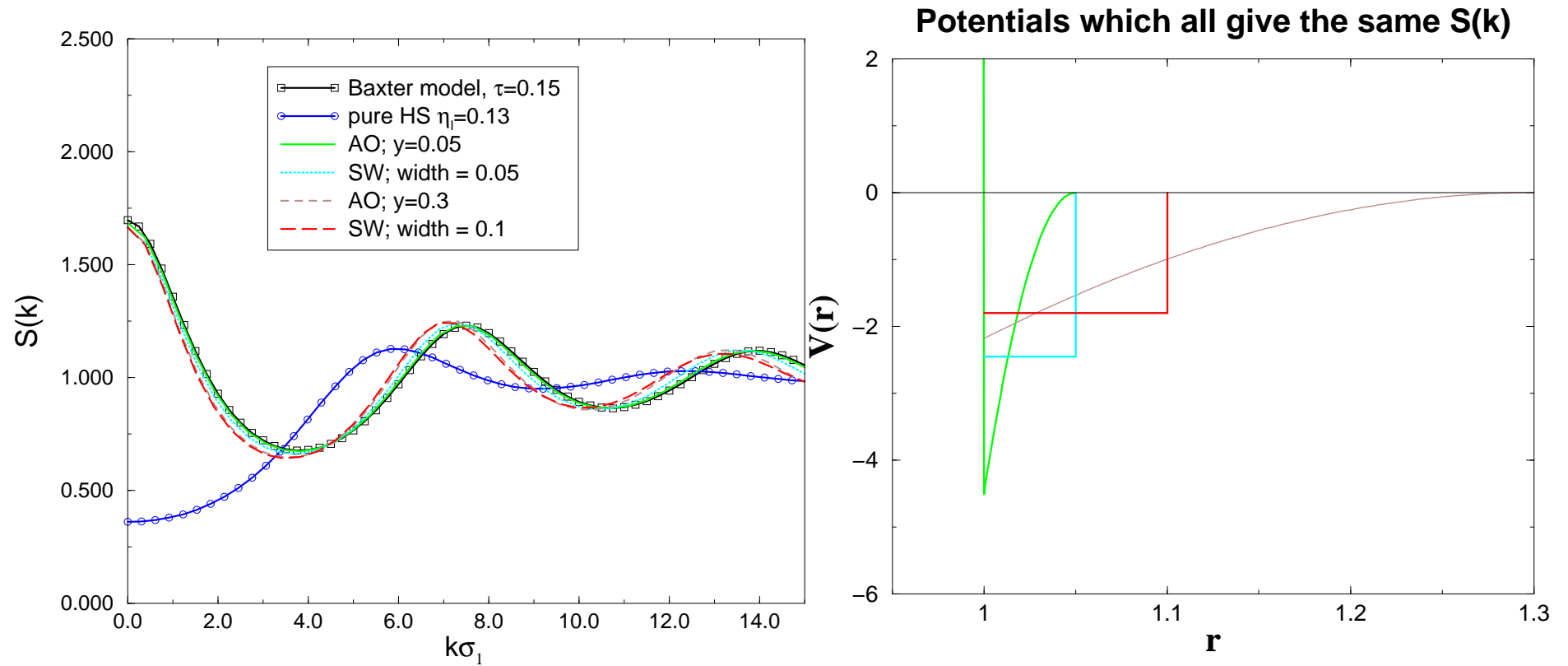
(range = $0.1\sigma_b$)



Again, **structure is not like the van der Waals picture!**

The potential is very important in determining phase-behaviour and $g(r)$. Can one now easily find it from inverting the structure?

Inversions are as hard as for van der Waals fluids.

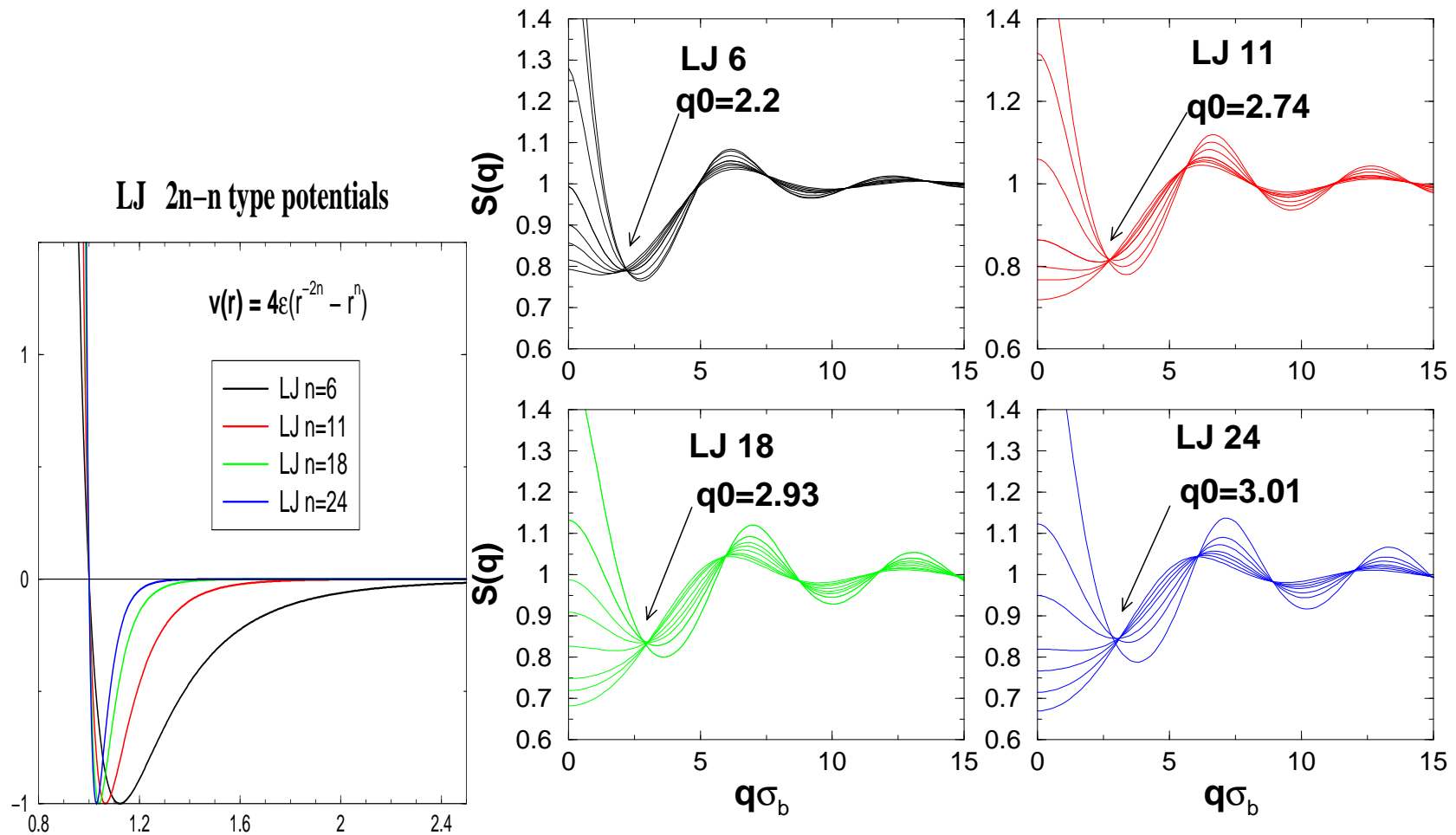


New underlying fluid is Baxter model, not HS.

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Isosbestic points in structure factors

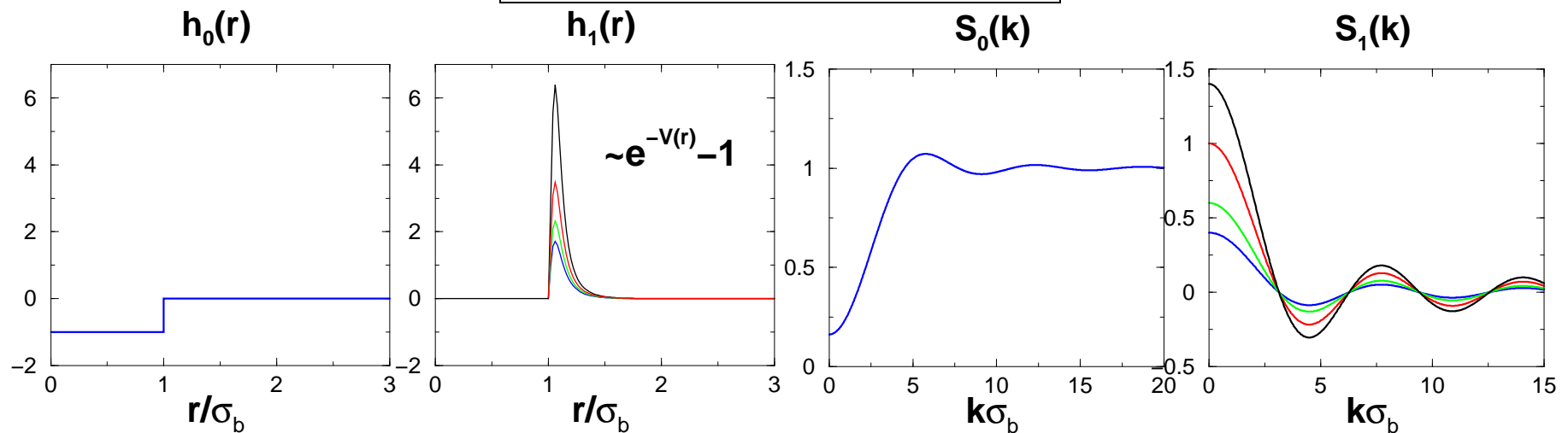


Why Isosbestic points?

$$S(k) = 1 + \rho \hat{h}(k)$$

$$h(r) = h_0(r) + h_1(r)$$

$$S(k) = \frac{4\pi}{k} j_1(k) + S_1(k)$$

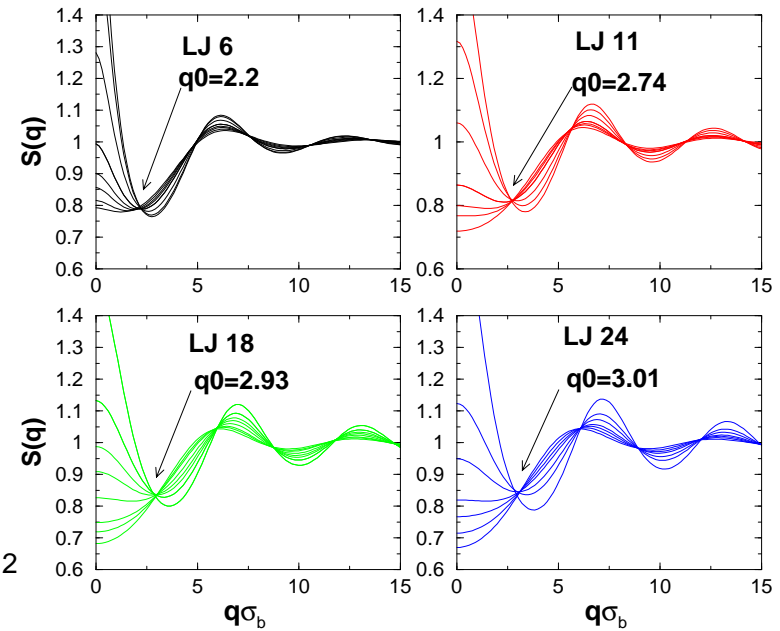
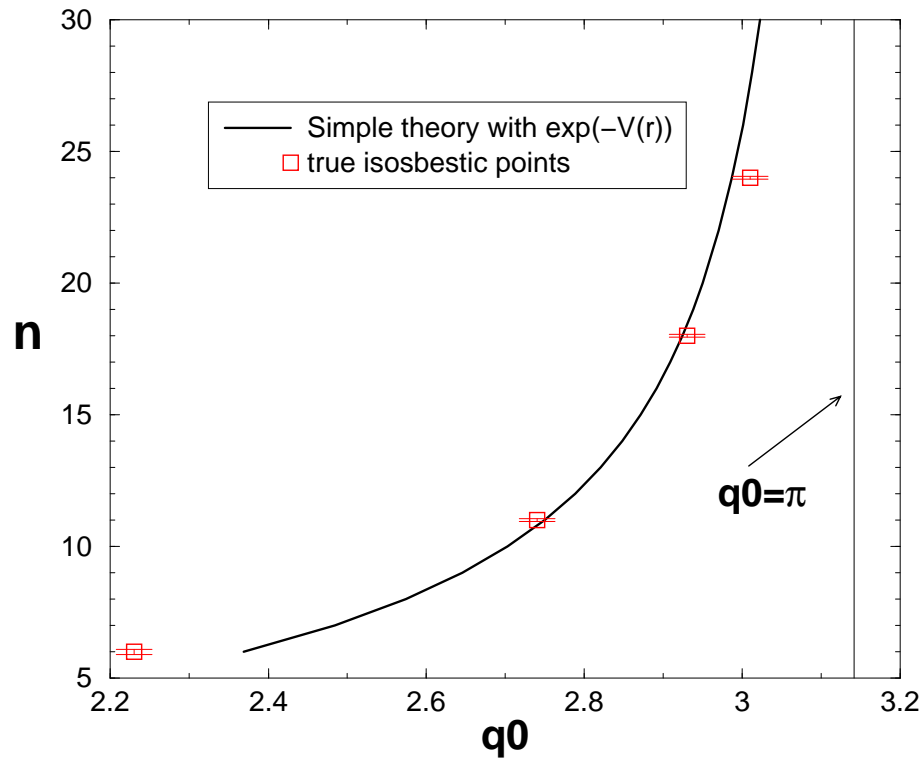


Finding potential range from Isosbestic points?

The position of q_0 is directly related to the potential range (it's a phase-shift)

1st Isosbestic point q_0 v.s. LJ n

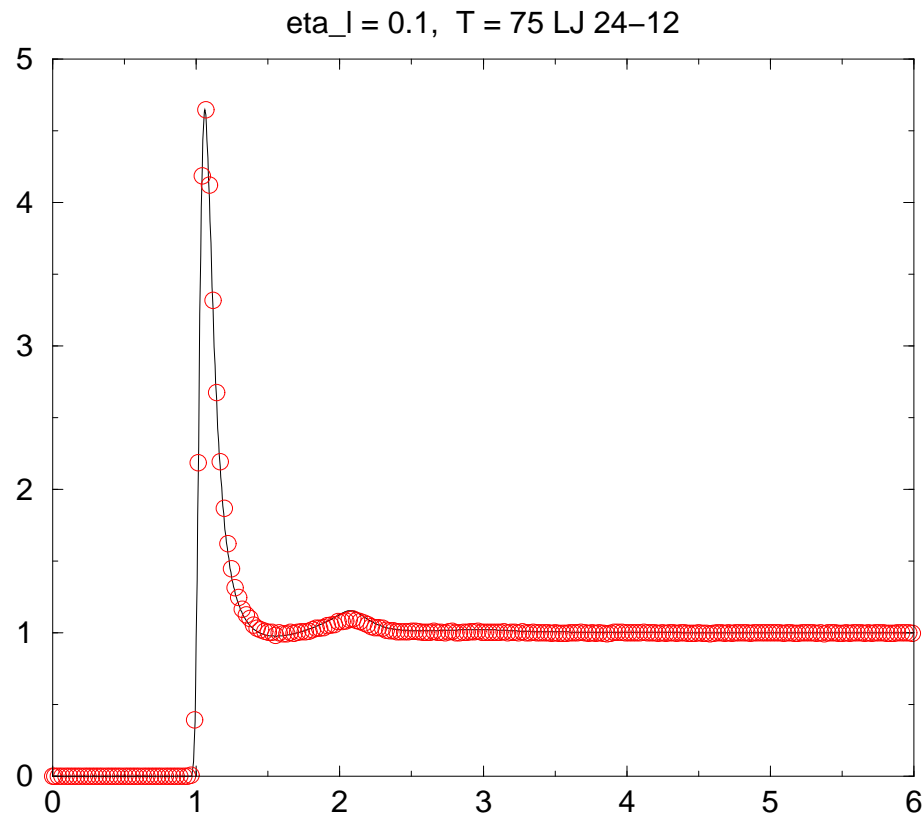
$$v(r) = 4\epsilon(r^{-2n} - r^{-n})$$



How good is PY?

PY should be trustworthy in the energetic/enthalpic fluid regime, as long as one stays away from spinodals (specialty of the Messina group)

PY v.s. simulations (symbols)



Conclusions

- **Entropic phase transitions** - are ubiquitous in soft matter
- **Colloids as model atoms?** – a very useful picture
 - be careful about using normal liquid state theory though
AAL Phil. Trans. R. Soc. A. 359, 939 (2001).
- **Energetic Fluids** –Are a new paradigm for particles in solution
 - **Freezing driven by potentials**
 - **Structure driven by potentials**
- **Isosbestic points can help invert potentials from structure**