PATH-INTEGRAL MONTE CARLO AND STATIC STRUCTURES IN CONDENSED MATTER

LUIS M. SESÉ

UNED, SPAIN

PIMD School – CECAM
Toulouse, FRANCE

June 8, 2012

P-2009 / ESP-1691

B. J. Berne and D. Thirumalai, Annu. Rev. Phys. Chem. 37, 401 (1986)
On the Simulation of Quantum Systems: Path Integral Methods

R. P. Feynman, *Statistical Mechanics* (Benjamin, Reading, 1972)

K. Singer and W. Smith, Molec. Phys. 64, 1215 (1988)
Path Integral Simulations of Condensed Phase Lennard Jones Systems

E. L. Pollock and D. M. Ceperley, Phys. Rev. B 30, 2555 (1984)
Simulation of Quantum Many-Body Systems by Path-integral Methods

D. L. Chandler and P. G. Wolynes, J. Chem. Phys. 74, 4078 (1981)
Exploiting the Isomorphism between Quantum Theory and Classical Statistical Mechanics of polyatomic fluids

Ricardo Ledesma (PhD)
Lorna Bailey (UNED)

Rafael Ramírez (ICMM)
Carlos Vega (UCM)

PATH-INTEGRAL MONTE CARLO AND STATIC STRUCTURES IN CONDENSED MATTER

CONTENTS

- I. Introduction

The idea behind MC simulations:

-Stochastic game for very difficult or non-analytic problems
-Use in condensed matter based on Metropolis sampling scheme (1953)

<u>Classical Statistical Mechanics (canonical ensemble)</u>

$$\langle B \rangle_{N,V,T} = \frac{\int d\mathbf{R}_1 d\mathbf{R}_2 ... d\mathbf{R}_N \exp\{-\beta U_N\} B(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N)}{\int d\mathbf{R}_1 d\mathbf{R}_2 ... d\mathbf{R}_N \exp\{-\beta U_N\}} \qquad \beta = \frac{1}{k_B T}$$

Numerical evaluation
Metropolis sampling $\rightarrow$

$$\textit{probability density: } \exp\{-\beta U_N\} \geq 0$$

$$(\mathbf{R}_{1n}, \mathbf{R}_{2n}, ..., \mathbf{R}_{Nn}) \leftrightarrow \exp\{-\beta U_N\}$$

$$\langle B \rangle \approx \frac{1}{M} \sum_{n=1}^{M} B_n(\mathbf{R}_{1n}, \mathbf{R}_{2n}, ..., \mathbf{R}_{Nn}); \ \textit{error} \sim \frac{1}{\sqrt{M}}$$

<u>Main advantage</u>: insensitivity to the dimensionality

<u>The price to pay</u>: Only Static / Equilibrium properties

Quantum Statistical Mechanics

$$\rho = \exp(-\beta H_N) = \textit{density operator}$$

$$\textit{Bloch equation:}\ \frac{\partial \rho}{\partial \beta} = -H_N \rho\ ;\ \ \rho(\beta=0)=1$$

$$Z_{N,V,T} = Tr(\rho) = Tr\left(\exp(-\beta H_N)\right) = \sum_n \psi_n(\mathbf{r}^N)\ \exp\{-\beta E_n\}\psi_n^*(\tilde{\mathbf{r}}^N) =$$

$$\frac{1}{N!}\int d\mathbf{r}^N \ \left\langle \mathbf{r}^N \left| \exp(-\beta H_N) \right| \mathbf{r}^N \right\rangle$$

Coordinate Representation

$$\left\{\left|\mathbf{r}^N\right\rangle\right\} = \left\{\left|\mathbf{r}_1\right\rangle, \left|\mathbf{r}_2\right\rangle, \left|\mathbf{r}_3\right\rangle, \ldots\ldots, \left|\mathbf{r}_N\right\rangle\right\}$$

Completeness

$$\int d\mathbf{r}_i \left|\mathbf{r}_i\right\rangle \left\langle \mathbf{r}_i\right| = \mathbf{1}$$

$$\langle B\rangle_{N,V,T} = \frac{Tr(\rho B)}{Tr(\rho)} = \frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N \left\langle \mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N \right| \exp\{-\beta H_N\}\, B(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \left| \mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N \right\rangle}{\int d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N \left\langle \mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N \right| \exp\{-\beta H_N\} \left| \mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N \right\rangle} = ?$$

Quantum Statistical Mechanics

$$\rho = \exp(-\beta H_N) = \textit{density operator} \quad \leftrightarrow \quad \exp\left[-\frac{it\,H_N}{\hbar}\right]$$

$$H_N = T + U$$

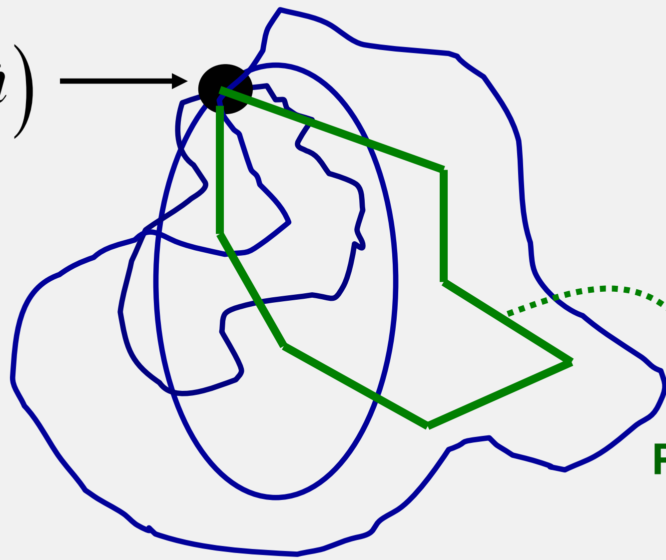
Feynman's paths in QSM (1948, 1965, 1972)

Every (continuous) closed path in imaginary time $\beta\hbar$

starting and ending at $\mathbf{r}(0) = \mathbf{r}(\beta\hbar)$

$$Z = Tr(\rho) = \oint D\mathbf{r}(\tau) \times \exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \left\{\frac{\mu}{2}\frac{d\mathbf{r}(\tau)}{d\tau} + U(\mathbf{r}(\tau))\right\}\right]$$

$\mathbf{r}(0) = \mathbf{r}(\beta\hbar)$ →



$\beta\hbar \to 0 \quad (T \to \infty)$

Classical case

Quantum case

PI discretized paths

Main Quantum Subject of this Lecture :

Equilibrium Structures in the Fluid and Solid Phases

There are direct connections with measurable properties

-***Equation of state***
-***Elastic scattering experiments (X-Ray, neutron scattering)***

$$\lambda \approx 1\,\text{Å}$$

Conditions

- particles $\equiv$ atoms
- dispersion effects only
***- canonical ensemble* (N, V, T) [+ (μ, V, T)]**

- II. General Concepts

- **II.1 The classical isomorphism**

Barker (1979); Chandler & Wolynes (1981)

Canonical partition function (N, V, T) $\begin{cases} \rho_N = N/V \\ \beta = 1/k_B T \end{cases}$

Structureless particles

$$Z_Q = Tr(\rho) = Tr\{\exp(-\beta H_N)\} \leftrightarrow A = -k_B T \ln Z_Q$$

$$H_N = T + U = Hamiltonian$$

$$T = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 \qquad U = \sum_{i<j} u(r_{ij}) \qquad (for\ simplicity)$$

$$A = Helmholtz\ free\ energy$$

Step 1: Splitting into P factors -exact-

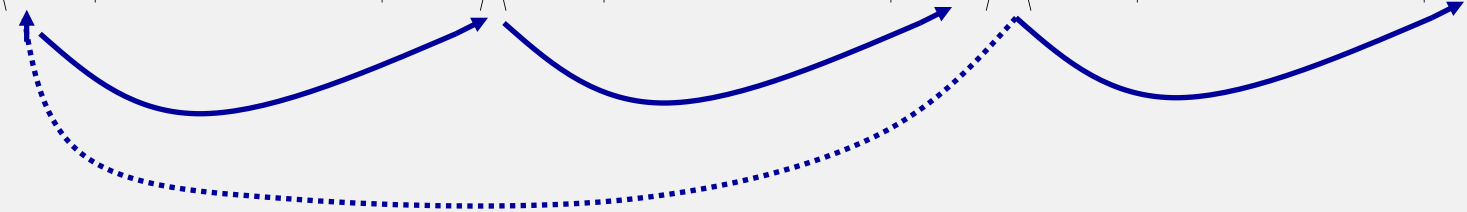
$$Z_Q = \frac{1}{N!}\int d\mathbf{r}^N \left\langle \mathbf{r}^N \right| \exp(-\beta H_N) \left| \mathbf{r}^N \right\rangle = \frac{1}{N!}\int d\mathbf{r}^N \rho\left(\mathbf{r}^N, \mathbf{r}^N; \beta\right)$$

$$\exp(-\beta H_N) = \exp(-\beta H_N / P)\exp(-\beta H_N / P)\ldots\exp(-\beta H_N / P)$$

$$\int d\mathbf{r}_i \left|\mathbf{r}_i\right\rangle \left\langle \mathbf{r}_i\right| = \mathbf{1} \qquad \int d\mathbf{r}^N \left|\mathbf{r}^N\right\rangle \left\langle \mathbf{r}^N\right| = \int d\mathbf{r}_1 \left|\mathbf{r}_1\right\rangle \left\langle \mathbf{r}_1\right| \ldots \int d\mathbf{r}_N \left|\mathbf{r}_N\right\rangle \left\langle \mathbf{r}_N\right| = \mathbf{1}$$

$$Z_Q = \frac{1}{N!}\int d\mathbf{r}^{N,1} \int d\mathbf{r}^{N,2} \times \int d\mathbf{r}^{N,3} \times \ldots\ldots \int d\mathbf{r}^{N,P} \times$$

$$\left\langle \mathbf{r}^{N,1} \right| \exp(-\beta H_N / P) \left| \mathbf{r}^{N,2} \right\rangle \left\langle \mathbf{r}^{N,2} \right| \exp(-\beta H_N / P) \left| \mathbf{r}^{N,3} \right\rangle \ldots \left\langle \mathbf{r}^{N,P} \right| \exp(-\beta H_N / P) \left| \mathbf{r}^{N,1} \right\rangle$$



Dimension: $3 \times N \rightarrow 3 \times N \times P$

$$\text{"}bead\text{"} = time\ slice\ t\,(1,2,3,\ldots,P) \rightarrow \frac{\beta\hbar}{P} t = \frac{\hbar}{k_B T P} t$$

As if T was higher (P × T)

Step 2:TROTTER'S approximation (1959) – Nelson (1964) -

Propagator: $\left\langle \mathbf{r}^{N,t} \right| \exp(-\beta H_N / P) \left| \mathbf{r}^{N,t+1} \right\rangle = \rho\left(\mathbf{r}^{N,t}, \mathbf{r}^{N,t+1}; \beta/P\right) \geq 0$

… probability density for the quantum problem → PIMC

Primitive Propagator (all the physics!!!):

$$\tau = \frac{\beta}{P} \; (small) \qquad \qquad [T, U] \neq 0$$

$$\left\langle \mathbf{r}^{N,t} \right| \exp\left(-\beta(T+U)/P\right) \left| \mathbf{r}^{N,t+1} \right\rangle = \left\langle \mathbf{r}^{N,t} \right| \exp\left(-\beta T/P - \beta U/P\right) \left| \mathbf{r}^{N,t+1} \right\rangle \approx$$

$$\left\langle \mathbf{r}^{N,t} \right| \exp(-\beta T/P) \exp(-\beta U/P) \left| \mathbf{r}^{N,t+1} \right\rangle; \; O(P^{-2})$$

$$\left\langle \mathbf{r}^{N,t} \right| \exp(-\beta U/2P) \exp(-\beta T/P) \exp(-\beta U/2P) \left| \mathbf{r}^{N,t+1} \right\rangle; \quad O(P^{-3})$$

PI primitive partition function

$$Z_Q \approx Z_{NP} = \frac{1}{N!}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{\frac{3NP}{2}} \int d\mathbf{r}^{N\times P} \times \exp(-\beta W_{NP}); \quad O(P^{-2})$$

$$W_{NP} = \frac{mP}{2\beta^2\hbar^2}\sum_{i=1}^{N}\sum_{t=1}^{P}{}^{/}(\mathbf{r}_i^{t+1} - \mathbf{r}_i^{t})^2 + \frac{1}{P}\sum_{i<j}\sum_{t=1}^{P} u(r_{ij}^{t})$$

↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑

FREE-PARTICLE CONTRIBUTIONS **Pairwise interact. assumed**

$$\langle E \rangle_{THERM.} \approx -\left[\frac{\partial \ln Z_{NP}}{\partial \beta}\right]_{N,V}, \ldots\ldots$$

Trotter's product formula

$$\exp\left[-\beta H_N\right] = \lim_{P\to\infty}\left\{\exp\left(-\beta T/P\right)\exp(-\beta U/P)\right\}^P$$

$$P \to \infty \Rightarrow Z_{NP}^{(PI)} \to Z_Q$$

MC (or MD) simulation
P = number of "<u>beads</u>"
Trotter's number, …
is a compromise, in practice!

PI primitive + Classical partition functions

Quantum PI primitive

$$Z_Q \approx Z_{NP} = \frac{1}{N!}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{\frac{3NP}{2}} \int d\mathbf{r}^{N\times P} \times \exp(-\beta W_{NP}); \quad O(P^{-2})$$

$$W_{NP} = \frac{mP}{2\beta^2\hbar^2}\sum_{i=1}^{N}\sum_{t=1}^{P}{}^{\prime}(\mathbf{r}_i^{t+1}-\mathbf{r}_i^{t})^2 + \frac{1}{P}\sum_{i<j}\sum_{t=1}^{P} u(r_{ij}^{t})$$

Classical (P =1)

$$Z_{N,CLASS.} = \frac{1}{N!}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{3N}{2}} \int d\mathbf{r}^{N} \times \exp(-\beta U_N)$$

$$U = \sum_{i<j} u(r_{ij})$$

Path-integral Model (P=4)

$$\exp(-\beta W_{NP})$$

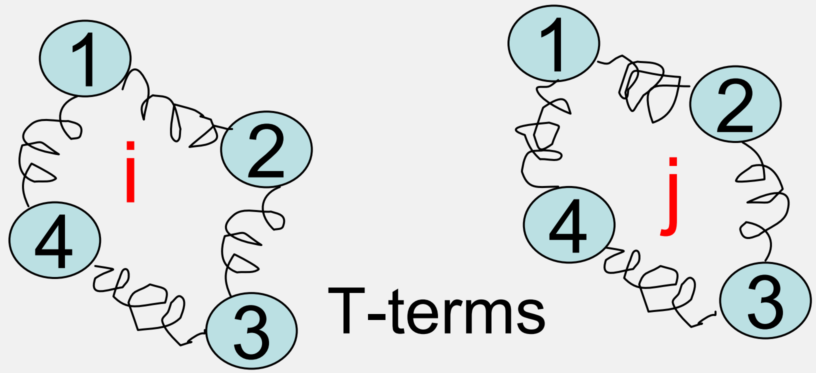
$$W_{NP} = W_1^F + W_2 =$$

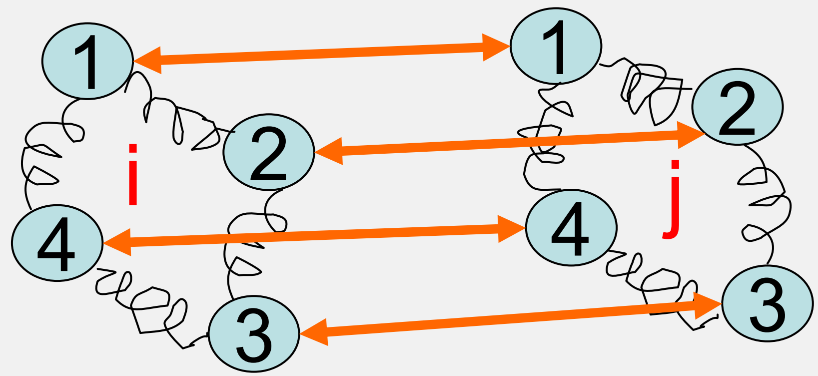
$$\frac{mP}{2\beta^2\hbar^2}\sum_{i=1}^{N}\sum_{t=1}^{P}(\mathbf{r}_i^{t+1}-\mathbf{r}_i^{t})^2$$

$$+$$

$$\frac{1}{P}\sum_{i<j}\sum_{t=1}^{P}u(r_{ij}^{t})$$

N *elastic necklaces* & P *beads*





U-terms

All beads are equivalent

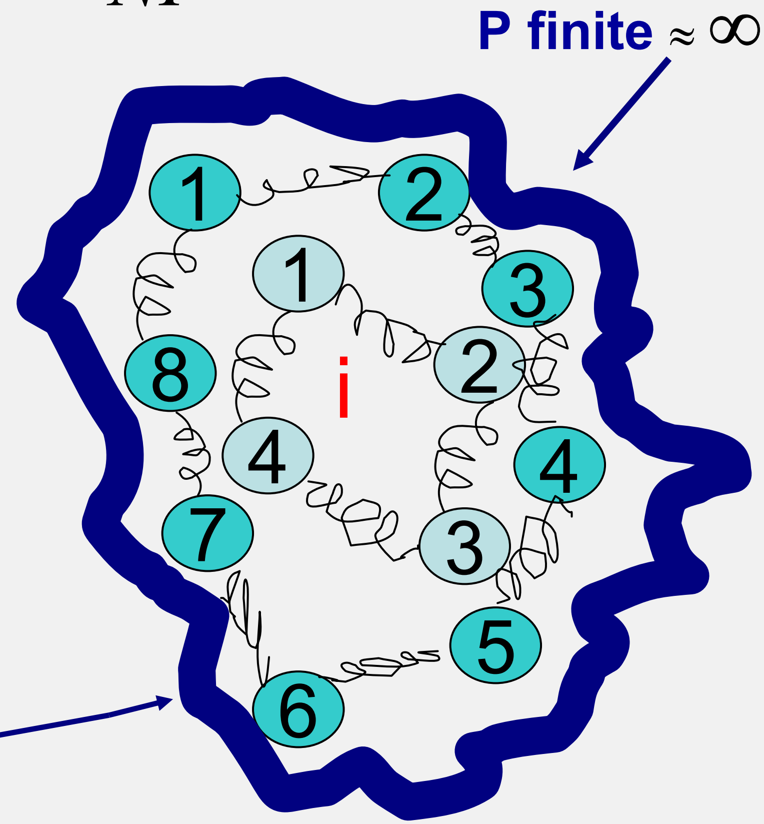
Discrete (bead) approximation to Feynman's path integral partition function

Classical Isomorphism

Path-integral Model (P=4,…∞)

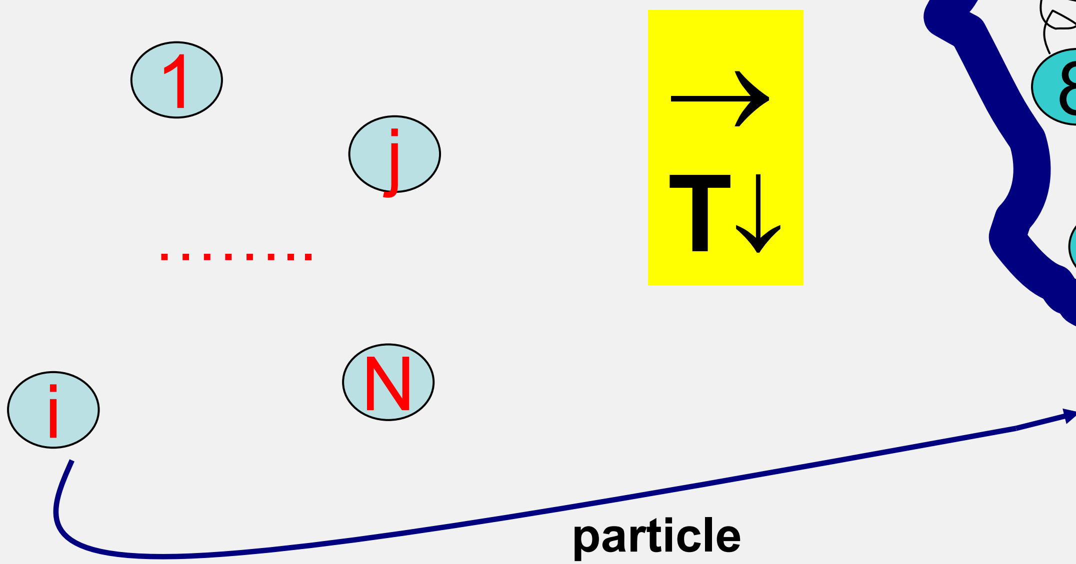
$$\exp(-\beta W_{NP})$$

Statistical convergence



Classical System (P=1)

$$\exp(-\beta U)$$



Discrete (bead) approximation to Feynman's path integral partition function

• II.2 Efficient propagators, ensembles, and algorithms

Quantum behaviour increases with the density and the inverse temperature

Large *P* are needed to describe these situations

But a large P may render the simulation impractical !!!

Besides, there is the problem of increasing variances with P (e.g. kinetic energy)

Although the Primitive Propagator contains all the physics,
the discretization *P turns out to be critical*

↓

Desing of Propagators:

(Primitive propagator)

Pair "action" propagators (free particles + reduced masses for pairs)

Ceperley's review article (1995)

Higher-order propagators (composite factorization schemes)

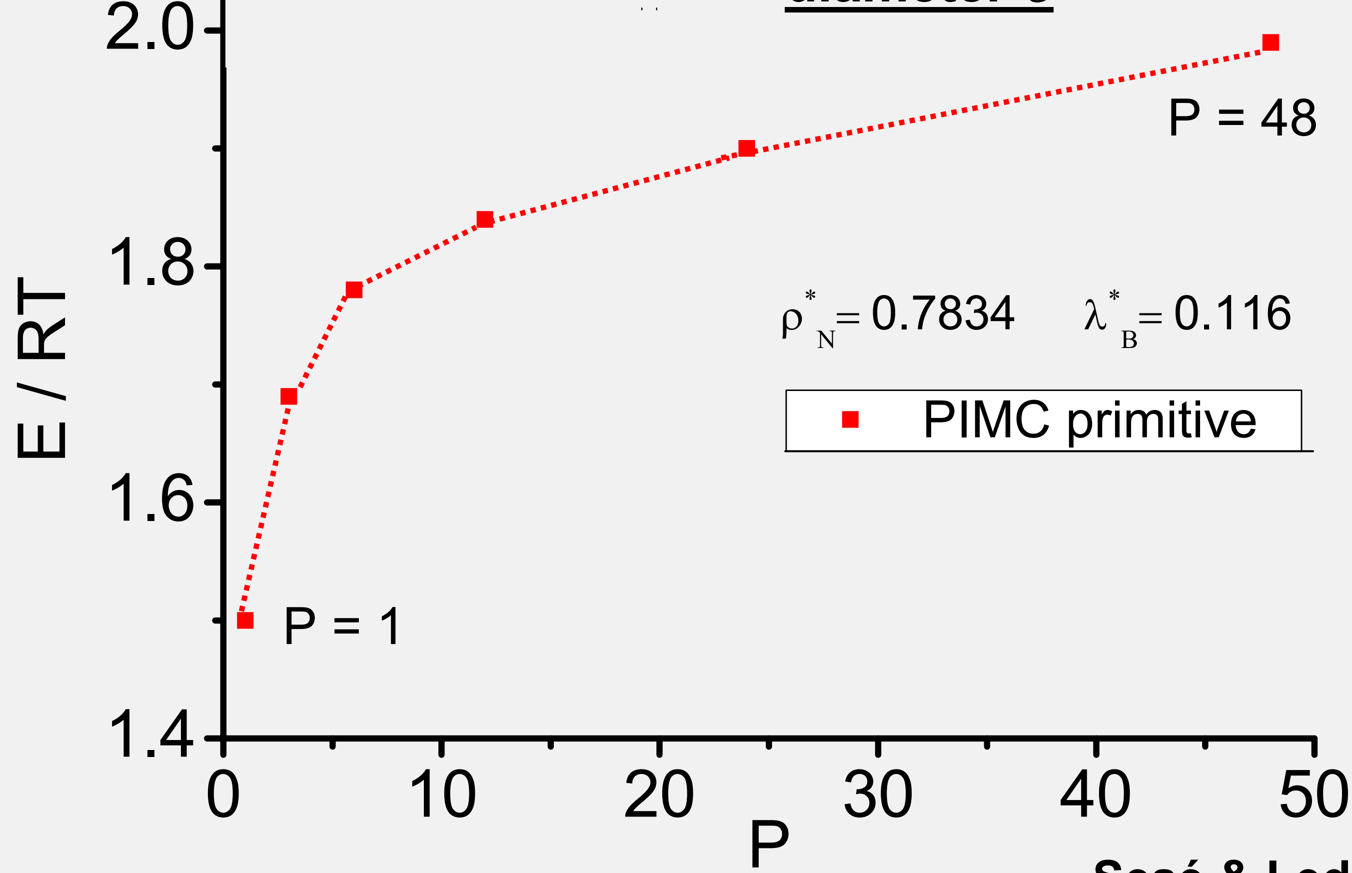
Suzuki's (1991), Chin's (2010)

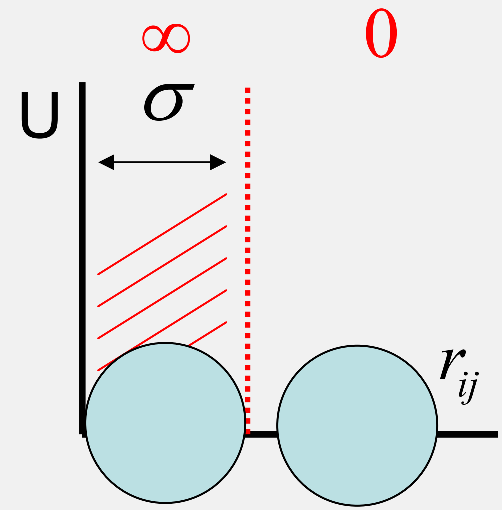
Primitive Propagator (energy)

$$W_{NP} = \frac{mP}{2\beta^2\hbar^2}\sum_{i=1}^{N}\sum_{t=1}^{P}(\mathbf{r}_i^{t+1}-\mathbf{r}_i^{t})^2 + \frac{1}{P}\sum_{i<j}\sum_{t=1}^{P}u(r_{ij}^{t})$$

Quantum Hard Spheres

diameter σ

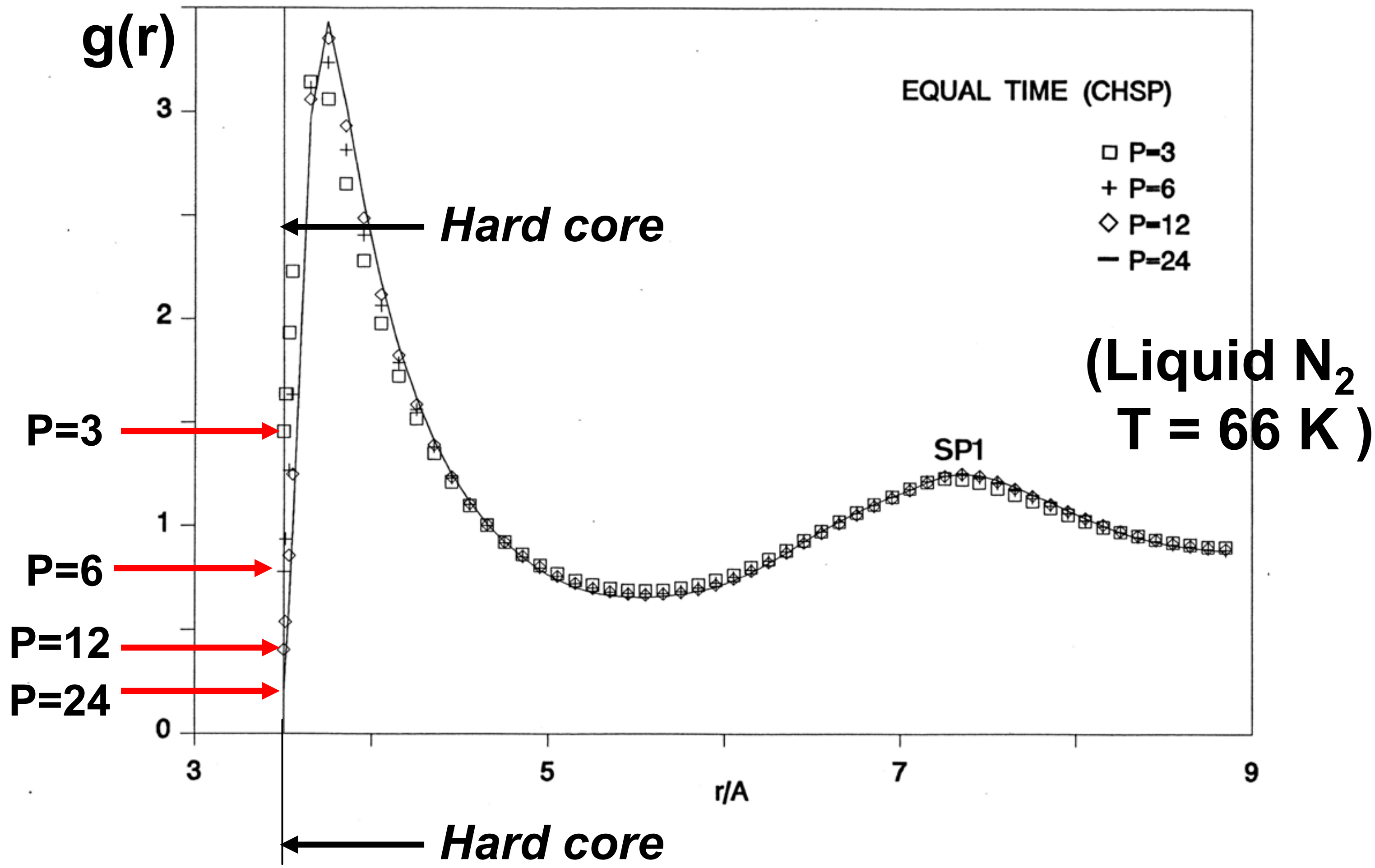




(Liquid N_2 T = 66 K)

Sesé & Ledesma (1995)

Primitive propagator (structure)



Sesé & Ledesma (1995)

Pair Actions

Quantum hard spheres –diameter σ -

- Barker (1979)
- Jacucci-Omerti simplification (1983) – **BJO**-
- Cao – Berne (1992) –**CB**-
- de Prunelé (2008)

Decompose the system into pairs and analyze each pair in terms of the Centre of Mass and The Reduced Mass then combine them in a physically significant manner

Superposition of terms:

one-body (free particle) × two-body (relative coordinate)

$$\rho\left(\mathbf{r}^{N,t},\mathbf{r}^{N,t+1};\beta/P\right)\approx\prod_{i=1}^{N}\rho_{free}\left(\mathbf{r}_i^t,\mathbf{r}_i^{t+1};\beta/P\right)\times\prod_{i<j}^{N}\tilde{\rho}_{ij}\left(\mathbf{r}_i^t-\mathbf{r}_j^t;\mathbf{r}_i^{t+1}-\mathbf{r}_j^{t+1};\beta/P\right)$$

$$W_{NP}(PA)=\underbrace{W_1^F+W_2^{HS}}_{\text{primitive}}+W_2^{PA}$$

----primitive-----

Pair Actions (QHS)

Barker (method of images) + Jacucci-Omerti simplification (BJO propagator, 1983)

$$W_{NP} = \frac{mP}{2\beta^2\hbar^2} \sum_{i=1}^{N} \sum_{t=1}^{P}{}' (\mathbf{r}_i^{t+1} - \mathbf{r}_i^t)^2 + \frac{1}{P} \sum_{i<j} \sum_{t=1}^{P} u(r_{ij}^t) +$$

$$- \frac{1}{\beta} \ln \prod_{i=1}^{N} \prod_{t=1}^{P}{}' \left\{ 1 - \exp\left(- \frac{mP}{\beta\hbar^2} \left(r_{ij}^t - \sigma \right) \left(r_{ij}^{t+1} - \sigma \right) \right) \right\}$$

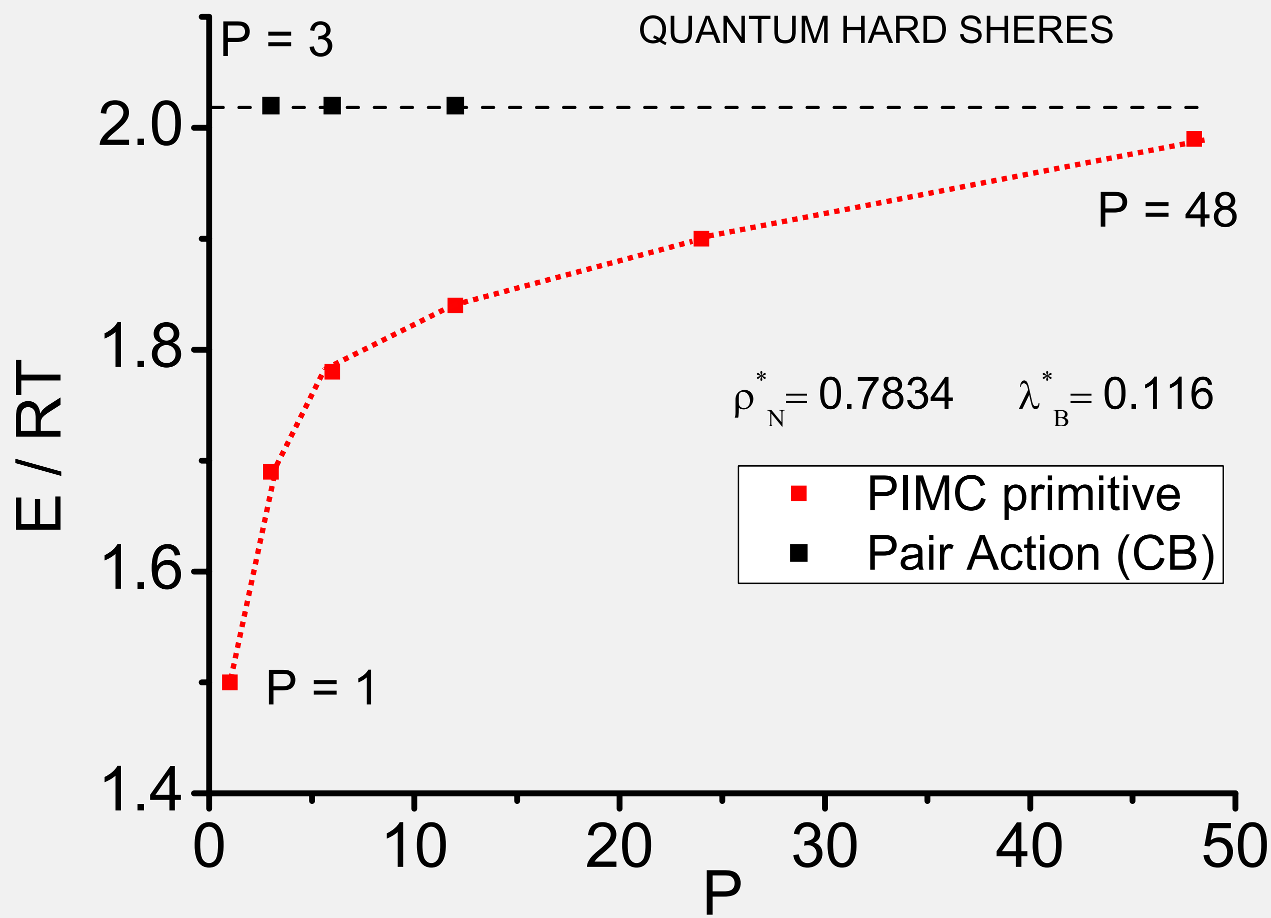
$$Z_{NP}(BJO) = \frac{1}{N!} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{\frac{3NP}{2}} \int d\mathbf{r}^{N\times P} \times \exp(-\beta W_{NP})$$

$\rho \to 0$ *smoothly, as* $r_{ij}^t \to \sigma$. *No contributions to Z.*

$$\langle E_P \rangle = -\left(\frac{\partial \ln Z_{NP}}{\partial \beta} \right)_{N,V} = \frac{3}{2} NPk_B T - \langle W_1^F \rangle + \frac{mP}{2\beta^2\hbar^2} \left\langle \sum_{i<j} \sum_{t=1}^{P}{}' K_{ij}^{t,t+1} \right\rangle$$

$$\langle p_P \rangle = k_B T \left(\frac{\partial \ln Z_{NP}}{\partial V} \right)_{N,T} = \frac{2}{3V} \langle E_P \rangle + \rho_N^2 \frac{\pi\sigma^3\hbar^2}{3m} g''_{t,P}(\sigma+)$$

Effectiveness of Pair Actions (QHS energy)



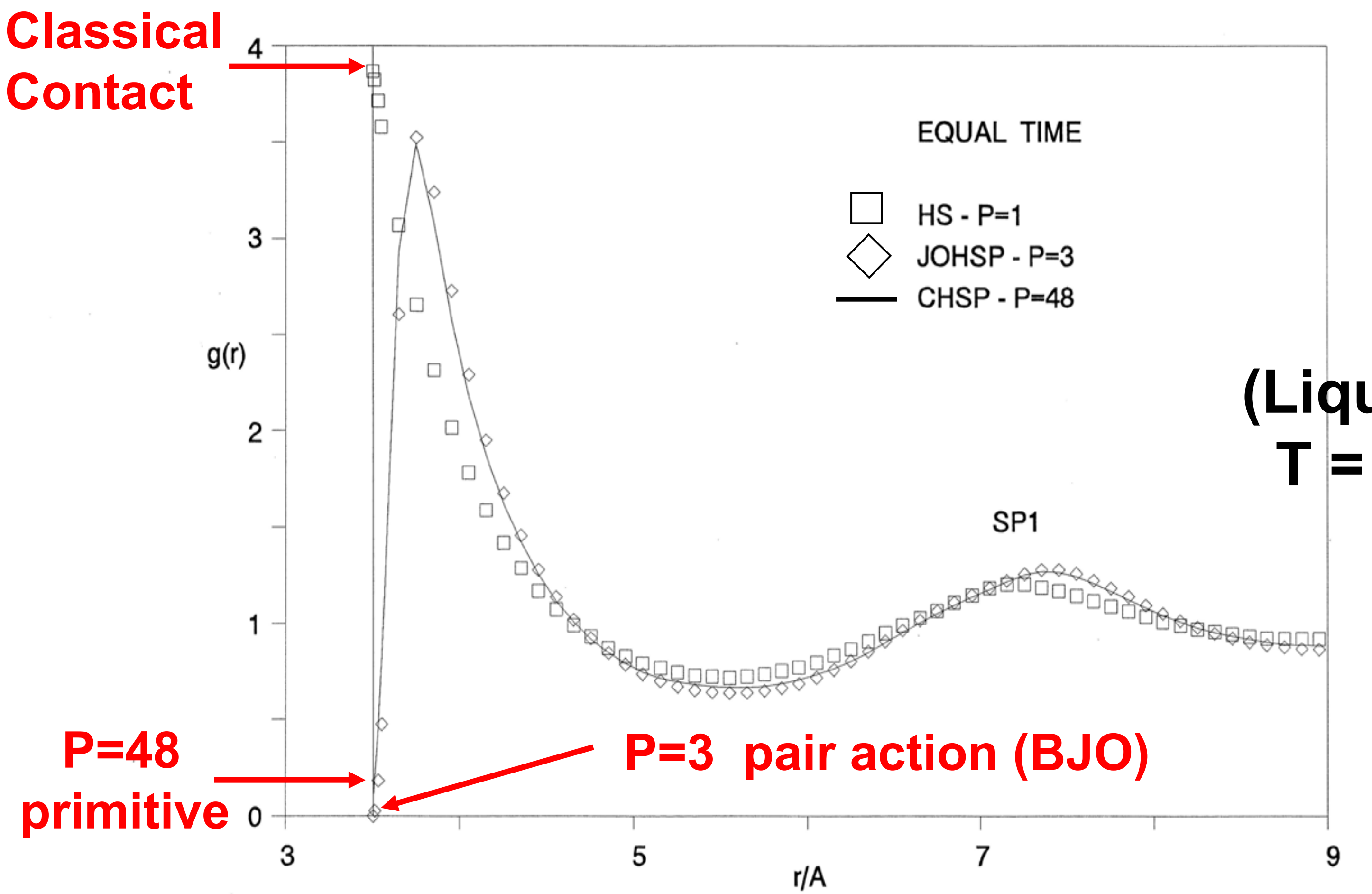
$$\rho_N^* = \rho_N \sigma^3$$

$$\lambda_B^* = \frac{h}{\sqrt{2\pi m k_B T \sigma^2}}$$

(Liquid N_2
T = 66 K)

Sesé & Ledesma (1995)

Effectiveness of Pair Actions (QHS structure)



(Liquid N_2
T = 66 K)

Higher-order propagators $[T, U] \neq 0$

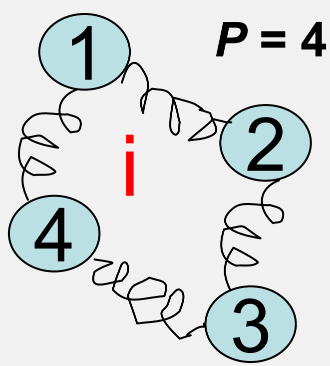
- Takahasi-Imada (1984) / Li-Broughton (1987) $O(P^{-3})$
- Suzuki (1995) - Chin(1997) fourth-order propagator $O(P^{-5})$ - P even!!

$$Z_Q = \frac{1}{N!}\left(\frac{mP}{2\pi\beta\hbar 2}\right)^{\frac{3NP}{2}} \int d\mathbf{r}^{N\times P} \times \exp(-\beta W^{(HO)}{}_{NP}) + O(P^{-4})$$

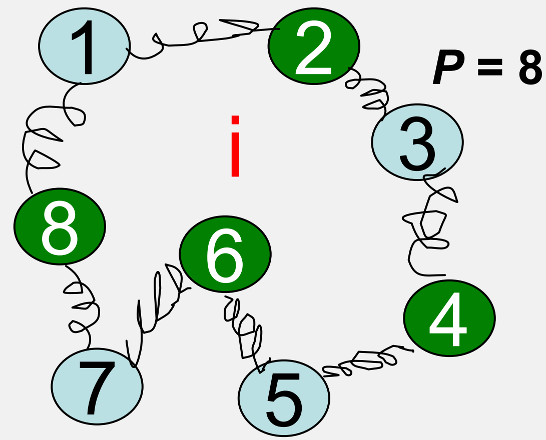
$$[[U,T],U] = \frac{\hbar^2}{m}\sum_{i=1}^{N}(\nabla_i U)^2$$

Forces included!

TI-LB (3)



SC (5)



Chin (2010): ***"This corrector propagator (TI-LB) is only second order, but yields a fourth-order trace, as explained in Ref. 3."***

Takahasi-Imada 1984 / Li-Broughton 1987

$$W_{NP}^{(TI-LB)} = \frac{mP}{2\beta^2\hbar^2}\sum_{i=1}^{N}\sum_{t=1}^{P}{}^{/}(\mathbf{r}_i^{t+1}-\mathbf{r}_i^{t})^2 + \frac{1}{P}\sum_{i<j}\left\{\sum_{t=1,2,3,\ldots,P} u(r_{ij}^{t})\right\} +$$

$$\frac{\beta^2\hbar^2}{24mP^3}\sum_{i=1}^{N}\left\{\sum_{t=1,2,3,\ldots,P}\left(\nabla_i^t \sum_{i\neq j} u(r_{ij}^{t})\right)^2\right\}$$

Bead symmetry kept

Suzuki (1995)-Chin(1997) fourth-order propagator

$$W_{NP}^{(4th)} = \frac{mP}{2\beta^2\hbar^2}\sum_{i=1}^{N}\sum_{t=1}^{P}{}^{/}(\mathbf{r}_i^{t+1}-\mathbf{r}_i^{t})^2 +$$

Bead symmetry lost

$0 \le \alpha \le 1$

$$\frac{2}{3P}\sum_{i<j}\left\{\sum_{t=1,3,5\ldots,P-1} u(r_{ij}^{t}) + 2\sum_{t=2,4,6\ldots,P} u(r_{ij}^{t})\right\} +$$

$$\frac{\beta^2\hbar^2}{9mP^3}\sum_{i=1}^{N}\left\{\alpha\sum_{t=1,3,5\ldots P-1}\left(\nabla_i^t \sum_{i\neq j} u(r_{ij}^{t})\right)^2 + (1-\alpha)\sum_{t=2,4,6\ldots,P}\left(\nabla_i^t \sum_{i\neq j} u(r_{ij}^{t})\right)^2\right\}$$

Higher-order propagators

Properties: Operator + Thermodynamic routes - Jang et al (2001)-

$$\left\langle E \right\rangle_{OPER.} = \frac{Tr\left\{ H_N \exp(-\beta H_N) \right\}}{Tr\left\{ \exp(-\beta H_N) \right\}} = \left\langle T \right\rangle + \left\langle U \right\rangle$$

$$\ldots\ldots \quad \left\langle E \right\rangle_{THERM.} = -\left[\frac{\partial \left(\ln Z_{NP} \right)}{\partial \beta} \right]_{N,V}$$

$$\left\langle B \right\rangle_{OPER.} = \frac{Tr\left\{ B \exp(-\beta H) \right\}}{Tr\left\{ \exp(-\beta H) \right\}} \quad \leftrightarrow \quad \left\langle B \right\rangle_{THERM.} = -k_B T \left(\frac{\partial \ln Z}{\partial X_B} \right)_Y$$

Pair Action against Higher-order propagator: which is better?

No systematic studies available

HO presents a route to improve results via the P reduction, but …

PA works very well, reduces P, deals with singular situations, but…

Ensembles & Algorithms

ENSEMBLES (equivalent in the T-lim)

- Canonical (N, V, T)
- Isothermal-Isobaric (N, P, T)
- Grand Canonical (μ, V, T) – theoretical developments for structures!!!-

-…..(Frenkel & Smit, 2002)

ALGORITHMS (Metropolis sampling)

DISCRETIZED: 3N $\rightarrow$ 3NP -dimension-
FOURIER: 3N $\rightarrow$ 3N(k_{max}+1) -dimension-
HYBRID MONTE CARLO (includes dynamics)

-Primitive algorithm (single bead movements) augmented with necklace overall translation and rotation
-Necklace normal (breathing) modes
-Fourier path-integral

-Staging
-Multilevel sampling
-Bisection
-…..

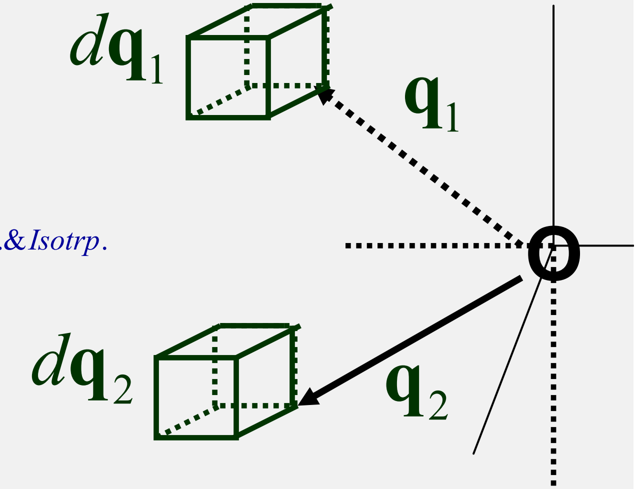
• II.3 Static Order in Classical Many-Body Systems (simulation)

Distribution & Correlation Functions (CANONICAL ENSEMBLE) -Hill (1956)-

- One-point density

$$\rho_N^{(1)}(\mathbf{q}_1) = \left\langle \sum_{i=1,2,\ldots,N} \delta(\mathbf{r}_i - \mathbf{q}_1) \right\rangle = \left\{\rho_N\right\}_{Homog.\&Isotrp.} = bulk\ density\ for\ HI\ fluids = \frac{N}{V}$$

probability density that one particle is at $\mathbf{q}_1 + d\mathbf{q}_1$



- Pair distribution / correlation function

$$\rho_N^{(2)}(\mathbf{q}_1,\mathbf{q}_2) = \left\langle \sum_{i\neq j} \delta(\mathbf{r}_i - \mathbf{q}_1)\delta(\mathbf{r}_j - \mathbf{q}_2) \right\rangle = \left\{\rho_N^2 g_2(r)\right\}_{Homog.\&Isotrp.}$$

probability density that : one particle is at $\mathbf{q}_1 + d\mathbf{q}_1$

and another is at $\mathbf{q}_2 + d\mathbf{q}_2$

- Triplet distribution / correlation function

$$\rho_N^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = \left\langle \sum_{i\neq j\neq k\neq i} \delta(\mathbf{r}_i - \mathbf{q}_1)\delta(\mathbf{r}_j - \mathbf{q}_2)\ \delta(\mathbf{r}_k - \mathbf{q}_3) \right\rangle = \left\{\rho_N^3 g_3(r,s,y)\right\}_{Homog.\&Isotrp.}$$

probability density that : one particle is at $\mathbf{q}_1 + d\mathbf{q}_1$

other is at $\mathbf{q}_2 + d\mathbf{q}_2$

and another is at $\mathbf{q}_3 + d\mathbf{q}_3$

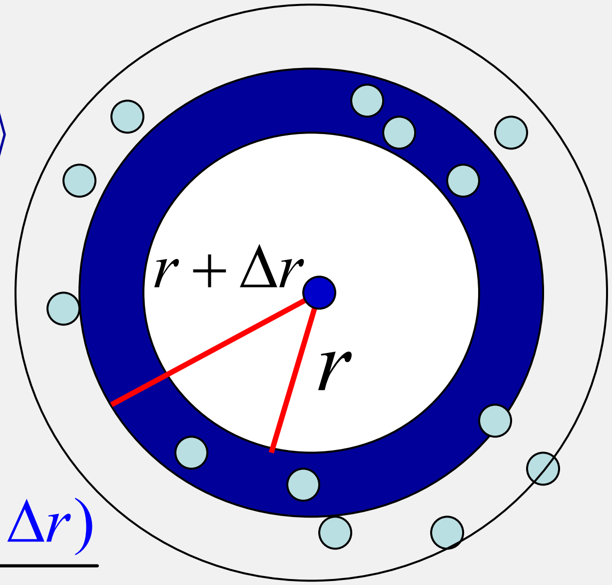
- ……

• II.3 Static Order in Classical Many-Body Systems (simulation)

Correlation Functions (CANONICAL ENSEMBLE)

-Pair correlation functions

$$\rho_N^{(2)}(\mathbf{q}_1,\mathbf{q}_2)=\left\{\rho_N^2 g_2(r)\right\}_{Homog.\&Isotrp.}=\left\langle \sum_{i\neq j}\delta(\mathbf{r}_i-\mathbf{q}_1)\delta(\mathbf{r}_j-\mathbf{q}_2)\right\rangle$$



Fluids (radial):

$$r=\left|\mathbf{q}_i-\mathbf{q}_j\right|$$

$$\pi_N(r)=\rho_N g_2(r)$$

$$\pi_N(r)=\rho_N \quad -ideal\ gas-$$

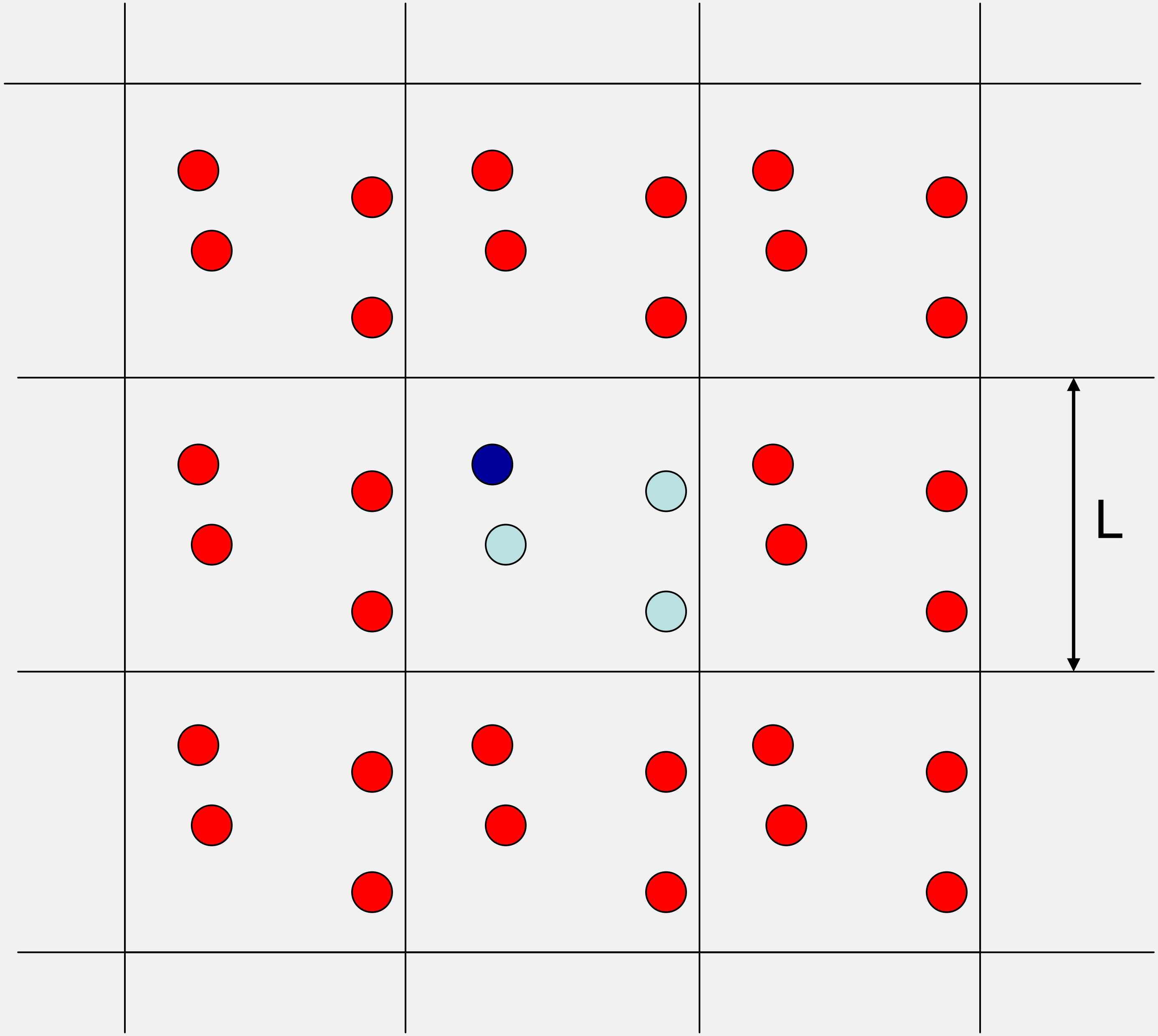
$$dN(r)=4\pi\rho_N g_2(r)r^2dr \rightarrow g_2(r)\approx\frac{\Delta N(r,r+\Delta r)}{4\pi\rho_N r^2\Delta r}$$

$$\Delta r\approx 0.1\,\text{Å}$$

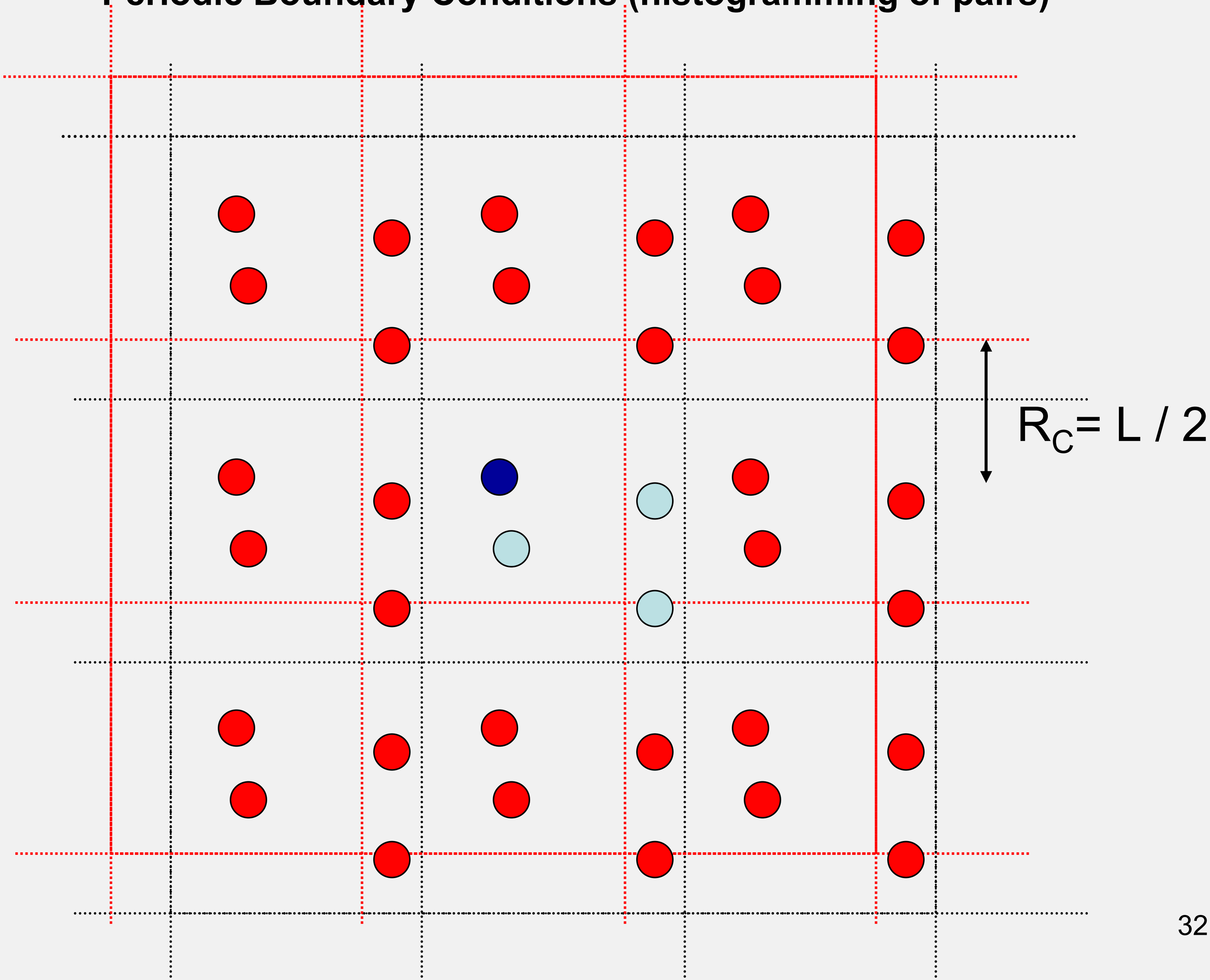
$$4\pi\rho_N\int_0^\infty g_2(r)r^2dr=N-1$$

AVERAGE OVER CENTRAL PARTICLES AND SPHERICALSHELLS,
i* < *j $\rightarrow$ **Double counting (pairs 2!)**
PBC $\rightarrow$ **cut-off distance *r* < *L/2* (*L* = box length)**
Finite-N effects (closed ensembles)!!!

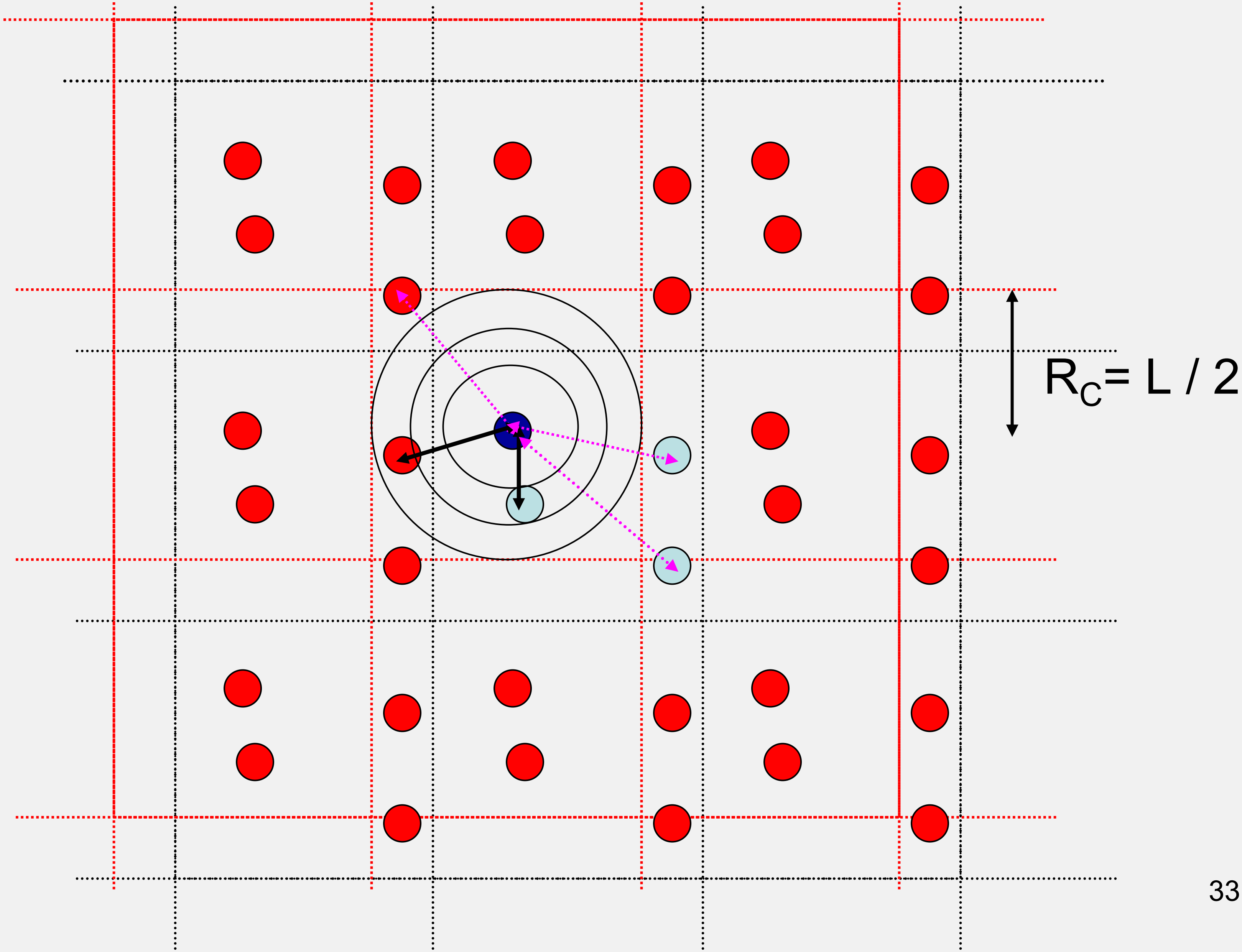
Periodic Boundary Conditions (histogramming of pairs)



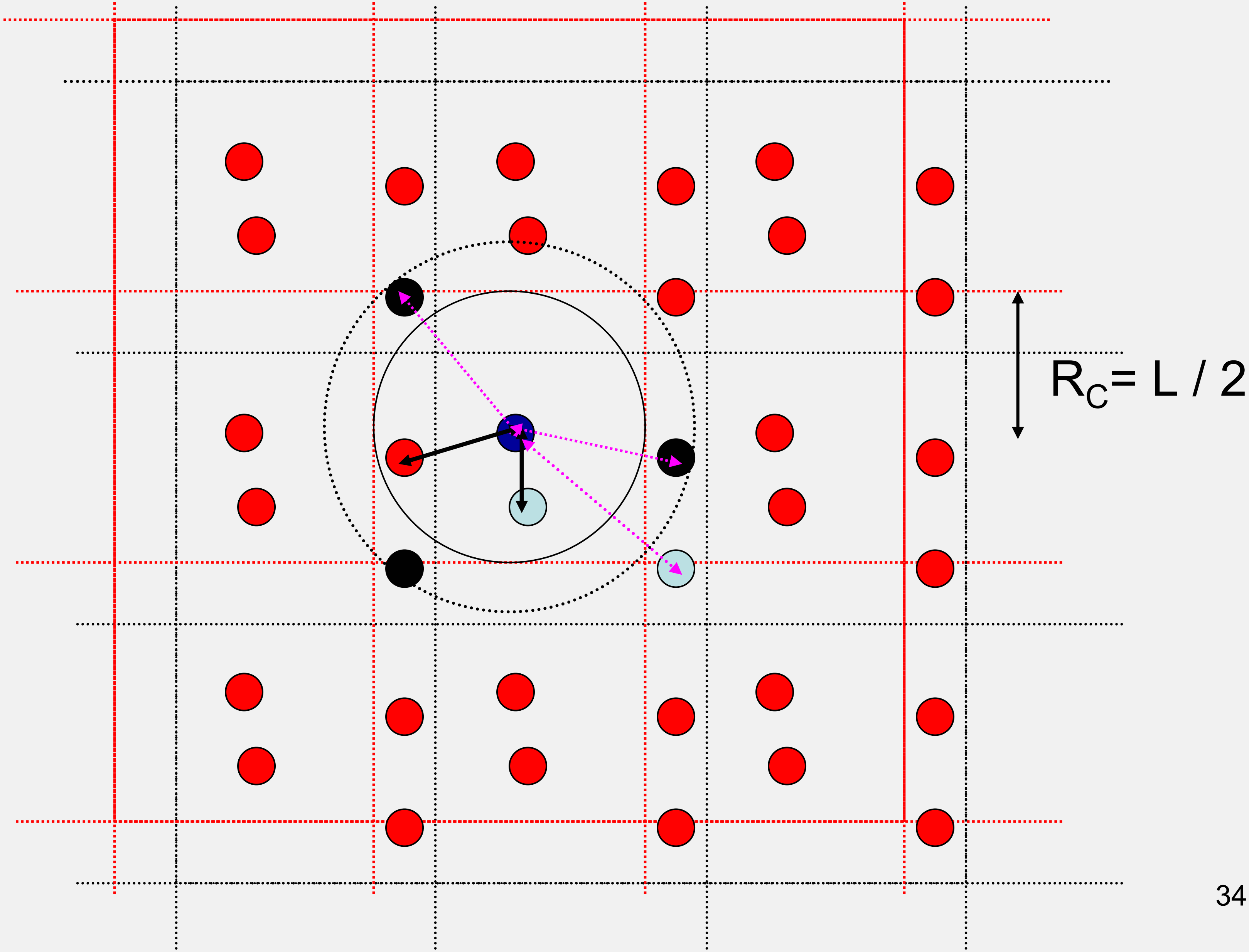
Periodic Boundary Conditions (histogramming of pairs)



Periodic Boundary Conditions (histogramming of pairs)



Periodic Boundary Conditions (histogramming of pairs)

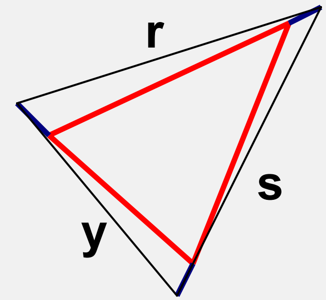


- Triplet correlation functions (Tanaka & Fukui, 1975)

$$\rho_N^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = \left\{\rho_N^3 g_3(r,s,y)\right\}_{Homog.\&Isotrp.} = \left\langle \sum_{i\neq j\neq k\neq i} \delta(\mathbf{r}_i-\mathbf{q}_1)\,\delta(\mathbf{r}_j-\mathbf{q}_2)\,\delta(\mathbf{r}_k-\mathbf{q}_3)\right\rangle$$

$$g_3(R,S,Y) \approx \frac{\Delta T_{Triplets\ in\ \Delta V}}{N\rho_N^2\left(\Delta V\right)_{R,S,Y}}$$

$$R-\Delta < r \leq R$$
$$S-\Delta < s \leq S$$
$$Y-\Delta < y \leq Y$$



Expected volume (bipolar coord.)

$$\left(\Delta V\right)_{RSY} = 8\pi^2\Delta^3\left(R-\Delta/2\right)\left(S-\Delta/2\right)\left(Y-\Delta/2\right)$$

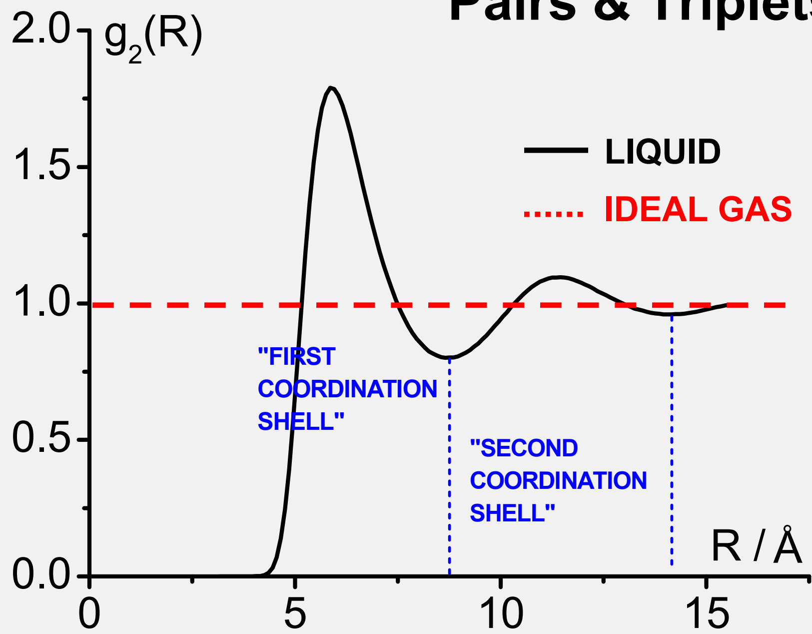
Equilateral ***r* = *s* = *y***
Isosceles ***r*, *s* = *y***
General ***r*, *s*, *y***

PBC → "cut-off distance" ***r* + *s* + *y* < *L***

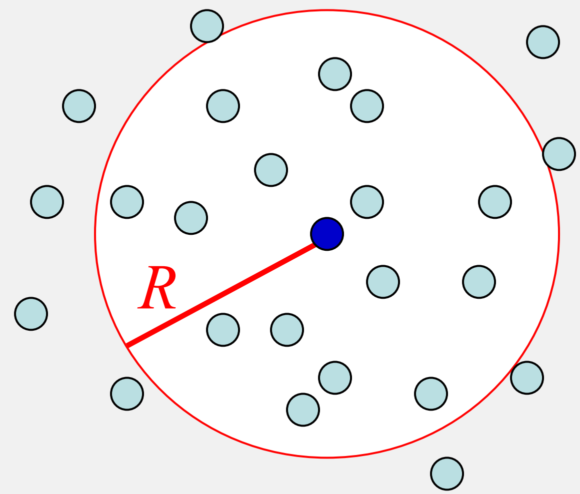
i < j < k → Sixfold counting (3!)

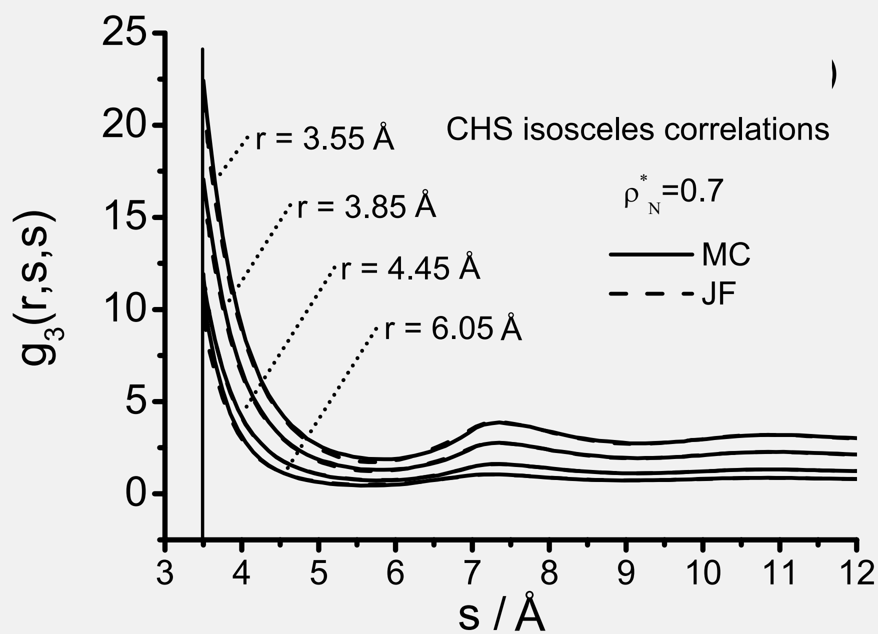
Fluids (Baranyai & Evans, 1990) →
special volume formulae for almost linear configurations !!!

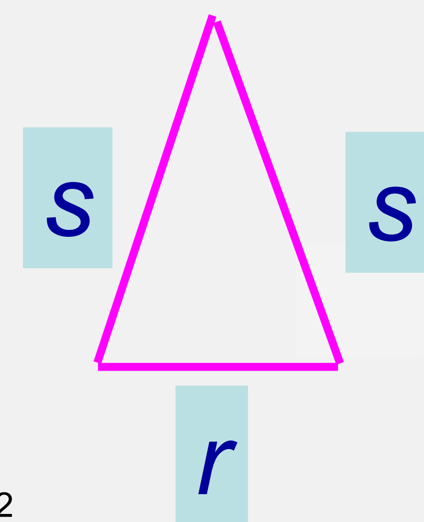
Pairs & Triplets in real space



$$N(R) = 4\pi\rho_N \int_0^R r^2 g_2(r)dr$$







Usefulness (Egelstaff, 1973, 1992):

- Fluids: X-ray, neutron diffraction (elastic scattering) – pair level -
- Information on crystallization (FREEZING THEORIES,…)
- Thermodynamic connection (equations of state)
- Hierarchies
- Use of closures for g_3
- …..

Thermodynamics

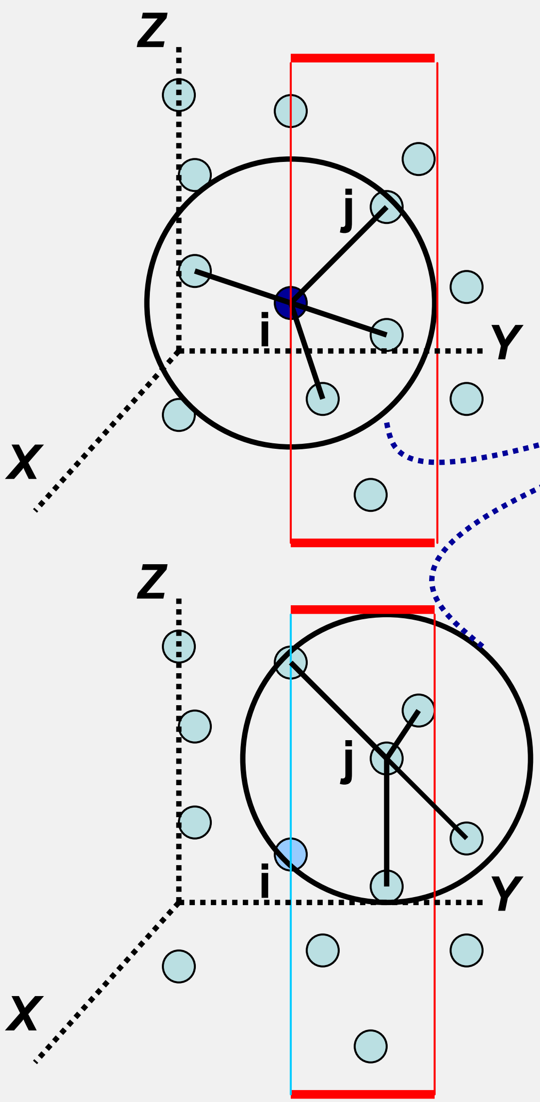
$$\langle E\rangle = \frac{3}{2}Nk_BT + \frac{1}{2}\int u_2(\mathbf{q}_1,\mathbf{q}_2)\rho_N^{(2)}(\mathbf{q}_1,\mathbf{q}_2;\rho_N,T)\,d\mathbf{q}_1 d\mathbf{q}_2 + $$
$$+\frac{1}{6}\int u_3(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\rho_N^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3;\rho_N,T)\,d\mathbf{q}_1 d\mathbf{q}_2 d\mathbf{q}_3 + \ldots$$

$$\langle p\rangle = \rho_N k_BT - \frac{\rho_N^2}{6}\int r\frac{du_2(r)}{dr}g_2(r;\rho_N,T)\,d\mathbf{r} -$$
$$-\frac{\rho_N^3}{6}\int r\frac{\partial u_3(\mathbf{r},\mathbf{s})}{\partial r}g_3(\mathbf{r},\mathbf{s};\rho_N,T)\,d\mathbf{r}d\mathbf{s} + \ldots$$

Hierarchies (BGY, density derivatives)

$$k_BT\chi_T\left(\frac{\partial\left\{\rho_N^2 g_2(\mathbf{q}_1,\mathbf{q}_2)\right\}}{\partial\rho_N}\right)_T = \rho_N\int d\mathbf{q}_3\left[g_3(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) - g_2(\mathbf{q}_1,\mathbf{q}_2)\right] + 2g_2(\mathbf{q}_1,\mathbf{q}_2)$$

Steinhardt *et al* Order Parameters (Configurational) – (1983)



$$i-j,\ N_b\ \text{"bonds" within}\ \frac{d_C}{\sigma}=1.2-1.5$$

$$Q_l=\left\{\frac{4\pi}{2l+1}\sum_{m=-l}^{+l}\left|N_b^{-1}\sum_b Y_{l,m}(\theta_{ij},\phi_{ij})\right|^2\right\}^{1/2}$$

l even

$l=4,\ 6,\ldots$

$$\langle Q_l\rangle_{RUN}$$

Very sentitive to orientational order (solids):

	Q_4 (≈)	Q_6 (≈)
FCC	0.19*	0.3 - 0.57*
BCC	0.04*	0.3 - 0.52*
HCP	0.10*	0.3 - 0.48*
Amorphous		0.07 – 0.2
Fluids		0.02 – 0.06

* = perfect lattice

$(\rho_N\uparrow)$

LANDAU's free energy $F(Q,T)_{NVT}$
(Lynden-Bell -1995-)

……….

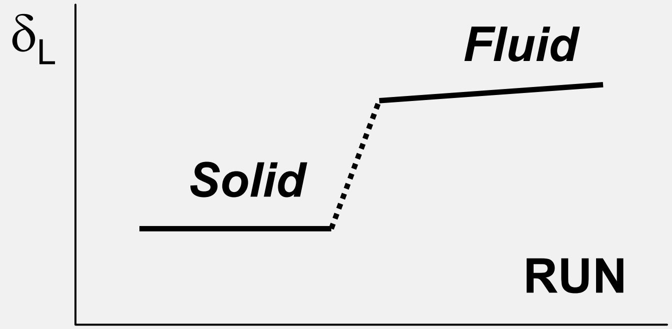
Lindemann's index (MELTING)

$$\delta_L = \frac{2}{N(N-1)} \sum_{i<j} \frac{\left(\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2 \right)^{1/2}}{\langle r_{ij} \rangle}$$

Entire-run evaluation

-Plateau for solids

-Jump (increase) for melting



Lindemann's RMS ratio (MELTING)

$$\gamma_L = \frac{1}{d_{nn}} \left\langle \frac{1}{N} \sum_{i=1}^{N} \left(\mathbf{r}_i - \mathbf{r}_i^{(0)} \right)^2 \right\rangle^{\frac{1}{2}}$$

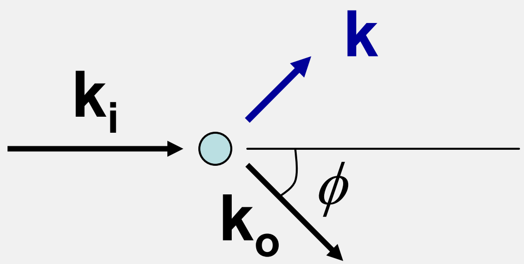
0.13 (CHS)

…

0.27 (He-4, LJ, T=0 K)

Static Structure Factor for Fluids ("elastic" scattering; Hansen & McDonald,1986)

Only momentum transfers: $\hbar\mathbf{k} = \hbar\left(\mathbf{k}_o - \mathbf{k}_i\right)$ $\quad \left\{E_i >> E_{particle}(a\ few\ k_B T)\right\}$



$|\mathbf{k}_i| = |\mathbf{k}_o|$

$$k_i = \frac{2\pi}{\lambda_i}$$

$$k = \frac{4\pi}{\lambda_i}\sin\frac{\phi}{2}$$

Intensity of the scattering:

$$S^{(2)}(k) = \frac{1}{N}\left\langle \left| \sum_{j=1}^{N} \exp\left(i\mathbf{k}\cdot\mathbf{r}_j\right) \right|^2 \right\rangle \rightarrow 1 + \rho_N \int d\mathbf{r}\, \exp(i\mathbf{k}\cdot\mathbf{r})\left[g_2(r) - 1\right] =$$

$$\left\{-(2\pi)^3 \delta(\mathbf{k})\, \rho_N\right\} \qquad 1 + 4\pi\rho_N \int_0^\infty dr\, \frac{\sin kr}{kr}\, r^2\left(g_2(r) - 1\right)$$

$$S^{(2)}(k=0) = \rho_N k_B T \chi_T = dimensionless\ isothermal\ compressibility$$

Static Structure Factor for Fluids ("elastic" scattering; Hansen & McDonald,1986)

$$\left(\frac{\partial S^{(2)}(k)}{\partial \rho_N}\right)_T = \frac{S^{(2)}(k)-1}{\rho_N} + \rho_N \int d\mathbf{r} \exp\left(-i\mathbf{k}\cdot\mathbf{r}\right)\left(\frac{\partial}{\partial \rho_N}\left(g_2(r)-1\right)\right)_T = f(g_2, g_3)$$

Simulation puts a limit on small *k due to the finite size of the box !!!*

$S^{(2)}(k)$ **is an average of** $S^{(2)}(\mathbf{k})$ **over a representative set of wave vectors**

$$\{\mathbf{k}_n\} = \frac{2\pi}{L}\{k_{nx}, k_{ny}, k_{nz}\}; \quad k^2 = \frac{4\pi^2}{L^2}\left(k_{nx}^2 + k_{ny}^2 + k_{nz}^2\right); \quad k_{nx}, \ldots \; integers$$

Alternative: Calculation of the Fourier Transform?

TRIPLETS

$$S^{(3)}(\mathbf{k}_1, \mathbf{k}_2) = N^{-1}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{m=1}^{N} \exp\left[i\left(\mathbf{k}_1\cdot\mathbf{r}_i + \mathbf{k}_2\cdot\mathbf{r}_j - (\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}_m\right)\right]\right\rangle$$

Static Structure Factor for Solids

Kittel (2005) + Mandell, McTague and Rahman (1977)

$$S^{(2)}_{hkl}(\mathbf{G}) = N^{-1}\sum_{j=1}^{N}\exp\left(i\mathbf{G}\cdot\mathbf{q}_j\right); \quad \mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3; \quad \mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot\mathbf{a}_2\times\mathbf{a}_3},\ldots$$

$$\mathbf{q}_j = j - particle\ position$$

$$\mathbf{G}\equiv\mathbf{k}$$

SIMULATION (COOLING-COMPRESSION)

INTENSITY

$$S^{(2)}(\mathbf{k}) = N_S^{-2}\left|\sum_{j=1}^{N}\exp\left(i\mathbf{k}\cdot\mathbf{q}_j\right)\right|^2$$

$$N_S = simulation\ sample\ size$$

For a perfect lattice: Bragg's system (cubic - 3 vectors)

$$S^{(2)}_{PL}(\mathbf{k}_{\max}) = 1 \qquad \left\{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3\right\}_n$$

$$\left|\mathbf{k}_1\cdot\left(\mathbf{k}_2\times\mathbf{k}_3\right)\right| = N_S\left(2\pi/L\right)^3$$

Static Structure Factor for Solids (Simulation)

Mandell, McTague and Rahman (1977)

SIMULATION: Searching for maximal wave vectors and comparison:

$$\mathbf{k} = \frac{2\pi}{L}\left(k_x, k_y, k_z\right); \; -10 \le k_\nu \le 10;$$

$$\left|\mathbf{k}_1 \cdot \left(\mathbf{k}_2 \times \mathbf{k}_3\right)\right| = N_S \left(2\pi / L\right)^3$$

Initial perfect lattice

$$S^{(2)}(\mathbf{k}_{\max imal}) < S^{(2)}_{PL}(\mathbf{k}_{\max}) = 1$$

	0.2	**liquids**
Maximal values	**0.2-0.5**	**amorphous**
	0.5-…	**partially crystalline**

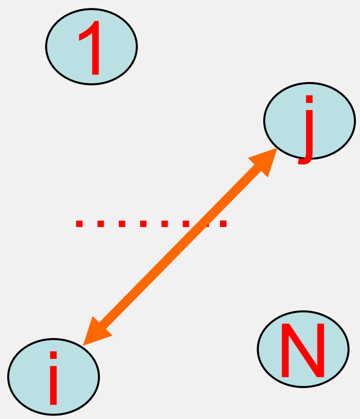
FCC		**BCC**	
$k_x k_y k_z$	*all odd* / *all even*	$k_x + k_y + k_z$ = *even integer*	…..

• II.4 Quantum Delocalization and Structural Complexity

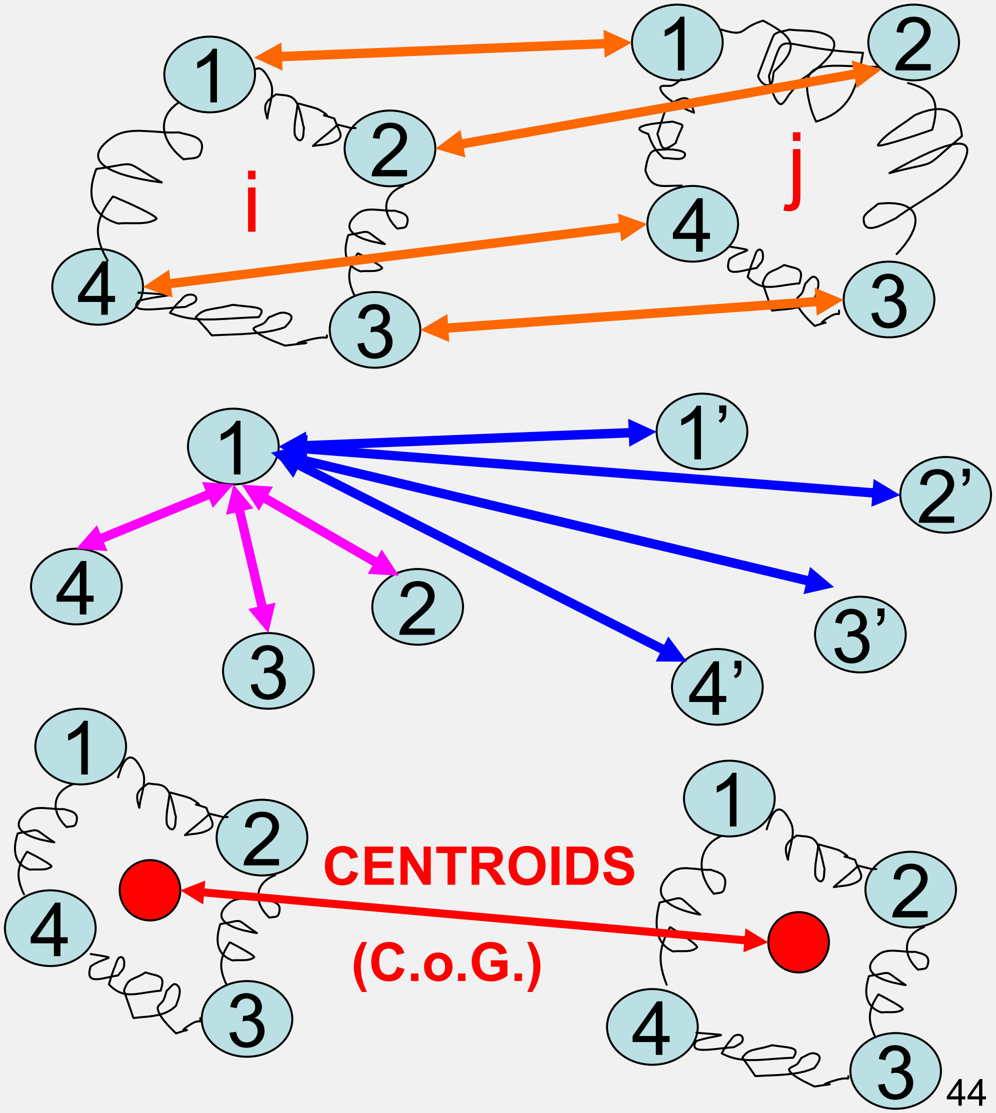
$$\rho_N = \frac{N}{V} \quad \leftrightarrow \quad \rho_N = \frac{1}{P}\frac{NP}{V} = \frac{N}{V}$$

Classical $\qquad$ *Path − integral*

Classical System



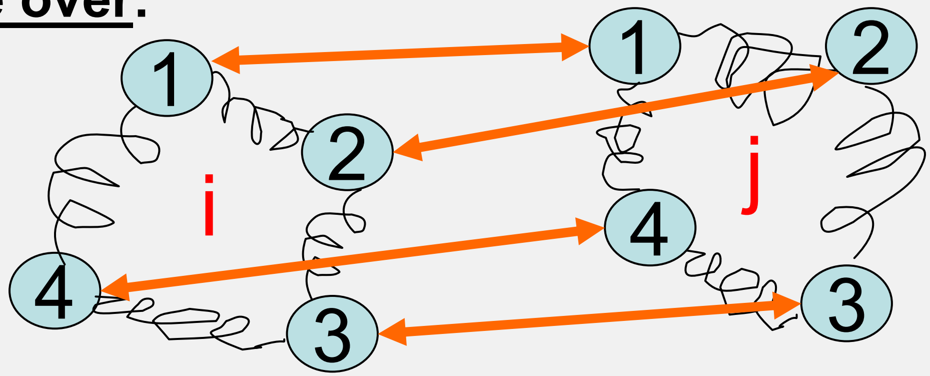
Path-integral Model (P=4)



- III. Static Quantum Structures in Real Space

• **III. 1 The "Standard" Instantaneous Pair Correlations**

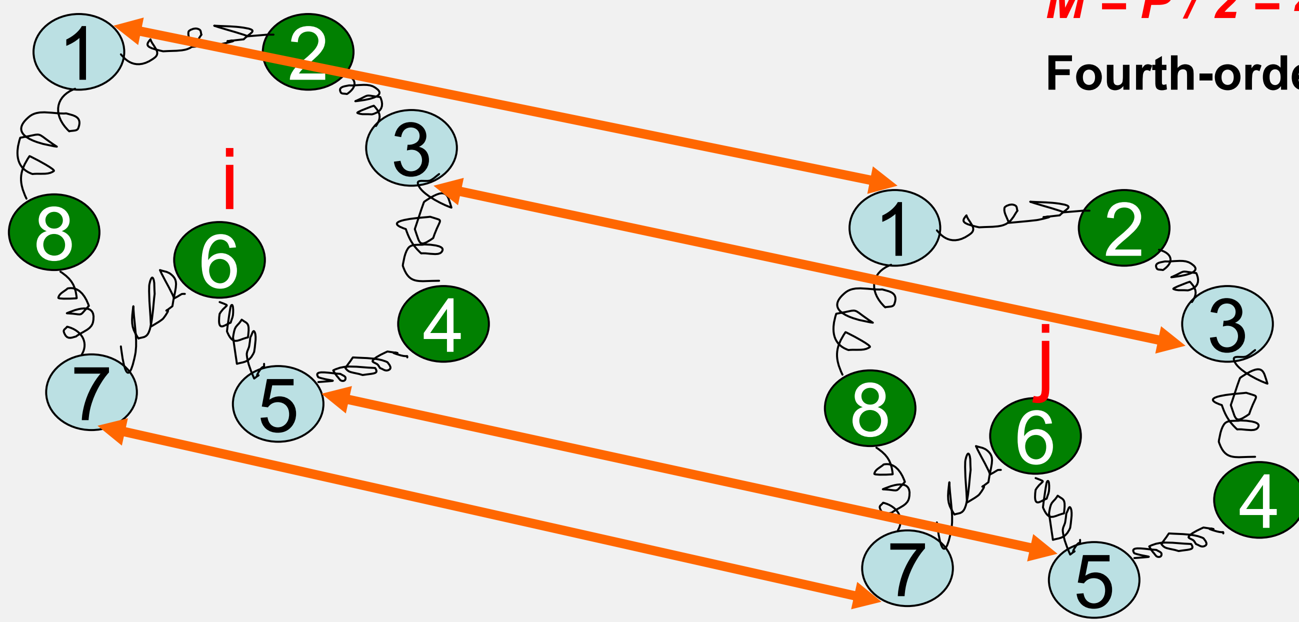
Average over:



M = P = 4

Primitive Pair actions

Average over:



M = P / 2 = 4

Fourth-order

Instantaneous = ET = equal time = "DIAGONAL"

Primitive Propagator

$$\rho^{(2)}_{N,ET}(\mathbf{q}_1,\mathbf{q}_2)=\left\{\rho_N^2 g_{2,ET}(r)\right\}_{Homog.\&Isotrp.}=\left\langle \sum_{i\neq j}\delta(\mathbf{r}_i-\mathbf{q}_1)\delta(\mathbf{r}_j-\mathbf{q}_2)\right\rangle=$$

$$\frac{Tr\left\{\left(\sum_{i\neq j}\delta(\mathbf{r}_i-\mathbf{q}_1)\delta(\mathbf{r}_j-\mathbf{q}_2)\right)\exp\left(-\beta H_N\right)\right\}}{Tr\left\{\exp\left(-\beta H_N\right)\right\}}=\frac{1}{Z_N N!}\int d\mathbf{r}^N\left\langle \mathbf{r}^N\left|\left(\sum_{i\neq j}\delta(\mathbf{r}_i-\mathbf{q}_1)\delta(\mathbf{r}_j-\mathbf{q}_2)\right)\exp\left(-\beta H_N\right)\right|\mathbf{r}^N\right\rangle=$$

$$\frac{1}{Z_N N!}\int d\mathbf{r}^N\left\langle \mathbf{r}^N\left|\left(\sum_{i\neq j}\delta(\mathbf{r}_i-\mathbf{q}_1)\delta(\mathbf{r}_j-\mathbf{q}_2)\right)\exp\left(-\frac{\beta H_N}{P}\right)\downarrow\exp\left(-\frac{\beta H_N}{P}\right)\downarrow\ldots\downarrow\exp\left(-\frac{\beta H_N}{P}\right)\right|\mathbf{r}^N\right\rangle=$$

$$\left\{P\ partitions\right\}\ and\ \left\{P-1\rightarrow\int d\mathbf{r}\ |\mathbf{r}\rangle\langle\mathbf{r}|=1\right\}$$

$$\frac{N(N-1)}{Z_N N!}\int d\mathbf{r}^{N,1}d\mathbf{r}^{N,2}\ldots d\mathbf{r}^{N,P}\left(\frac{1}{P}\sum_{t=1,2,\ldots,P}\delta(\mathbf{r}_1^t-\mathbf{q}_1)\delta(\mathbf{r}_2^t-\mathbf{q}_2)\right)\times\exp\left(-\beta W_{NP}\right)$$

$g_2(r)-t=1-$

$g_2(r)-t=2-$

.....

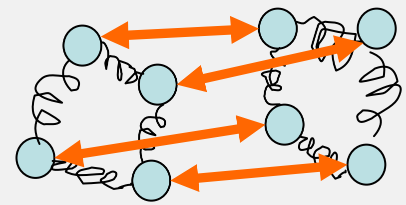
$g_2(r)-t=P-$

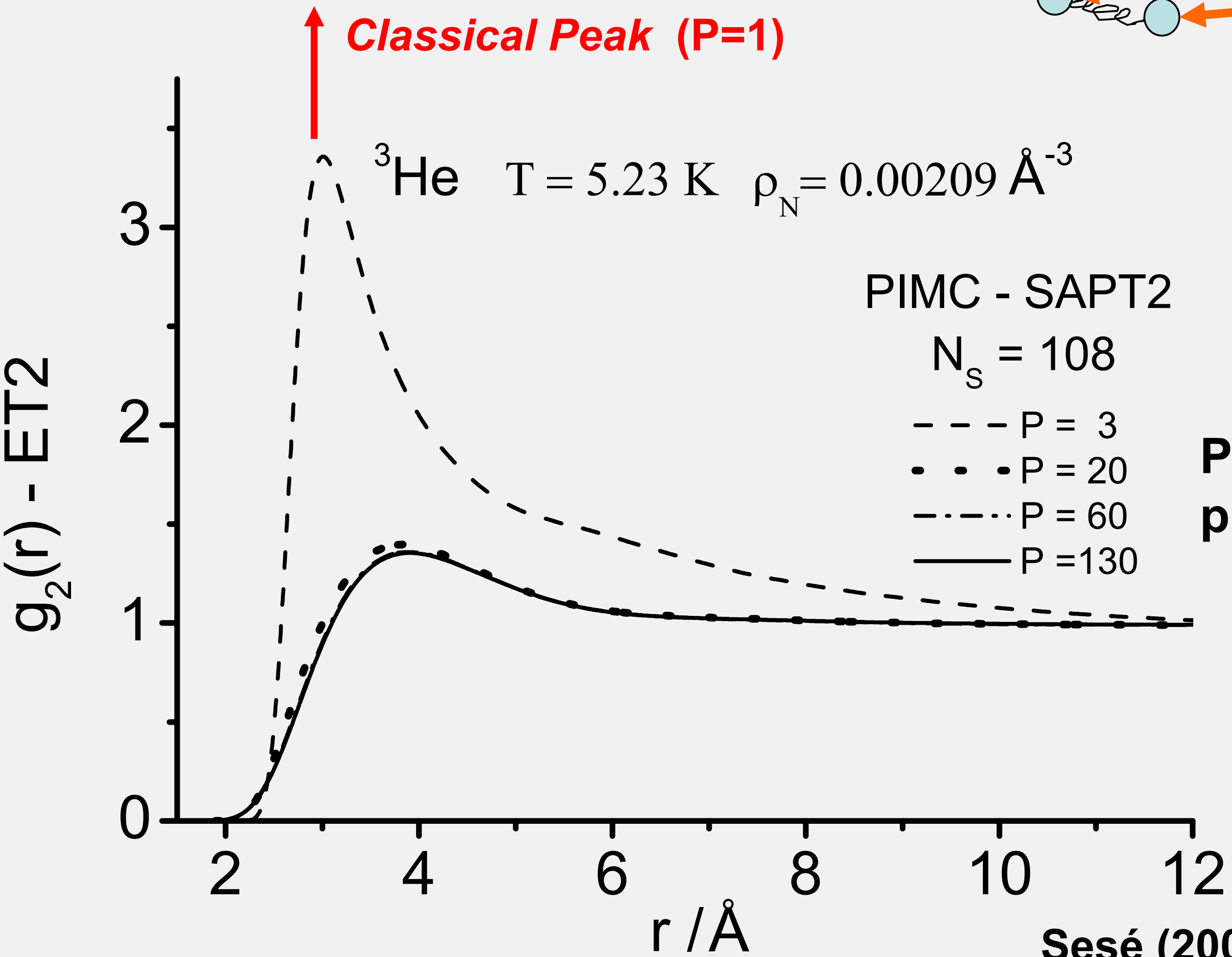
$$\rightarrow\left\langle\frac{1}{P}\sum_{t=1}^{P}\sum_{i\neq j}\delta(r-r_{ij}^t)\right\rangle\rightarrow g_{2,ET}(r)$$

(FLUID)

Helium-3 gas / PIMC convergence

Instantaneous





Primitive propagator

Sesé (2008)

• III. 2 External Fields and Functional Calculus

$$H_N = H_N^0 + \Psi_N = T + U + \Psi_N = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j} u(r_{ij}) + \sum_{i<j<l} u(r_{ij}, r_{il}, r_{lj}) + \ldots + \sum_{i=1}^{N}\Psi(\mathbf{r}_i)$$

Ψ is an external <u>weak continuous</u> field (w.c.f)

GRAND ENSEMBLE (For simplicity: Primitive Propagator + Fluids)

$$\Xi = \sum_{N\geq 0}\exp(\beta\mu N) Tr\left\{\exp(-\beta H_N)\right\} = \sum_{N\geq 0}\frac{\exp(\beta\mu N)}{N!}\int d\mathbf{r}^N \left\langle \mathbf{r}^N \middle| \exp(-\beta H_N) \middle| \mathbf{r}^N \right\rangle$$

PI $\quad H_N^0 \quad \Psi_N$

$$\Xi_P(\Psi) = \sum_{N\geq 0} C_N \frac{\exp(\beta\mu N)}{N!}\int \prod_{t=1}^{P}{}' d\mathbf{r}^{N,t} \times \exp\left(-\beta W_{NP}\right) \times \exp\left(-\frac{\beta}{P}\sum_{i=1}^{N}\sum_{t=1}^{P}\Psi(\mathbf{r}_i^t)\right)$$

Functional Variations and Derivatives of the Partition Function
(Hansen & McDonald, 1986)

$$\frac{\delta \ln \Xi_P(\Psi)}{\delta \Psi(\mathbf{q}_1)}, \quad \frac{\delta^2 \ln \Xi_P(\Psi)}{\delta \Psi(\mathbf{q}_1)\delta \Psi(\mathbf{q}_2)} ?$$

A very simple example:

$$J\left(y(x)\right) = \int_{\Omega} \theta\left(y(x)\right) dx \qquad J\left(y(x)\right) = \int_{-\infty}^{\infty} y^2 dx \quad (convergent)$$

$$\delta J\left(y(x)\right) = \frac{\partial}{\partial \alpha} J\left(y(x) + \alpha \delta y(x)\right)\Big|_{\alpha=0} \qquad \delta J\left(y(x)\right) = \frac{\partial}{\partial \alpha} \int_{-\infty}^{\infty} \left(y + \alpha \delta y\right)^2 dx\Big|_{\alpha=0} = \int_{-\infty}^{\infty} 2y(x)\, \delta y(x) dx$$

$$\frac{\delta J\left(y(x)\right)}{\delta y(x)} \qquad \frac{\delta J\left(y(x)\right)}{\delta y(x)} = 2y(x) \equiv \int_{-\infty}^{\infty} 2y(z)\, \delta(z-x) dz$$

$$\delta^2 J\left(y(x)\right) = \frac{\partial^2}{\partial \alpha^2} J\left(y(x) + \alpha \delta y(x)\right)\Big|_{\alpha=0} \qquad \delta^2 J\left(y(x)\right) = \frac{\partial^2}{\partial \alpha^2} \int_{-\infty}^{\infty} \left(y + \alpha \delta y\right)^2 dx\Big|_{\alpha=0} = \int_{-\infty}^{\infty} 2\delta y(x) \delta y(x) dx$$

$$\frac{\delta^2 J\left(y(x)\right)}{\delta y(x) \delta y(x)} \qquad \frac{\delta^2 J\left(y(x)\right)}{\delta y(x) \delta y(x)} = 2$$

• III. 3 Three More Basic Correlations up to the Pair Level

Chandler & Wolynes (1981) – Sesé (1995 …)

First Variation (one-body function; fluids)

$$-Pk_BT\frac{\delta \ln \Xi_P(\Psi)}{\delta\Psi(\mathbf{q}_1)}=\frac{1}{\Xi_P(\Psi)}\sum_{N\geq 0}\frac{z_P^N}{N!}\int\prod_{t=1}^{P}/d\mathbf{r}^{N,t}\times\exp\left(-\beta W_{NP}\right)\times\exp\left(-\frac{\beta}{P}\sum_{i=1}^{N}\sum_{t=1}^{P}\Psi(\mathbf{r}_i^t)\right)\left(\sum_{i=1}^{N}\sum_{t=1}^{P}\delta\left(\mathbf{r}_i^t-\mathbf{q}_1\right)\right)=$$

$$=\rho_{NP}^{(1)}(\mathbf{q}_1,\Psi)=P\rho_N^{(1)}(\mathbf{q}_1,\Psi)$$

$$-k_BT\frac{\delta \ln \Xi_P(\Psi)}{\delta\Psi(\mathbf{q}_1)}=\rho_N^{(1)}(\mathbf{q}_1,\Psi)$$

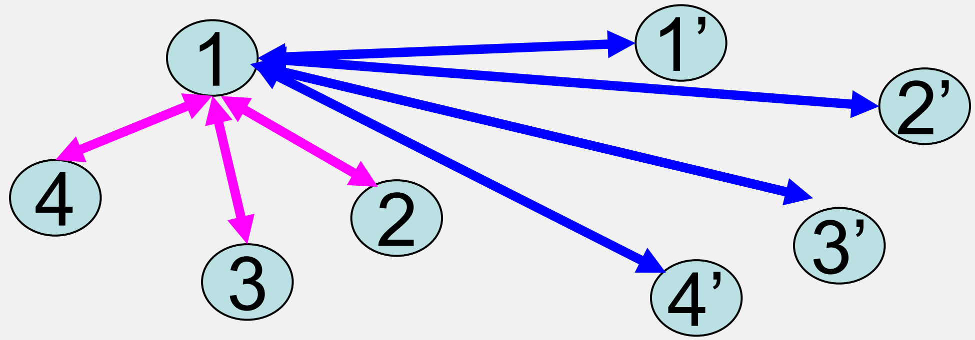
Homogeneity is lost!

Second Variation ("one/two"-body function; fluids)

$$\left(k_B T\right)^2 \frac{\delta^2 \ln \Xi_P(\Psi)}{\delta\Psi(\mathbf{q}_1)\delta\Psi(\mathbf{q}_2)} = -k_B T \frac{\delta\rho_N^{(1)}(\mathbf{q}_1;\Psi)}{\delta\Psi(\mathbf{q}_2)} =$$

$$\left(G_{2,TLR}(\mathbf{q}_1,\mathbf{q}_2;\Psi)-1\right)\rho_N^{(1)}(\mathbf{q}_1;\Psi)\rho_N^{(1)}(\mathbf{q}_2;\Psi)+\frac{1}{P}\rho_N^{(1)}(\mathbf{q}_1;\Psi)\delta\left(\mathbf{q}_1-\mathbf{q}_2\right)$$

Overall bead-bead correlation



Weak Field → LINEAR RESPONSE: ***Self Correlations + Pair CLR Correlations***

Total Continuous Linear Response

$$G_{2,TLR}(\mathbf{q}_1,\mathbf{q}_2;\Psi) \rightarrow G_{2,TLR}(r_{12}) = s_{(1)SC}(r_{12}) + g_{2,TLR}(r_{12})$$

$$\rho_N^{(1)}(\mathbf{q}_1;\Psi) \rightarrow \rho_N = \frac{\langle N \rangle}{V}$$

The Centroid Case –fluids-

What if Ψ is a field of constant strength f? (Ramírez & López-Ciudad, 1999)

$$\Psi_F \rightarrow \Psi_N = \sum_{i=1}^{N} \mathbf{f}\cdot\mathbf{r}_i \rightarrow \mathbf{PI} \rightarrow \frac{1}{P}\sum_{i=1}^{N}\sum_{t=1}^{P}\mathbf{f}\cdot\mathbf{r}_i^t = \sum_{i=1}^{N}\mathbf{f}\cdot\sum_{t=1}^{P}\frac{1}{P}\mathbf{r}_i^t = \sum_{i=1}^{N}\mathbf{f}\cdot\mathbf{R}_{CM,i}$$

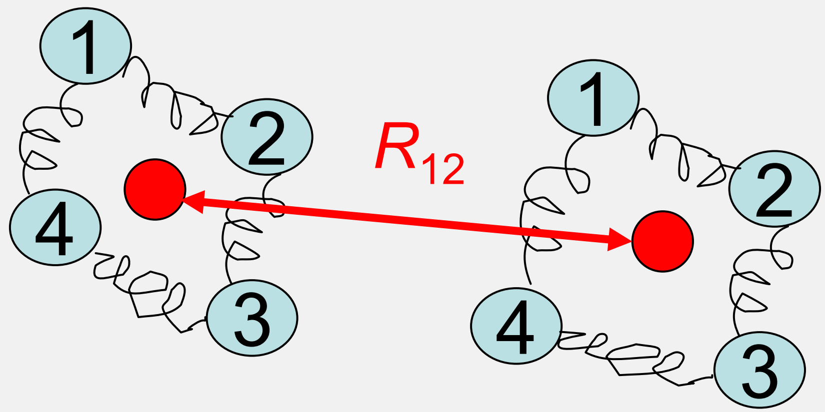
Everything can be worked out as if it was classical (Sesé, 2003)!!!

$$\Xi_P = \sum_{N\geq 0}\frac{z_P^N}{N!}\int\prod_{i=1}^{N}\prod_{t=1}^{P}{}' d\mathbf{r}_i^t \times \exp\left(-\beta W_{NP}(\mathbf{r}_i^t,\ldots)\right)\times\prod_{i=1}^{N}\delta\left(\mathbf{R}_i-\mathbf{R}_{CM,i}\right)d\mathbf{R}_i\times\exp\left(-\beta\sum_{i=1}^{N}\Psi_F(\mathbf{R}_i)\right)$$

$$-k_B T\frac{\delta \ln \Xi_P(\Psi_F)}{\delta\Psi_F(\mathbf{q}_1)} = \rho_{N,CM}^{(1)}(\mathbf{q}_1,\Psi_F)$$

$$-k_B T\frac{\delta\rho_N^{(1)}(\mathbf{q}_1;\Psi)}{\delta\Psi_F(\mathbf{q}_2)} =$$

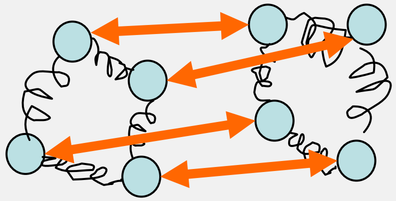
$$\left(g_{2,CM}(\mathbf{q}_1,\mathbf{q}_2;\Psi_F)-1\right)\rho_{N,CM}^{(1)}(\mathbf{q}_1;\Psi_F)\rho_{N,CM}^{(1)}(\mathbf{q}_2;\Psi)+\rho_{N,CM}^{(1)}(\mathbf{q}_1;\Psi_F)\delta\left(\mathbf{q}_1-\mathbf{q}_2\right)$$



LINEAR RESPONSE: …. $\rho_N = \frac{\langle N\rangle}{V}$ $\quad g_{2,CM}(R_{12})$

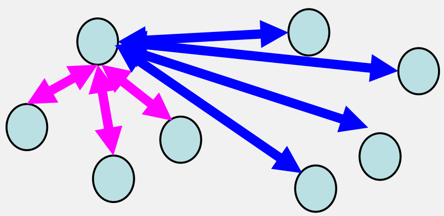
CANONICAL ENSEMBLE NORMALIZATIONS AND FEATURES

$$Instantaneous: \quad 4\pi\rho_N \int_0^\infty g_{2,ET}(r) r^2 dr = N-1$$



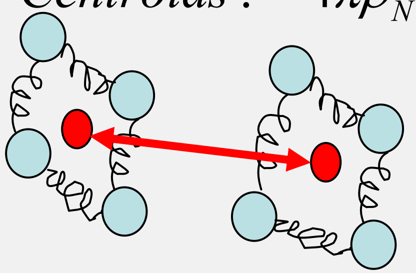
Linear response to a δ external field
Measurable via elastic scattering
Hansen & McDonald (1986)

$$\left\{ \begin{array}{l} Self-correlation: \quad 4\pi\rho_N P \int_0^\infty s_{SC,P}(r) r^2 dr = P-1 \\ Pair\ continuous\ linear\ response: \quad 4\pi\rho_N P \int_0^\infty g_{2,TLR}(r) r^2 dr = (N-1)P \end{array} \right\} NP-1$$



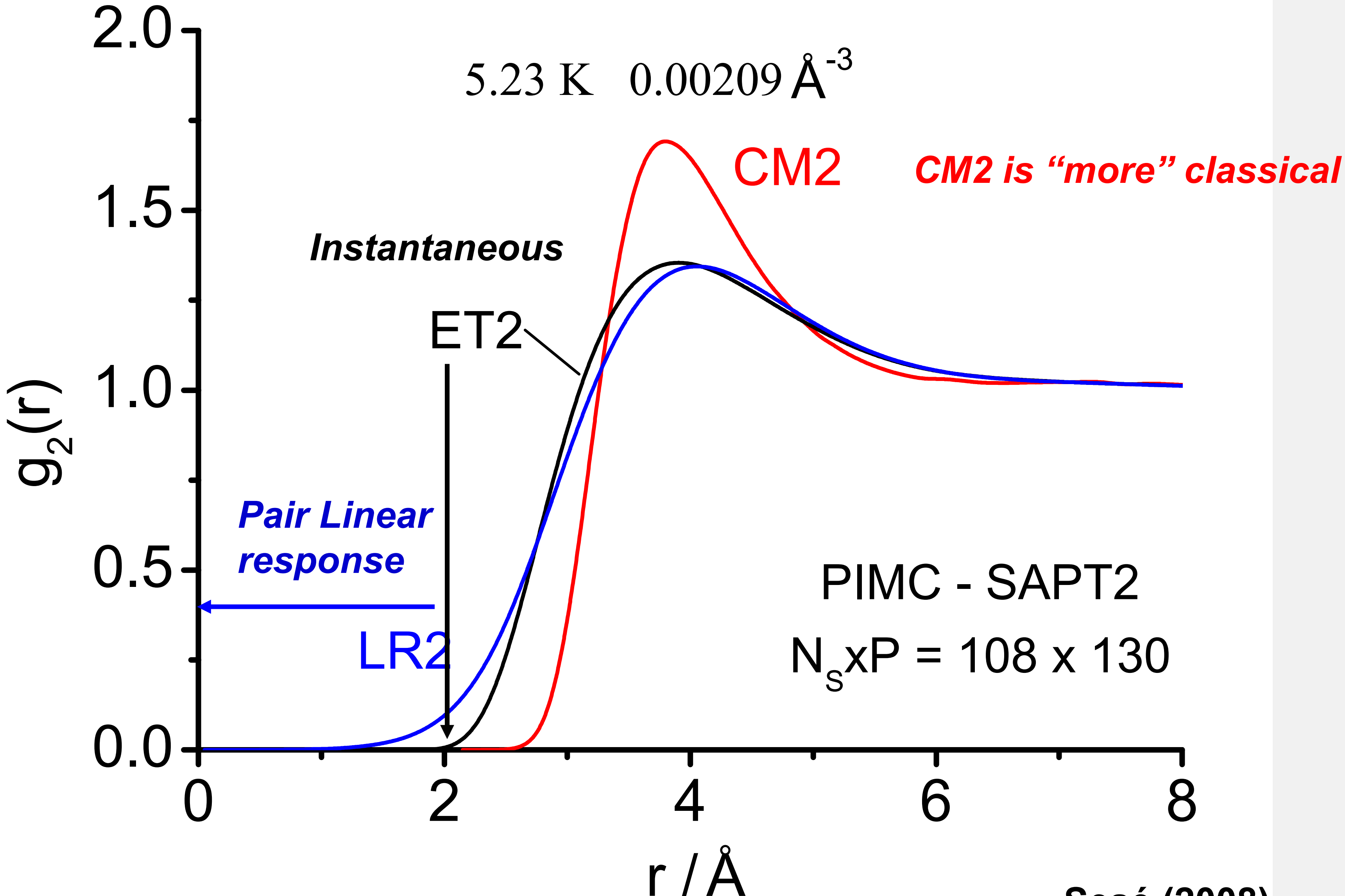
Linear response to an e.c.f. of constant force
Measurable via density relaxation, sum rules,…
Lovesey (1987)

$$Centroids: \quad 4\pi\rho_N \int_0^\infty g_{2,CM}(R) R^2 dr = N-1$$



Related to the linear response to an e.c.f.
Not directly measurable, but …

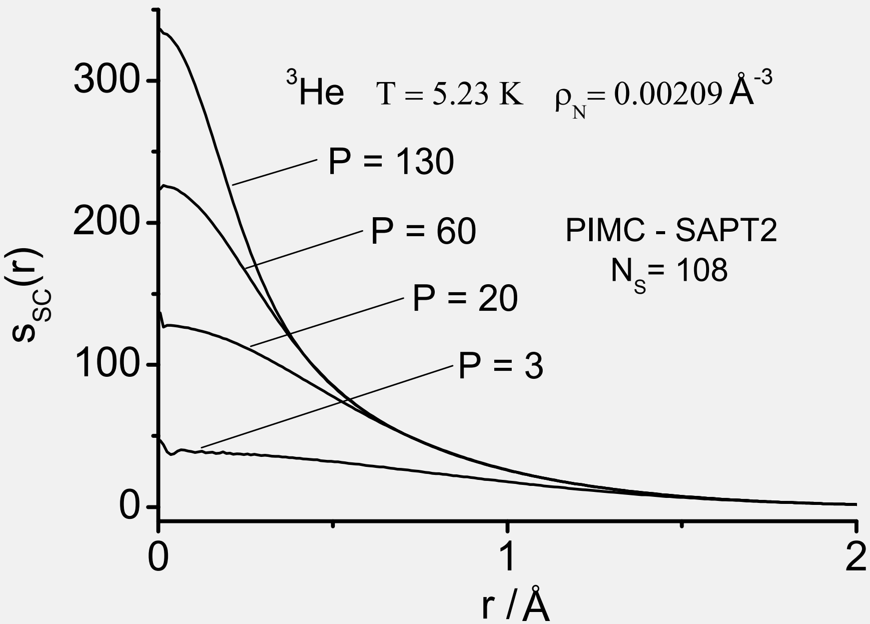
Helium-3



Sesé (2008)

Self-correlations and slow-P convergence

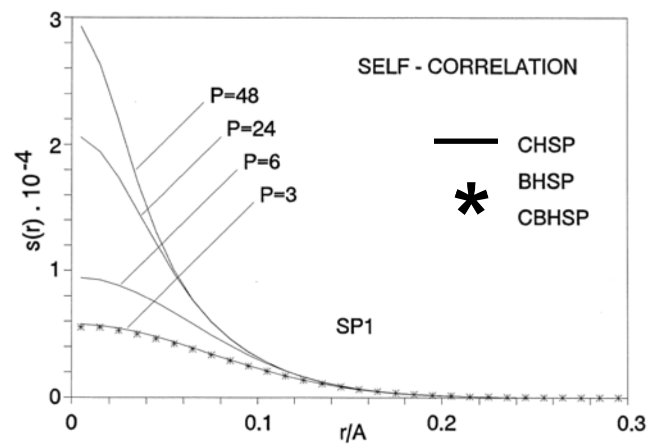
Helium-3 gas



Sesé (2008)

Quantum Hard Spheres

(Liquid N_2, T = 66 K)



Sesé & Ledesma (1995)

Influence on TLR k-space properties

- **III. 4 Order Parameters and Correlations Beyond the Pair Level**

The size of the problem increases in going to the PI approach :

-<u>Pairs</u>:

Different order parameters (Steinhardt et al, Lindemann's, structure factors,etc.) depending upon de sort of basic pair correlation).

-<u>Triplets (Sesé, 2005-2009)</u>:

g_3 instantaneous and centroids are analogous to classical

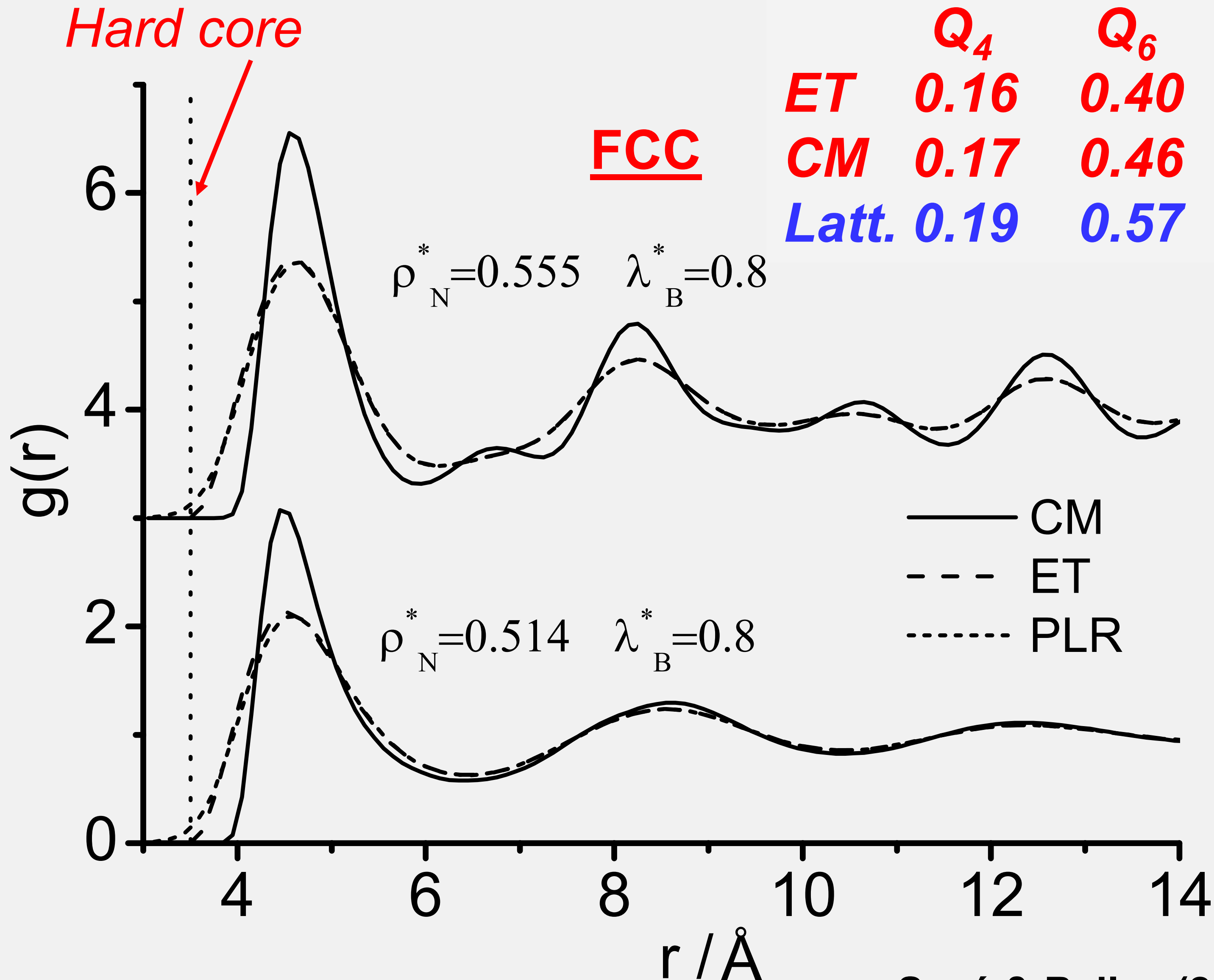
The continuous linear response turns out to be highly involved

- <u>Quadruplets</u>: ?

Computation of Static Structure Factors for Fluids and All That …

Quantum hard spheres (fluid – fcc phase transition)

	Q_4	Q_6	$S(k_{max})$
ET	0.16	0.40	0.656
CM	0.17	0.46	0.773
Latt.	0.19	0.57	1

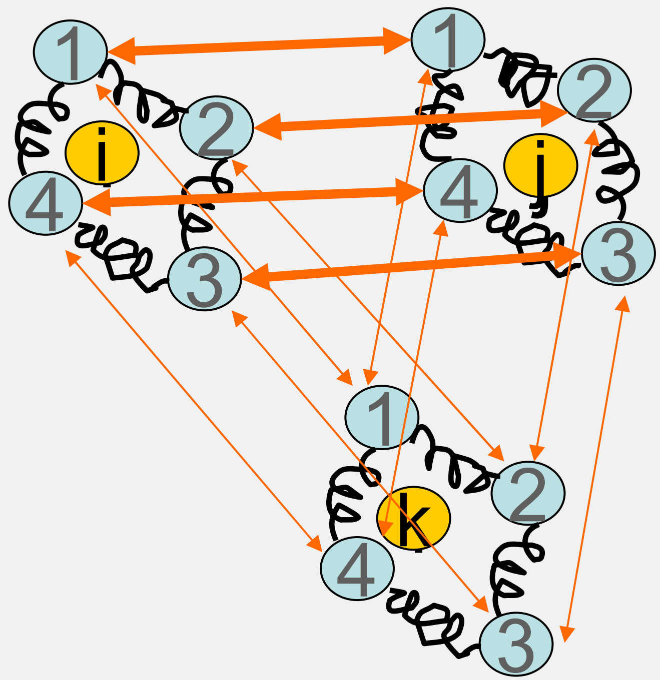


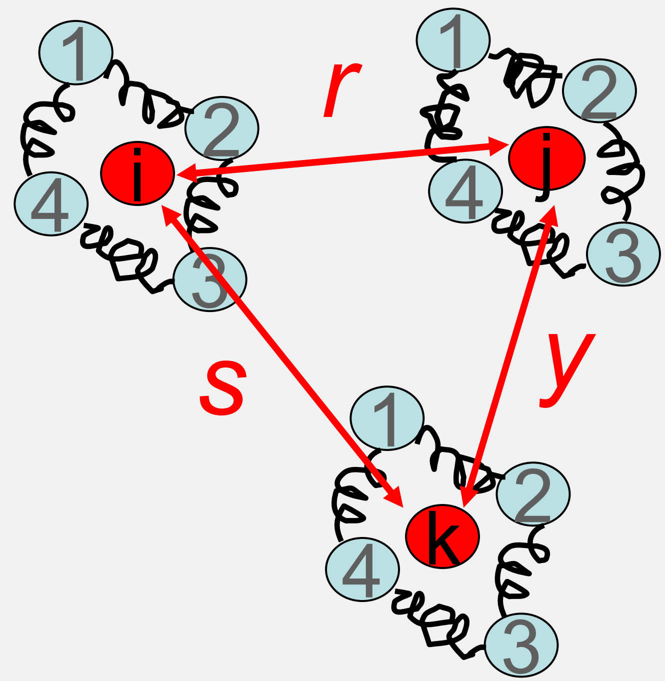
Fluid side

Sesé & Bailey (2007)

Triplet Correlations

Instantaneous (ET3)

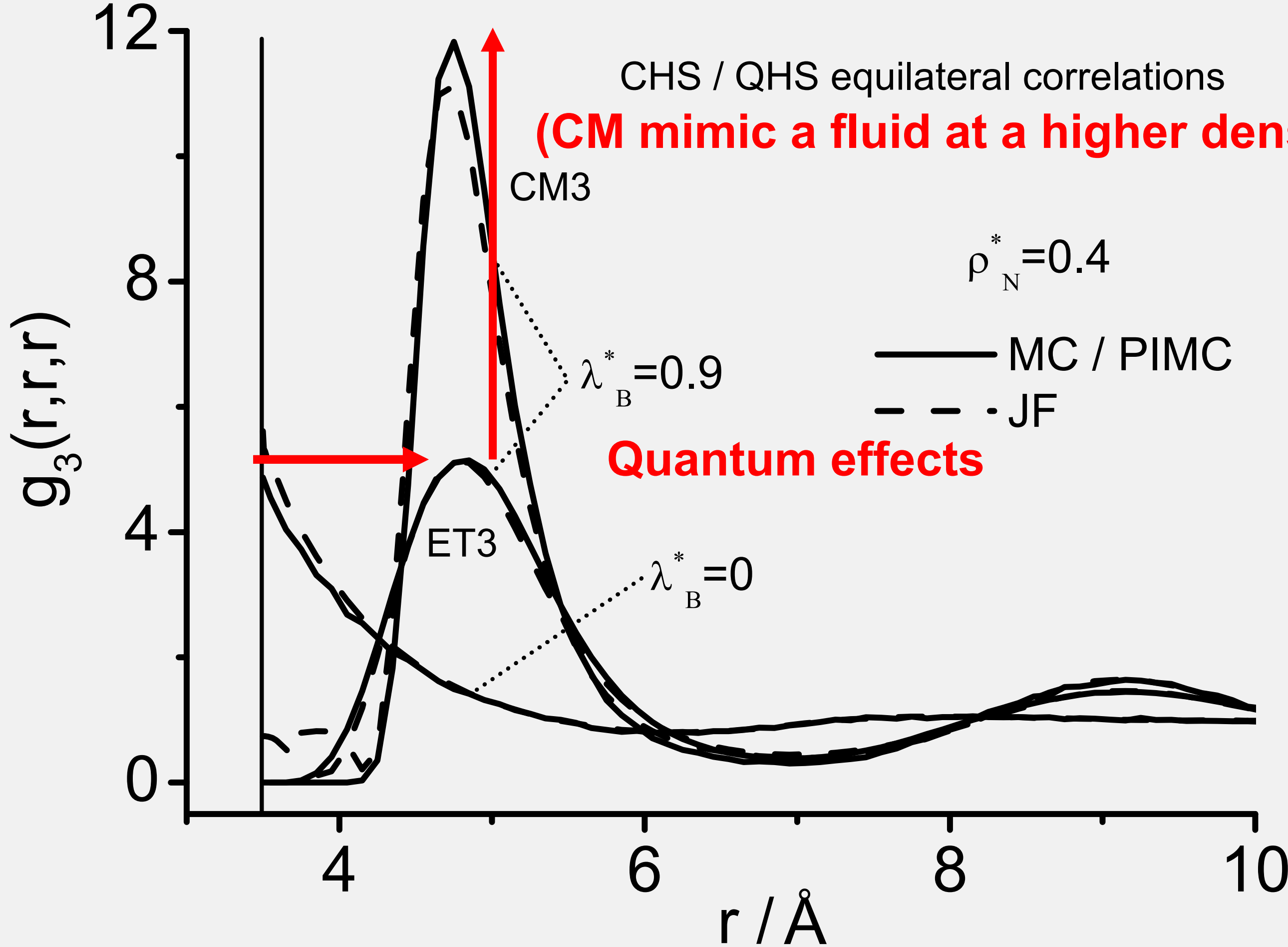


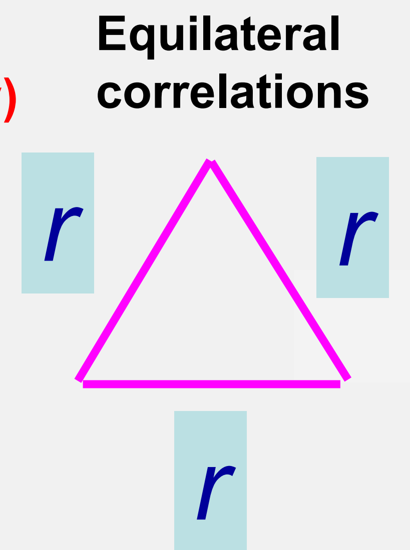


Centroids (CM3)

Total linear response …..

Classical / Quantum hard spheres





Sesé (2005)

- IV. Static Quantum Fluid Structures in Fourier Space

- **IV. 1 Static Structure Factors at the Pair Level**

Linear response development (Yvon, 1935; Hansen&McDonald, 1986)

$$-k_B T \frac{\delta \rho_N^{(1)}(\mathbf{q}_1;\Psi)}{\delta \Psi(\mathbf{q}_2)} = \left(g_2(\mathbf{q}_1,\mathbf{q}_2;\Psi)-1\right)\rho_N^{(1)}(\mathbf{q}_1;\Psi)\rho_N^{(1)}(\mathbf{q}_2;\Psi)+\rho_N^{(1)}(\mathbf{q}_1;\Psi)\delta\left(\mathbf{q}_1-\mathbf{q}_2\right)$$

↓ Linear Response (Fluids)

$$-k_B T \frac{\delta \rho_N^{(1)}(\mathbf{q}_1;\Psi)}{\delta \Psi(\mathbf{q}_2)} \approx \left(g_2(R_{12})-1\right)\rho_N^2+\rho_N\delta\left(\mathbf{q}_1-\mathbf{q}_2\right)$$

$$-k_B T\, \delta \rho_N^{(1)}(\mathbf{q}_1;\Psi) \approx \int d\mathbf{q}_2 \delta\Psi(\mathbf{q}_2)\left\{\left(g_2(\mathbf{q}_1-\mathbf{q}_2)-1\right)\rho_N^2+\rho_N\delta\left(\mathbf{q}_1-\mathbf{q}_2\right)\right\}$$

$$-k_B T \int d\mathbf{q}_1 \exp\left[i\mathbf{k}\cdot\mathbf{q}_1\right]\delta \rho_N^{(1)}(\mathbf{q}_1;\Psi) \approx$$
$$\int d\mathbf{q}_1 d\mathbf{q}_2 \exp\left[i\mathbf{k}\cdot\mathbf{q}_1\right]\left\{\left(g_2(\mathbf{q}_1-\mathbf{q}_2)-1\right)\rho_N^2+\rho_N\delta\left(\mathbf{q}_1-\mathbf{q}_2\right)\right\}\delta\Psi(\mathbf{q}_2)$$

- **IV. 1 Static Structure Factors at the Pair Level**

Linear response development (Yvon, 1935; Hansen&McDonald, 1986)

$$-k_B T \int d\mathbf{q}_1 \exp\left[i\mathbf{k}\cdot\mathbf{q}_1\right]\delta\rho_N^{(1)}(\mathbf{q}_1;\Psi)\approx$$

$$\int d\mathbf{q}_1 d\mathbf{q}_2 \exp\left[i\mathbf{k}\cdot\mathbf{q}_1\right]\left\{\left(g_2(\mathbf{q}_1-\mathbf{q}_2)-1\right)\rho_N^2+\rho_N\delta\left(\mathbf{q}_1-\mathbf{q}_2\right)\right\}\delta\Psi(\mathbf{q}_2)$$

$$\delta\rho_N^{(1)}(\mathbf{k};\Psi)\approx-\beta\rho_N S^{(2)}(\mathbf{k})\delta\Psi(\mathbf{k})$$

$$\boxed{S^{(2)}(k)=1+\rho_N\int d\mathbf{R}\exp(i\mathbf{k}\cdot\mathbf{R})\left(g_2(R)-1\right)}$$

- **IV. 1 Static Structure Factors at the Pair Level (fluids)**

Centroids (Sesé, 1996-…, 2003-…)

$$S^{(2)}_{CM,P}(k)=1+\rho_N\int d\mathbf{R}\,\exp(i\mathbf{k}\cdot\mathbf{R})\,(g_{2,CM}(R)-1)$$

Total continuous linear response (Chandler & Wolynes, 1981; Sesé, 1995-…)

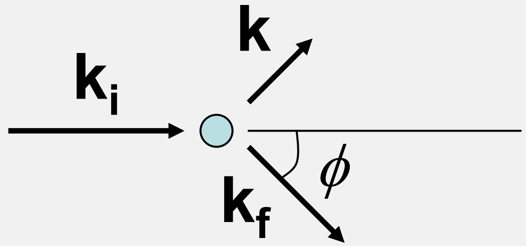
$$S^{(1,2)}_{TLR,P}(k)=P^{-1}+\rho_N\int d\mathbf{r}\,\exp(i\mathbf{k}\cdot\mathbf{r})\,(s_{(1),SC}(r)+g_{2,TLR}(r)-1)$$

Instantaneous (Hansen&McDonald, 1986; Ceperley, 1995; Sesé, 2002)

$$S^{(2)}_{ET,P}(k)=1+\rho_N\int d\mathbf{r}\,\exp(i\mathbf{k}\cdot\mathbf{r})\,(g_{2,ET}(r)-1)$$ **(***)**

(***) ET Standard derivation: golden rule (PT) + Fermi potential +…

<u>Simulation - Strictly</u>: $g_2(r)$ free from finite-size effects
(fixed in the grand ensemble or with a sufficiently large canonical sample,…)



EXTERNAL WEAK FIELD
$\Psi(\mathbf{r}_i)$

$\hbar\mathbf{k}$ = momentum transfer

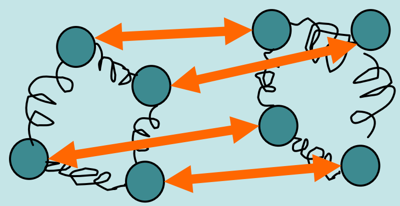
LINEAR RESPONSE FUNCTION

<u>δ-localizing</u> → $g_{2,ET}(r)$ → $S_{ET}^{(2)}(k)$ **measurable**

Neutron
(zero-spin atoms)

X-ray

QUANTUM FLUID



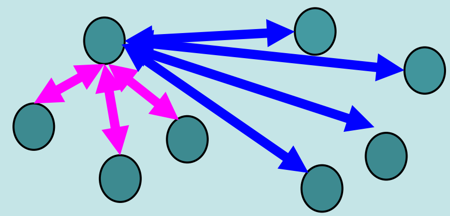
(+ form factor of atoms in X-ray)

EXTERNAL WEAK FIELD
$\Psi(\mathbf{r}_i)$

Continuous

General
Constant force

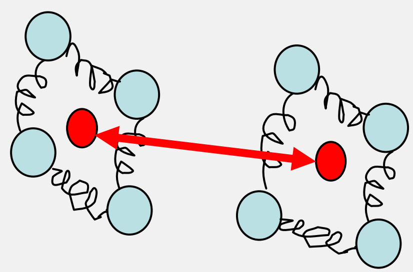
$\hbar\mathbf{k}$ = momentum transfer



QUANTUM FLUID

$G_{2,TLR}(r)$

$g_{2,CM}(R)$



LINEAR RESPONSE FUNCTION

$S^{(1,2)}_{TLR}(k)$ **measurable**

$S^{(2)}_{CM}(k)$ **non-measurable but related to ET and TLR**

Origins, Computational Problems, and Thermodynamics

Instantaneous:

- Elastic scattering of radiation (X-Rays, fast neutrons –spinless nuclei-)
- Only momentum transfers from radiation to sample
- Coherent scattering (interference between waves scattered from atoms)
- Numerical problems if directly simulated (low k and 2π/L, etc.)
- Numerical problems at small k with the Fourier transform of simulated $g_2(r)$

Total continuous linear response:

- Weak continuous field
- Only momentum transfers from field to sample
- Numerical problems at small k ….
- Numerical problems at low r with the computation of $s_{SC}(r)$ (P-dependence)

Centroids:

- Weak continuous field of constant strength
- Only momentum transfers from field to sample
- Numerical problems at small k …

$$S^{(2)}(k) \rightarrow \int d\mathbf{R} \exp(i\mathbf{k}\cdot\mathbf{R}) \left(g_2(R)-1\right)$$

Number Fluctuations (Sesé, …- 2003)

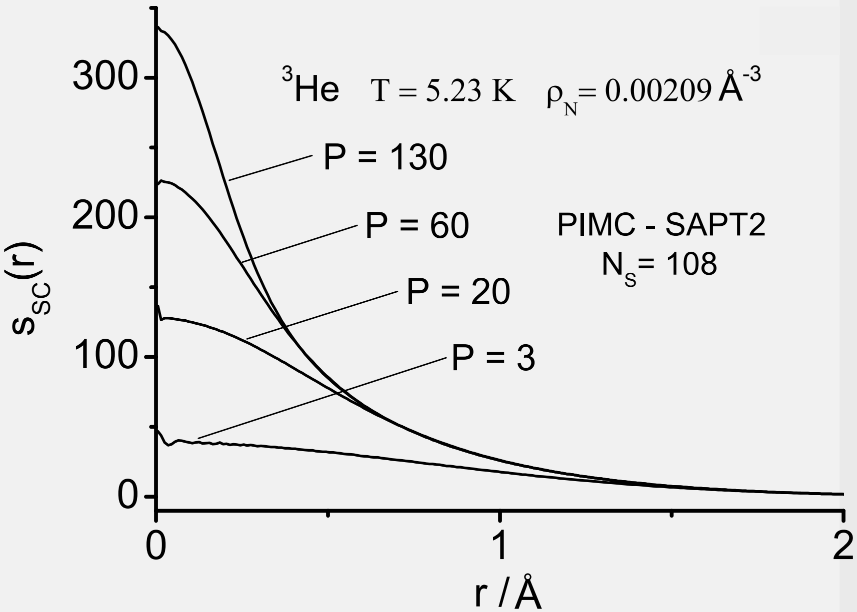
$$S^{(2)}_{ET}(k=0) = S^{(2)}_{TLR}(k=0) = S^{(2)}_{CM}(k=0) = \rho_N k_B T \chi_T$$

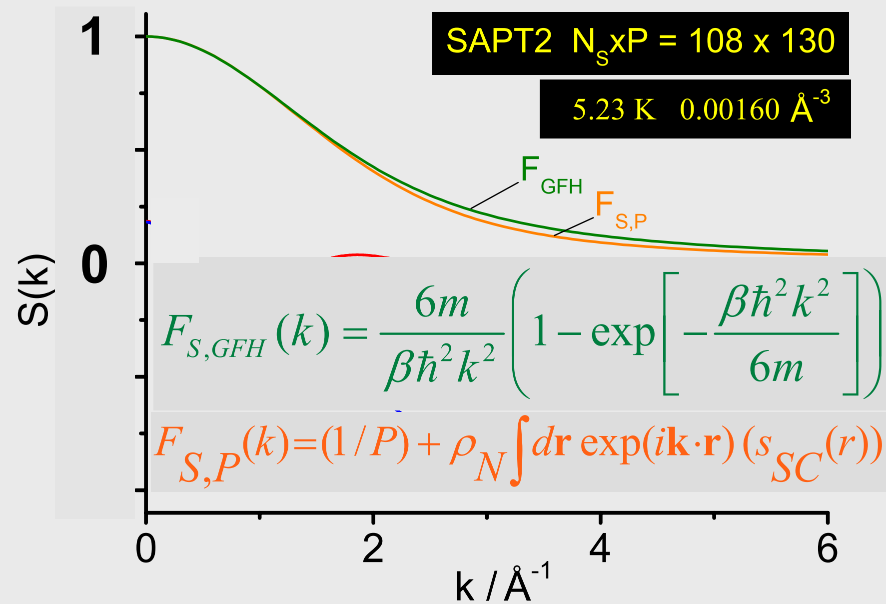
• IV. 2 Tackling the S(k) Problems

(1) Self-correlations

- **Do not contribute to S(k=0) in (N,V,T), (μ,V,T)**
- **A) Increasing *P* + *PIMC***

Helium-3 gas





- B) Feynman-Hibbs picture (GFH)

Sesé (1996, 2008)

(2) : Fourier Transforms and Direct Correlation Functions (Fluids)

(Chandler & Wolynes, 1981 + Shinoda et al, 2001; Sesé, 1996-…)

Classical Ornstein-Zernike equation (Hansen & McDonald, 1986)

OZ2: $h(r_{12}) = c(r_{12}) + \rho_N \int d\mathbf{r}_3\, h(r_{13})\, c(r_{23})$ $\qquad h(r) = g_2(r) - 1$

1- 2 Total Correlation = 1- 2 Direct Correlation + 1- 3 - 2 Mediated Correlations

c(r) is short ranged → no problems with its Fourier transform

$$S^{(2)}(k) = 1 + \rho_N \int d\mathbf{r} \exp(i\mathbf{k}\cdot\mathbf{r})\, h(r) = \frac{1}{1 - \rho_N c(\mathbf{k})}$$

C(r) Functional Definition (Percus, 1962; Lee, 1974)

Computation of the Quantum Fluid S(k)

$$h(r_{12}) = c(r_{12}) + \rho_N \int d\mathbf{r}_3\, h(r_{13})\, c(r_{23}); \quad \left\{ \begin{array}{l} h_{2,ET}(r) = g_{2,ET}(r) - 1 \\ h_{2,TLR}(r) = g_{2,TLR}(r) - 1 \\ h_{2,CM}(R) = g_{2,CM}(r) - 1 \end{array} \right\}$$

***P* dependence !!!**
Grand ensemble!!!

CM Exact OZ2!!!

$$S^{(2)}_{CM,P}(\mathbf{k}) = \frac{1}{1 - \rho_N c_{2,CM}(\mathbf{k})}$$

$$S^{(2)}_{CM,P}(\mathbf{k}=0) = \rho_N k_B T \chi_{T,P}$$

Equation of State of Fluids

$$\langle p \rangle$$

Approximations

$$S^{(2)}_{ET,P}(\mathbf{k}) \approx \frac{1}{1 - \rho_N c_{2,ET}(\mathbf{k})}$$

$$S^{(1,2)}_{TLR,P}(\mathbf{k}) \approx F^{(1)}_{SC,P}(\mathbf{k}) + \frac{\rho_N c_{2,TLR}(\mathbf{k})}{1 - \rho_N c_{2,TLR}(\mathbf{k})}$$

$$\approx F_S^{GFH}(\mathbf{k}) + \frac{\rho_N c_{2,TLR}(\mathbf{k})}{1 - \rho_N c_{2,TLR}(\mathbf{k})}$$

- **IV. 3 Determination of direct correlation functions**

Baxter-Dixon-Hutchinson method (BDH, 1968,1977)

Fast computational method specially suitable for:
Feynman_Hibbs picture // OZ2 is exact (Sesé, 1996)
Path-integral quantum computations (Sesé, 1997-…)

Instantaneous
k – space: Total continuous linear response
Centroids – thermodynamics (EXACT)

BDH INPUT: bulk density + pair radial correlation function !

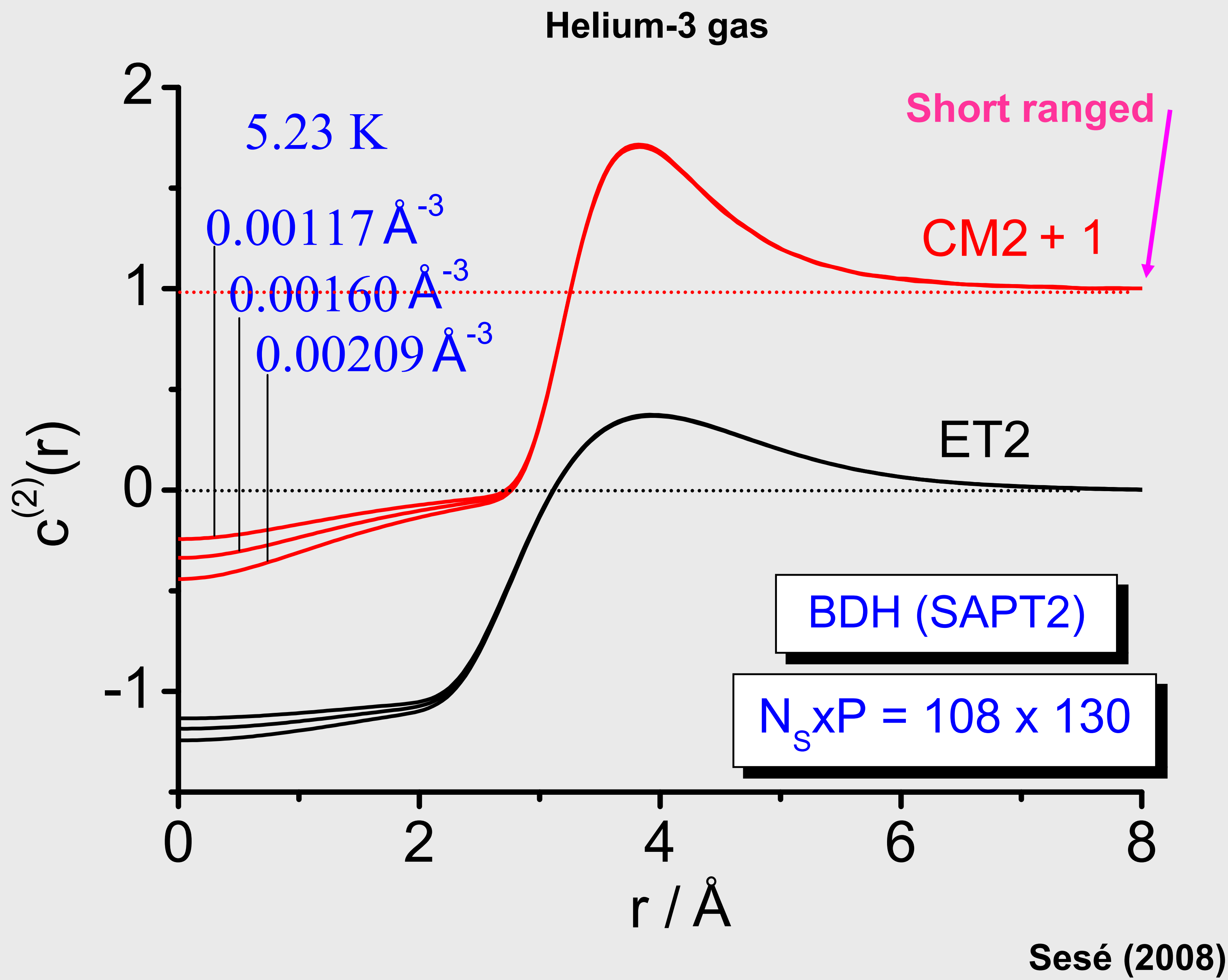
COMPUTATIONAL EFFORT: the whole *S(k)* answer takes (today):

FROM SECONDS TO A FEW HOURS!

- RISM equations (Chandler & Wolynes, 1981; Shinoda et al, 2001)

Only total continuous linear response

- Simulation/Theory approach for freezing theories (Haymet et al, 1990, 1992)



Helium-3 gas
5.23 K
0.00117 Å-3
0.00160 Å-3
0.00209 Å-3
Short ranged
CM2 + 1
ET2
BDH (SAPT2)
NSxP = 108 x 130
c(2)(r)
r / Å
2
1
0
-1
0
2
4
6
8
Sesé (2008)

Liquid Helium-4 (path-integrals + BDH)

SVP line   T = 4.2 K

Figure 2

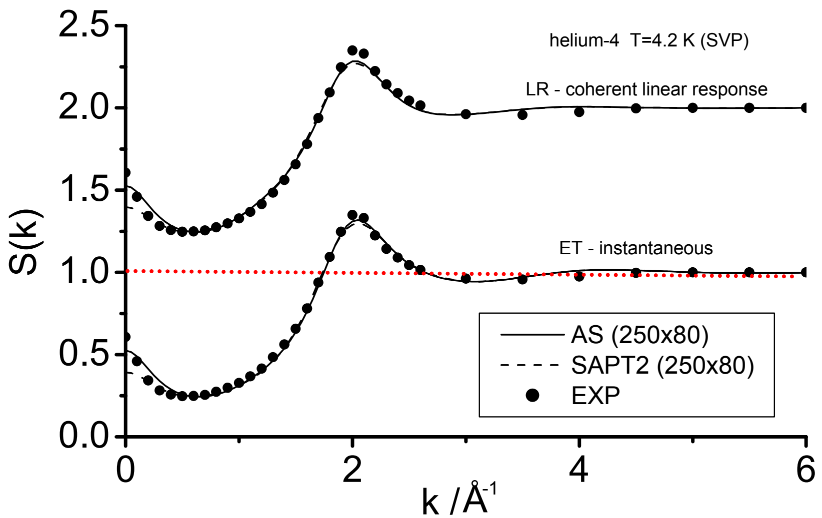
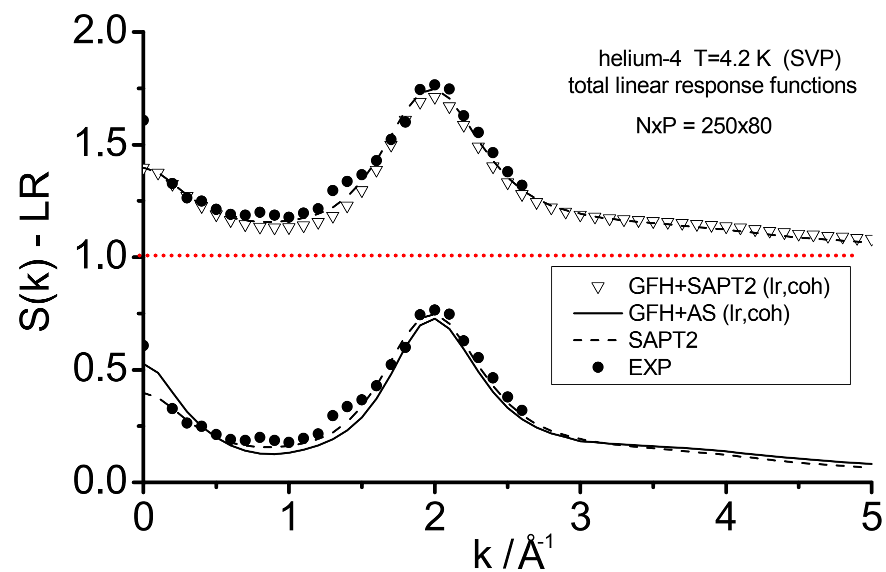


Figure 3



Instantaneous

$$S(k \to \infty) \to 1$$

Total C. Linear Response

$$S(k \to \infty) \to 0$$

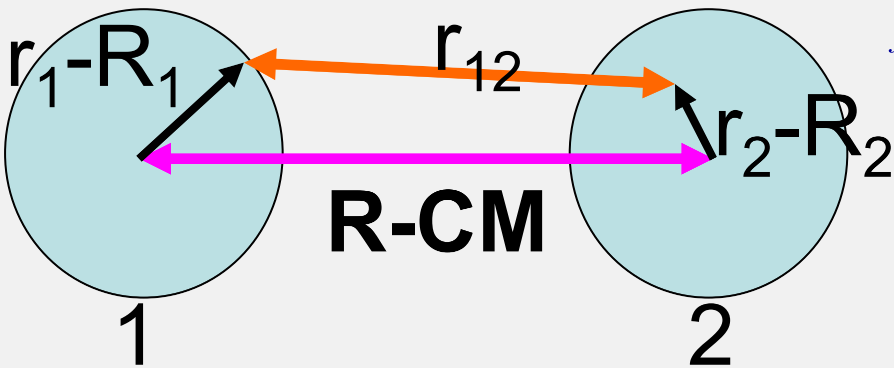
Sesé (2002)

- **IV. 4 The key role of centroid correlations (at equilibrium)**

- (1) Intermediate role in the computation of measurable structures (Sesé, 1993, 1996; Blinov and Roy (2004))

<u>Feynman-Hibbs picture (Sesé, 1993-1996…)</u>:

$$g_q^{GFH}(\mathbf{r}_1,\mathbf{r}_2)=\int d\mathbf{R}_1 d\mathbf{R}_2\; f_1^{GFH}(\mathbf{r}_1-\mathbf{R}_1)\,g_{CM}^{GFH}(\mathbf{R}_1,\mathbf{R}_2)\,f_2^{GFH}(\mathbf{r}_2-\mathbf{R}_2)$$



$$f_i^{GFH}(\mathbf{r}_i-\mathbf{R}_i)=\left(\frac{6m}{\pi\beta\hbar^2}\right)^{3/2}\exp\left[-\frac{6m}{\beta\hbar^2}(\mathbf{r}_i-\mathbf{R}_i)^2\right]$$

Instantaneous (ET2)

$$S_q^{GFH}(\mathbf{k})=1+\exp\left(-\frac{\beta\hbar^2}{12m}k^2\right)\left(S_{CM}^{GFH}(\mathbf{k})-1\right)$$

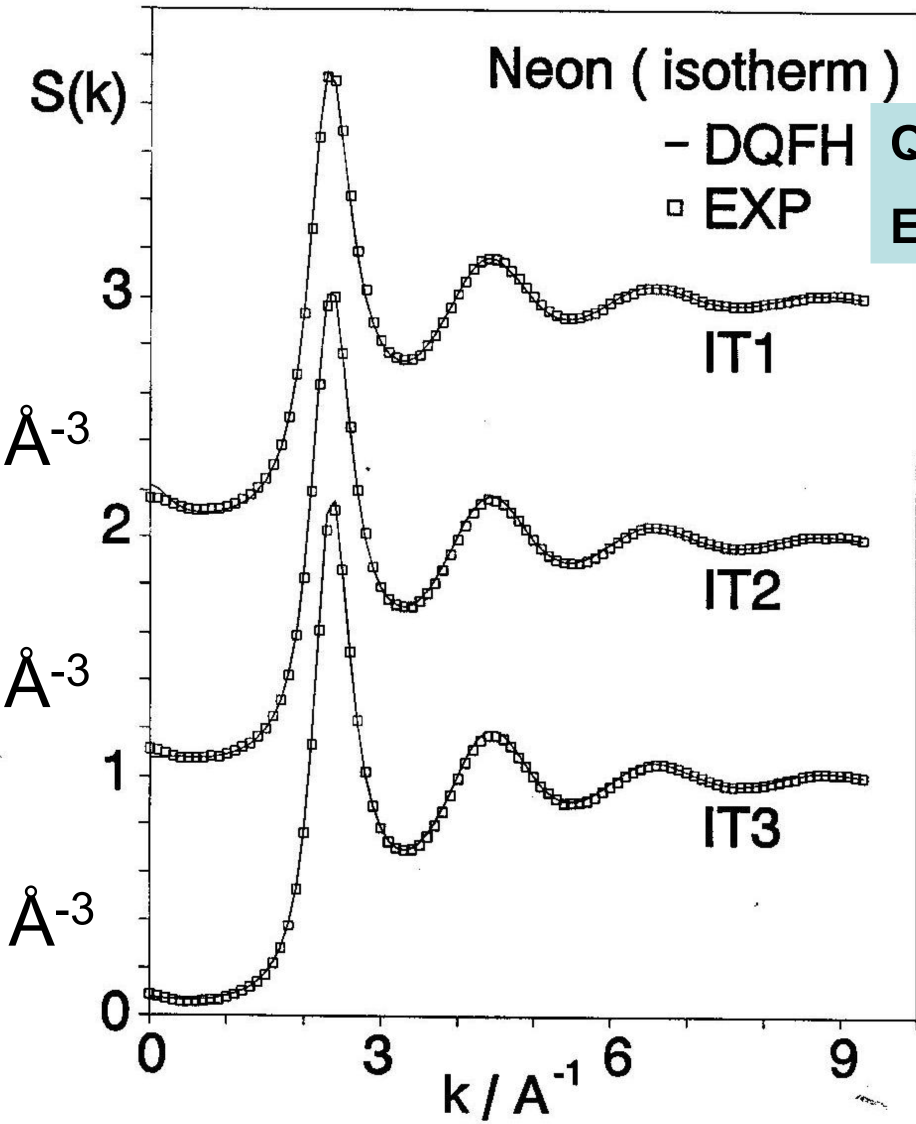
T = 35.05 K

Neutron Diffraction

ρ_N=0.0317 Å^{-3}

ρ_N=0.0334 Å^{-3}

ρ_N=0.0347 Å^{-3}



Quantum

Experimental

Sesé (1996)

- (2) Usefulness of Centroids at Equilibrium (eos)….

$$S^{(2)}_{ET}(k=0)=S^{(2)}_{TLR}(k=0)=S^{(2)}_{CM}(k=0)=\rho_N k_B T \chi_T=\rho_N k_B T\left[\frac{1}{\rho_N}\left(\frac{\partial \rho_N}{\partial p}\right)_T\right]$$

$$S^{(2)}_{CM}(k=0)=\rho_N k_B T\left[\frac{1}{\rho_N}\left(\frac{\partial \rho_N}{\partial p}\right)_T\right]=\frac{\langle N^2\rangle-\langle N\rangle^2}{\langle N\rangle}$$

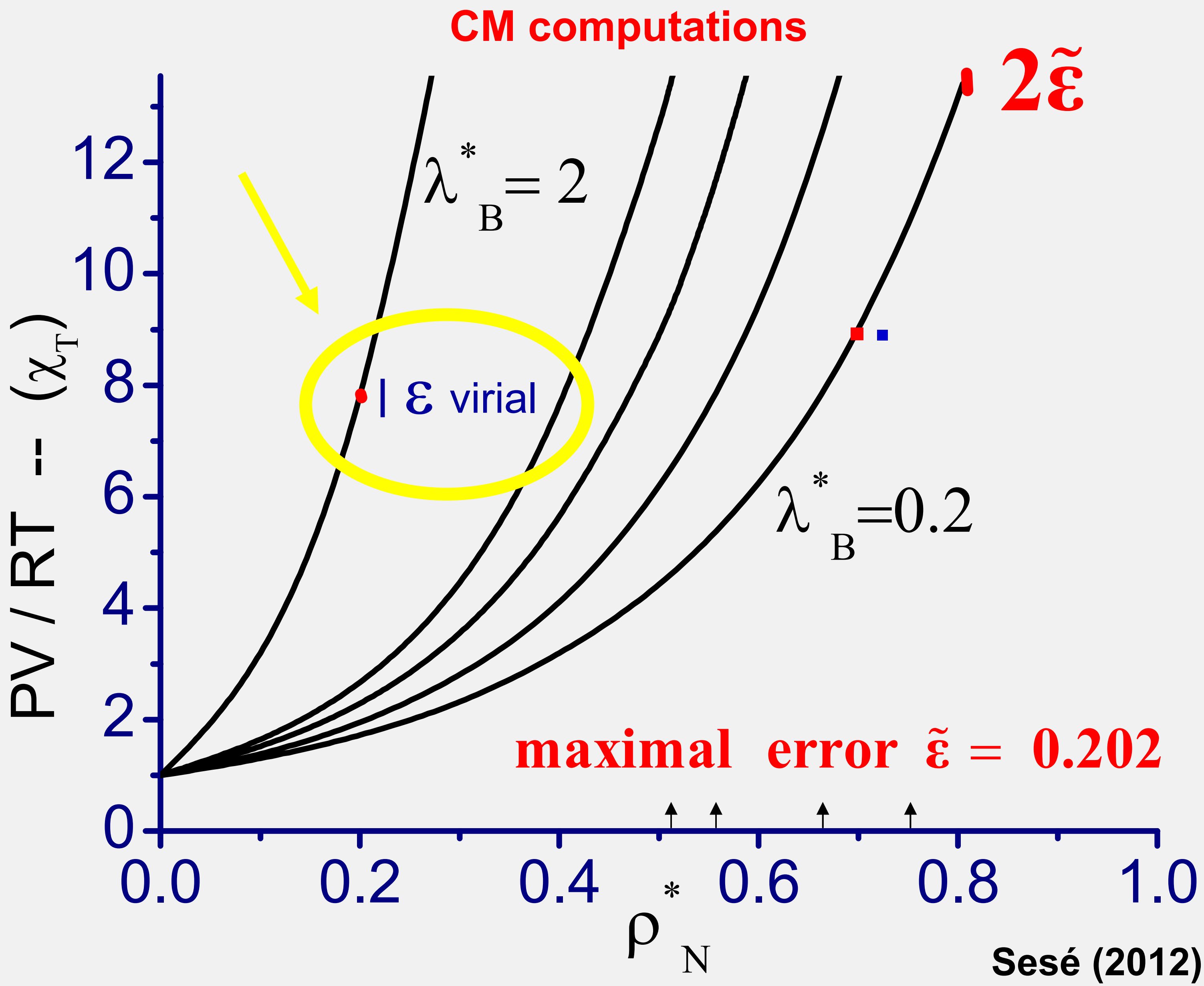
↓

Equation of state: $p = p(V,T)$

Centroids are:

a useful means for counting number fluctuations OZ2!!!
present a deep connection with classical statistical mechanics
in a sense this is an extension of the classical isomorphism

Quantum Hard Sphere Fluid (eos)

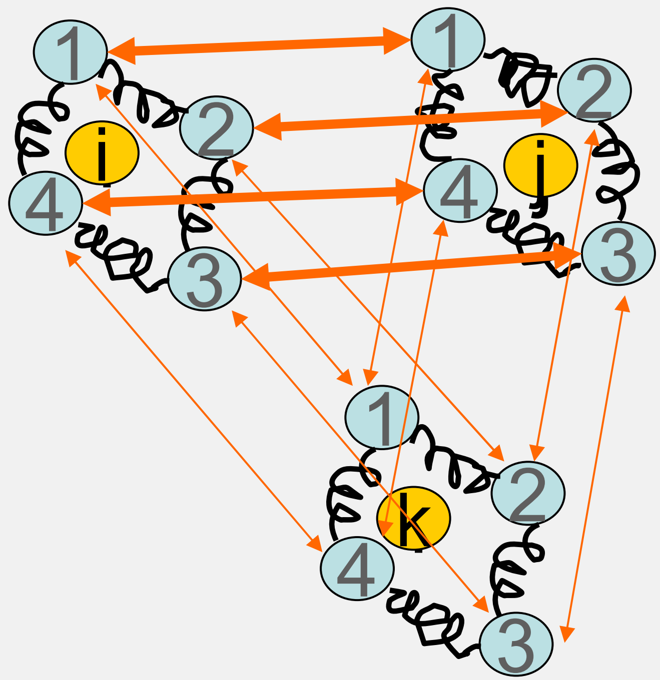


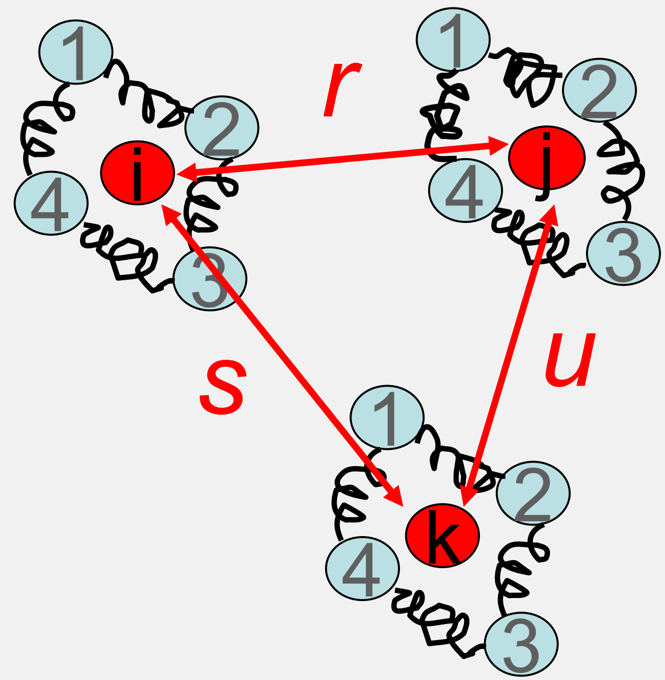
Sesé (2012)

- **IV. 5 Beyond the Pair Level**

Triplets

Instantaneous





Centroids

Continuous linear response …

Fluid Triplets in k space (directly from functional derivatives)

$$S^{(3)}(\mathbf{k}_1,\mathbf{k}_2)=\frac{1}{\rho_N}H^{(3)}(\mathbf{k}_1,\mathbf{k}_2); \qquad H^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)=\left\langle \prod_{n=1}^{3}\left(\sum_{j=1}^{N}\delta(\mathbf{r}_j-\mathbf{q}_n)-\left\langle \sum_{j=1}^{N}\delta(\mathbf{r}_j-\mathbf{q}_n)\right\rangle \right)\right\rangle$$

Instantaneous Triplets:

$$S_{ET}^{(3)}(\mathbf{k}_1,\mathbf{k}_2)=\left(NP\right)^{-1}\left\langle \sum_{t=1}^{P}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{m=1}^{N}\exp\left[i\left(\mathbf{k}_1\cdot\mathbf{r}_i^t+\mathbf{k}_2\cdot\mathbf{r}_j^t-(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}_m^t\right)\right]\right\rangle$$

Centroid Triplets:

$$S_{CM}^{(3)}(\mathbf{k}_1,\mathbf{k}_2)=N^{-1}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{m=1}^{N}\exp\left[i\left(\mathbf{k}_1\cdot\mathbf{R}_{CM,i}+\mathbf{k}_2\cdot\mathbf{R}_{CM,j}-(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}_{CM,m}\right)\right]\right\rangle$$

PIMC …

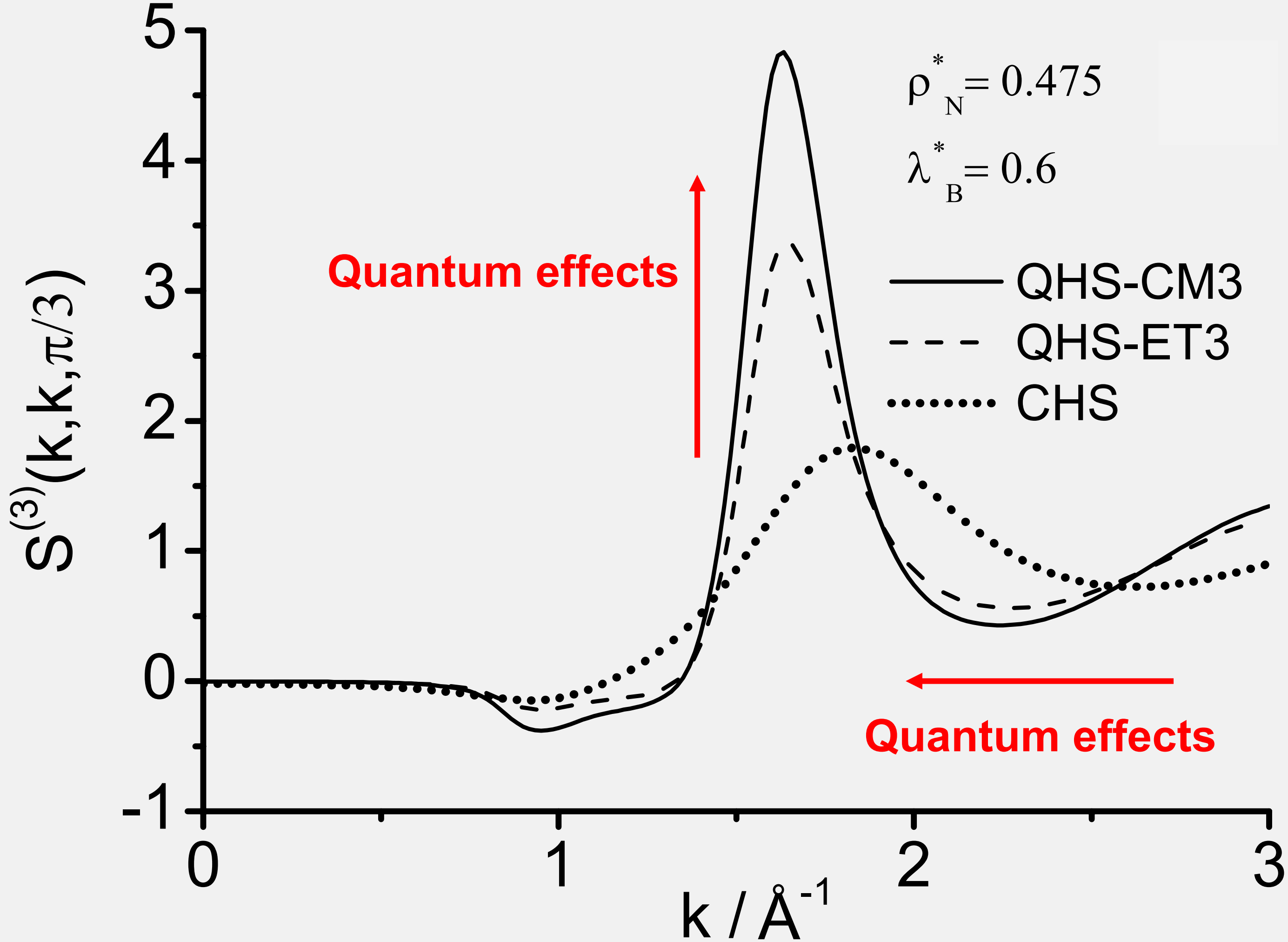
Fluids & Direct Correlation Functions (Barrat et al, 1988; Sesé, 2008-2009):

$$S^{(3)}(\mathbf{k}_1,\mathbf{k}_2)=S^{(2)}(\mathbf{k}_1)S^{(2)}(\mathbf{k}_2)S^{(2)}(|\mathbf{k}_1+\mathbf{k}_2|)\left\{1+\rho_N^2c^{(3)}(\mathbf{k}_1,\mathbf{k}_2)\right\}$$

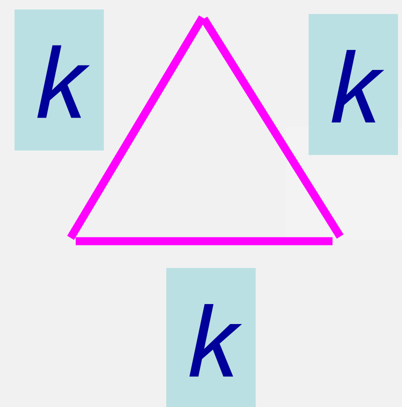
Baxter's (1964):

(new hierarchy!) $$\frac{\partial c^{(2)}(r)}{\partial\rho_N}=\int d\mathbf{s}\,c^{(3)}(\mathbf{r},\mathbf{s}), \quad \frac{\partial c^{(2)}(\mathbf{k}_1)}{\partial\rho_N}=c^{(3)}(\mathbf{k}_1,\mathbf{k}_2=0)$$

Quantum / Classical Hard spheres



Equilateral correlations



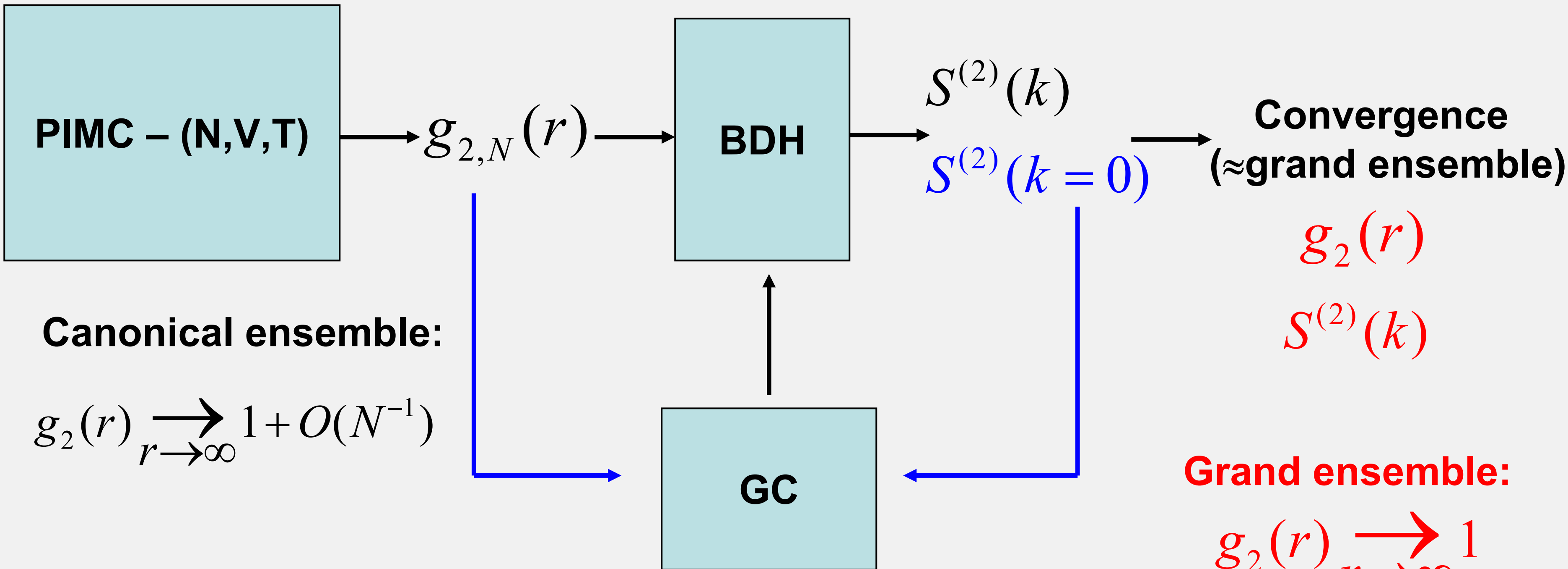
Sesé (2009)

- V. Other Topics

• V. 1 Finite-size *N* effects

Grand Ensemble Corrections (GC) to Canonical $g_2(r)$

(Salacuse et al, 1996; Baumketner and Hiwatari, 2001; Sesé, 2008)



Canonical ensemble:

$$g_2(r) \underset{r\to\infty}{\longrightarrow} 1 + O(N^{-1})$$

Grand ensemble:

$$g_2(r) \underset{r\to\infty}{\longrightarrow} 1$$

$$g_2(r_{12})_{GE} \approx g_{2,N}(r_{12}) + \frac{S^{(2)}(k=0)}{N} g_{2,N}(r_{12})$$

BDH + GC takes from seconds to a few hours
(stable fluid state points)

- **V. 2 The dynamic connection (Lovesey, 1988; Shinoda et al, 2001)**

Neutron Scattering

Sum rules: $S_{ET}^{(2)}(\mathbf{k}) = \int_{-\infty}^{\infty} d\omega \, S(\mathbf{k},\omega)$ **Instantaneous**

$$S_{TLR}^{(2)}(\mathbf{k}) = 2\int_{0}^{\infty} d\omega \frac{1-\exp(-\beta\hbar\omega)}{\beta\hbar\omega} S(\mathbf{k},\omega)$$

Static Susceptibility

(Relaxation of Density)

- **V. 3 (N,P,T) simulations (Scharf et al , 1993;…)**

Calculations of isothermal compressibilities via fluctuations of the volume

$$\frac{\langle V^2\rangle - \langle V\rangle^2}{\langle V\rangle} = k_B T \chi_T$$

(finite-N effects also affect these simulations)

- **V. 4**

  - ….

VI. Bibliography

R. Aziz and M. Slaman, Metrologia, 27, 211 (1990)
A. Baranyai and D. J. Evans, Phys. Rev. A, 42, 849 (1990)
J. A. Barker, J. Chem. Phys., 70, 2914 (1979)
J. L. Barrat, J. P. Hansen and G. Pastore, Molec. Phys. 63, 747 (1988)
A. Baumketner and Y. Hiwatari, Phys. Rev. E, 63, 061201 (2001)
R. J. Baxter, Aust. J. Phys. 21, 563 (1968)
B. J. Berne and D. Thirumalai, Annu. Rev. Phys. Chem. 37, 401 (1986)
N. Blinov and P. N. Roy, J. Chem. Phys. 120, 3759 (2004)
D. M. Ceperley, Rev. Mod. Phys. 67, 279 (1995)
C. Chakravarty and R. M. Lynden-Bell, J. Chem. Phys. 113, 9239 (2000)
S. A. Chin, Phys. Rev. E 69, 046118 (2004); R. E. Zilich, J. M. Mayrhofer and S. A. Chin, J. Chem. Phys. 132, 044103 (2010)
D. L. Chandler and P. G. Wolynes, J. Chem. Phys. 74, 4078 (1981)
M. Dixon and P. Hutchinson, Molec. Phys. 33,1663 (1977)
P. A. Egelstaff, Introduction to the Liquid State (Clarendon, Oxford, 1994)
R. P. Feynman, Rev. Mod. Phys. 20, 367 (1948)
R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path integrals* (McGraw-Hill, New York, 1965)
R. P. Feynman, *Statistical Mechanics* (Benjamin, Reading, 1972)
D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, San Diego, 2002)
R. B. Hallock, Phys. Rev. A 8, 2143 (1973)
J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986)
A. D. J. Haymet, Fundamentals of Inhomogeneous Fluids, Chp. 9 (M. Dekker, New York, 1992)
T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956)
G. Jaccuci and E. Omerti, J. Chem. Phys. 79, 3051 (1983)
H. W. Jackson and E. Feenberg, Rev. Mod. Phys. 34, 686 (1962)
S. Jang, S. Jang and G. Voth, J. Chem. Phys. 115, 7832 (2001)

J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935)
C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 2005)
L. L. Lee, J. Chem. Phys. 60, 1197 (1974)
X-P Li and J. Q. Broughton, J. Chem. Phys. 86, 5094 (1987)
R. M. Lynden-Bell, Molec. Phys. 86, 1353 (1995)
S. W. Lovesey, *Theory of Neutron Scattering from Condensed Matter*, (Clarendon, Oxford, 1987)
M. J. Mandell, J. P. McTague and A. Rahman, J. Chem. Phys. 64, 3699 (1976)
N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, J. Chem. Phys, 21, 1087 (1953)
E. Nelson, J. Math. Phys. 5, 332 (1964)
J. K. Percus, Phys. Rev. Lett. 8, 462 (1962)
E. L. Pollock and D. M. Ceperley, Phys. Rev. B 30, 2555 (1984)
E. de Prunelé, J. Phys. A Math. Theor. 41, 255305 (2008)
R. Ramírez and T. López-Ciudad, J. Chem. Phys. 111, 3339 (1999)
J. J. Salacuse, A. R. Denton and P. A. Egelstaff, Phys. Rev. E 53, 2382 (1996)
D. Scharf, G. J. Martyna and M. L. Klein, J. Chem. Phys. 99, 8997 (1993); G. J. Martyna, A. Hughes and M. E. Tuckerman, 110, 3275 (1999)
L. M. Sesé, Molec. Phys. 78, 1167, (1993); 85, 931 (1995); 89, 1783 (1996); 100, 927 (2002); 101, 1455 (2003)
L. M. Sesé, J. Chem. Phys. 108, 9086 (1998); 114, 1732 (2001); 116, 8492 (2002); 123, 104507 (2005); 126, 164508 (2007); 130, 074504 (2009)
L. M. Sesé, J. Phys. Chem. B 112, 10241 (2008)
L. M. Sesé and L. E. Bailey, J. Chem. Phys. 119, 10256 (2003); 126, 164509 (2007)
L. M. Sesé and R. Ledesma, J. Chem. Phys. 102, 3776 (1995); 106, 1134 (1997)
K. Shinoda, S. Miura and S. Okazaki, J. Chem. Phys. 114, 7497 (2001)
K. Singer and W. Smith, Molec. Phys. 64, 1215 (1988)
P. J. Steinhardt, D. R. Nelson and M. Ronchetti,. Phys. Rev. B, 28, 784 (1983)
M. Suzuki, J. Math. Phys. 32, 400 (1991)
M. Takahasi and M. Imada, J. Phys. Soc. Japan, 53, 3765 (1984)
M. Tanaka and Y Fukui, Prog. Theor. Phys. 53, 1547 (1975)
H. F. Trotter, Proc. Am. Math. Soc. 10, 345 (1959)
J. Yvon, *La Theorie Statisque des Fluides et l'equation d'Etat* (Hermann, Paris, 1935)