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Van der Waals clusters: solid or liquid ?

Highorder actions and their applications in manybody, Fewbody and classical problems
In honor to
Siu A. Chin
at the occasion of his 60th birthday
March 24-26, 2009 Universidad Politécnica de Cataluña

Characterizing a cluster as solid or liquid

- Motivation: para-Hydrogen clusters
- A simple model of a cluster switching from liquid to solid
- Lindemann parameter: classical
- New Lindemann parameter: quantum mechanical
- Solid-Liquid behavior
- Application: Lennard-Jones clusters
- Conclusions

Motivation: para-Hydrogen clusters

- **EXPERIMENT**
- G. Tejeda, J.M. Fernández, S. Montero, D. Blume and J. P. Toennies, Phys. Rev. Lett. **92**, 223401 (2004)

- **Light clusters:**
- Ph. Sindzingre, D. M. Ceperley, and M. L. Klein, Phys. Rev. Lett. **67**, 1871 (1991).
- M. V. Rama Krishna and K. B. Whaley, Z. Phys. D 20, 223 (1991).
- Daphna Scharf, Michael L. Klein and Glenn J. Martyna, J. Chem. Phys. **97**, 3590 (1992).
- \Michele A. McMahon, Robert N. Barnett, and K. Birgitta Whaley, J. Chem. Phys. **99**, 8818 (1993).
- Michele A. McMahon and K. Birgitta Whaley, Chemical Physics 182, 119 (1994) .

- **Two dimensional**
- M. C. Gordillo and D. M. Ceperley, Phys. Rev. **65**, 174527 (2002)

Motivation: para-Hydrogen clusters

- Systematic studies
- F. Mezzacapo and M. Boninsegni, Phys. Rev. Lett. **97**, 045301 (2006).
- R. Guardiola and J. Navarro, Phys. Rev. A **74**, 025201 (2006).
- J. E. Cuervo and P.N. Roy, J. Chem. Phys. **125**, 124314 (2006).
- F. Mezzacapo and M. Boninsegni, Phys. Rev. A **75**, 033201 (2007).
- S. A. Khairallah, M. B. Sevryuk, D. M. Ceperley, and J. P. Toennies,
- Phys. Rev. Lett. **98**, 183401 (2007).
- R. Guardiola and J. Navarro, Cent. Eur. J. Phys. 6, 33 (2008).
- F. Mezzacapo and M. Boninsegni, Phys. Rev. A **76**, 021201 (2007).
- J. E. Cuervo and P.-N. Roy, J. Chem. Phys. **128**, 224509 (2008).

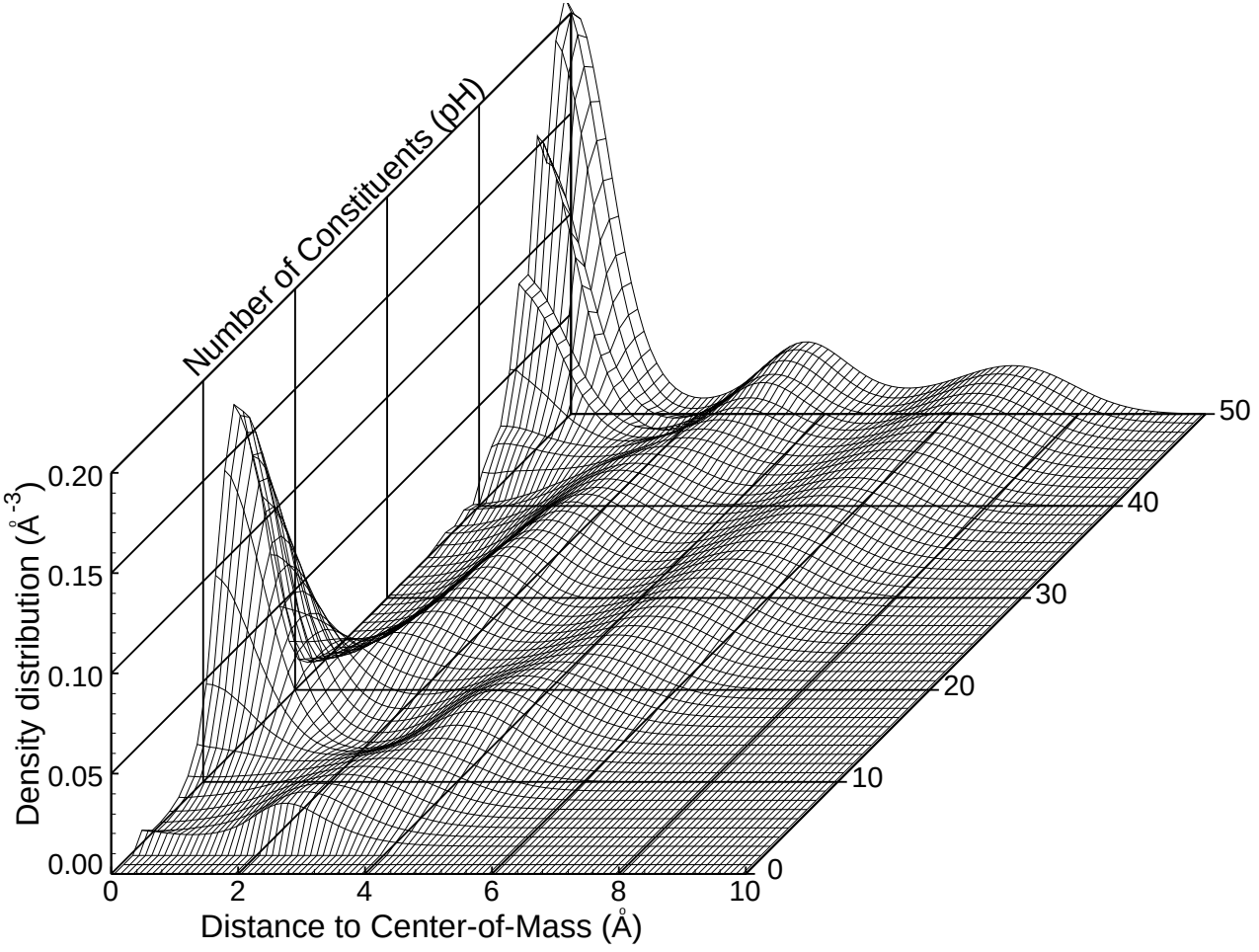
para-Hydrogen clusters: Main results - 1

- Experiment: Magical cluster at N=13
- Theory up to N=40
- DMC: only N=13 is magical
- PIGS and PIMC: many othe magical clusters

- MAGICAL defined as a peak in the dissociation energy

para-Hydrogen clusters: Main results - 2

- HIGHLY STRUCTURED DENSITY with defined shells



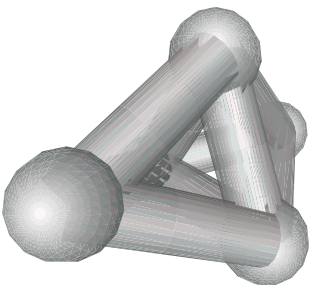
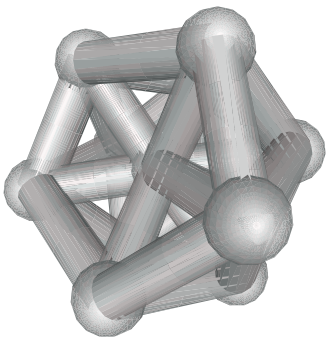
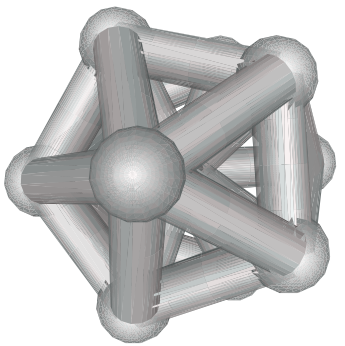
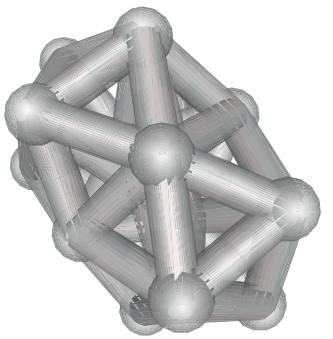
MacKay Polyhedra

Constituents coordinates obtained by minimizing the 6-12 Lennard-Jones potential (static problem)

A. L. Mackay, Acta Crystallogr. **15**, 916 (1962).
M. R. Hoare and P. Pal, Adv. Phys. **20**, 161 (1971).
M. R. Hoare, Adv. Chem. Phys. **40**, 49 (1979).
J. Dana Honeycutt and Hans C. Andersen, Phys. Chem. **91** , 4950, (1987).
The Cambridge Cluster Database, D. J. Wales, J. P. K. Doye, A. Dullweber, M. P. Hodges, F. Y. Naumkin, F. Calvo, J. Hernández-Rojas and T. F. Middleton, URL http://www-wales.ch.cam.ac.uk/CCD.html

..\Qmol\Qmol.exe

N=5 N=12 N=13 N=19

Simple cluster model

c : cluster coordinates

r : constituent coordinates

Single particle wave functions

$$\phi_k(\mathbf{r}) = \frac{\alpha^{3/2}}{\pi^{3/4}} \exp\left[-\frac{1}{2}\alpha^2(\mathbf{r}-\mathbf{c}_k)^2\right]$$

Bose symmetrized cluster wave function

$$\Psi_B = \mathrm{perm}|\phi_i(j)| = \mathrm{perm}\begin{vmatrix} \phi_1(1) & \phi_2(1) & \phi_3(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \phi_3(2) & \cdots & \phi_N(2) \\ \phi_1(3) & \phi_2(3) & \phi_3(3) & \cdots & \phi_N(3) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \phi_1(N) & \phi_2(N) & \phi_3(N) & \cdots & \phi_N(N) \end{vmatrix}$$

Parameters: Harmonic vibrations: ▫▭▭

Cluster size: $d = 2^{1/6}\sigma \approx 1.12\sigma$

Dimensionless: ~d

Limits of model cluster wave function

Small HO parameter is equivalent to null C – cluster coordinates -> Liquid

$$|\Psi_{B,\alpha\to 0}|^2 \equiv \left(\frac{\alpha^{3/2}}{\pi^{3/4}}\right)^N \exp\left[-\alpha^2 \sum_i \mathbf{r}_i^2\right]$$

Large HO parameter is equivalent to point-like cluster wave function -> SOLID

$$|\Psi_{B,\alpha\to\infty}|^2 \equiv \sum_{\mathbf{P}} \prod \delta(\mathbf{r}_i - \mathbf{c}_{\mathbf{P}i}).$$

Where is the liquid-solid transition? Compute the probability of finding the particle in a sphere of radiusd/2:

$$\int_{r<d/2} |\phi(r)|^2 d\mathbf{r} = \mathrm{erf}(\alpha d/2) - \frac{\alpha d}{\sqrt{\pi}} \exp(-\alpha^2 d^2/4)$$

To have a probability of 0.9 the required value of □=3.20 (SOLID).
For a probability of 0.7 then □=2.40 (LIQUID)

Model independent parameter: Lindemann parameter

- F. A. Lindemann, Phys. Z. {\bf 11}, 609 (1910)

PHYSIKALISCHE ZEITSCHRIFT

No. 14. 15. Juli 1910. Redaktionsschluß für No. 15 am 18. Juli 1910. 11. Jahrgang.

Über die Berechnung molekularer Eigenfrequenzen [1]).

Von F. A. Lindemann.

The average of the oscillations of single atoms divided by the distance to the nearest neighbors

$$\delta = \frac{\sqrt{\langle r^2 \rangle}}{d}$$

Reasonable for quasi-classical description of solids, but not for quantum-mechanical cluster

Related to measurable quantities:
J.J. Gilvarry, Phys. Rev. 103, 1700 (1956).
R.D. Etters and Jaya Kaelberer, Phys. Rev. A {\bf 11}, 1068 (1975).

Lindemann parameter: forms used in quantum mechanical studies

- Thomas L. Beck, J.D. Doll and David L. Freeman, J. Chem. Phys. 190, 5851 (1989)
- Works on para-Hydrogen already mentioned (K. Birgitta Whaley)
- Based on mean bond length fluctuations

$$\delta = \frac{2}{N(N-1)} \sum_{i<j} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle}$$

Uncompatible with Bose symmetry

A generic form has been recently introduced

J. E. Cuervo and P.-N. Roy, J. Chem. Phys. 128, 224509 (2008)

$$\delta = \frac{\sqrt{\langle \sum_{i<j} r_{ij}^2 / N_p \rangle - \langle \sum_{i<j} r_{ij} / N_p \rangle^2}}{\langle \sum_{i<j} r_{ij} / N_p \rangle} \qquad N_p = N(N-1)/2$$

Some comments on Bose symmetry

Particles are called identical if the hamiltonian is invariant under the permutation of particle coordinates, like in the case of typical N-body problems for which the hamiltonian is

$$H = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_{i<j} V_{ij}$$

with all masses equal and the two-body interaction is symmetric. The Spin-Statistics connection principle establishes that among all solutions of the eigenvalue equation

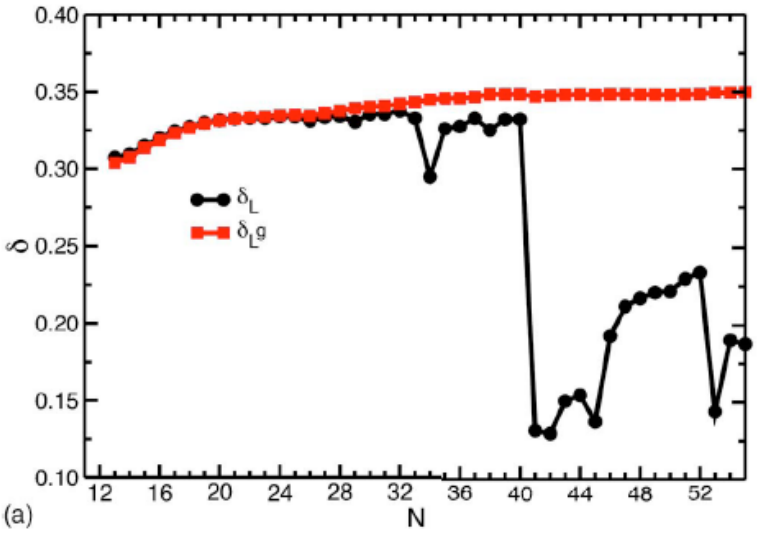
$$H\Psi = E\Psi$$

only those which are fully symmetric (bosons) or fully antisymmetric (fermions) appear in nature. In both cases the probability density is a symmetric function, and when computing the expectation value of any operator it acts as a projector, extracting from this operator exclusively the symmetric part.
In other words, relevant quantum mechanical operators in a system of identical particles must be symmetric. At the same time, the use of particles labels has not sense, apart from being a way of labelling the 3N dummy coordinates of the wave function.

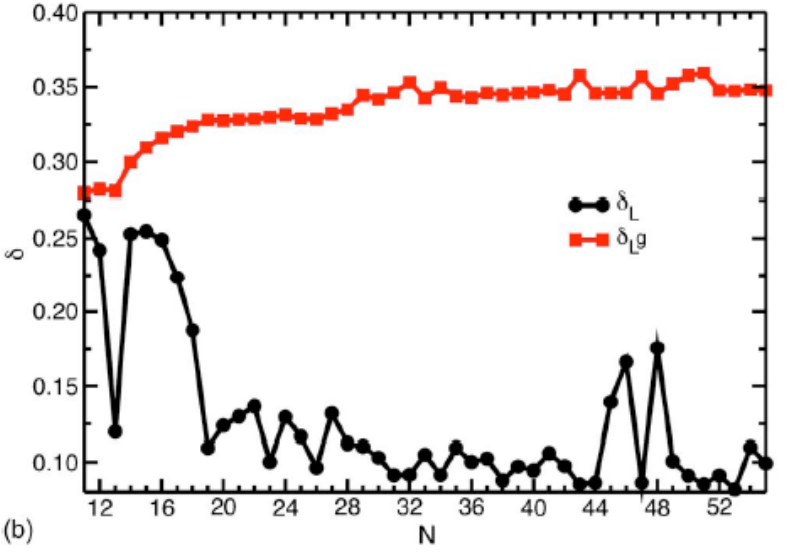
Limits of Generic Lindemann parameter for our model

- Solid Limit: 0.27 (N=10) to 0.34 (N=40)
- Liquid Limit (N indep.): 0.422: very small interval
- Troubles with Bose symmetry (Cuervo and LeRoy)

para-H



ortho-D



New Lindemann parameter

For a given operator *O* the quantum incertitude (i.e., the standard deviation for the Copenhagen interpretation of quantum mechanics) is given by

$$\Delta\mathcal{O} = \sqrt{\langle\Psi_B|\mathcal{O}^2|\Psi_B\rangle - \langle\Psi_B|\mathcal{O}|\Psi_B\rangle^2}$$

Use the relativeincertitude of the mean square pair distance

$$\mathcal{O} = \sum_{i<j} r_{ij}^2 / N_p$$

Limit solid=0

Limit liquid= $\lim_{\alpha\to 0} \frac{\Delta O}{\langle O\rangle} = \sqrt{\frac{2}{3(N-1)}}$

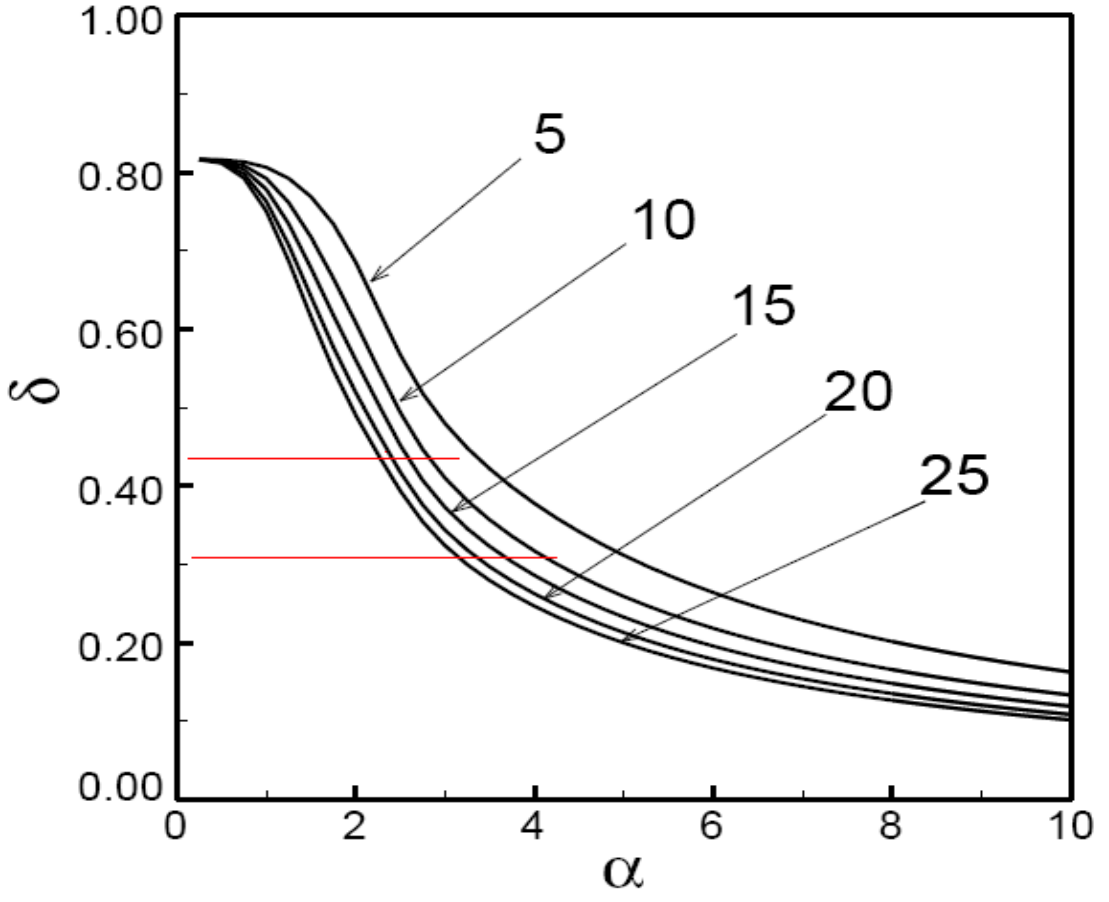
Specific proposal of new Lindemann parameter

$$\delta = \sqrt{N-1}\frac{\sqrt{\left\langle \left[\sum_{i<j} r_{ij}^2\right]^2 \right\rangle - \left\langle \left[\sum_{i<j} r_{ij}^2\right] \right\rangle^2}}{\left\langle \left[\sum_{i<j} r_{ij}^2\right] \right\rangle}$$

Limit liquid: 0.8165

Limit solid: 0

Transition: use model wave function (exact calculation)



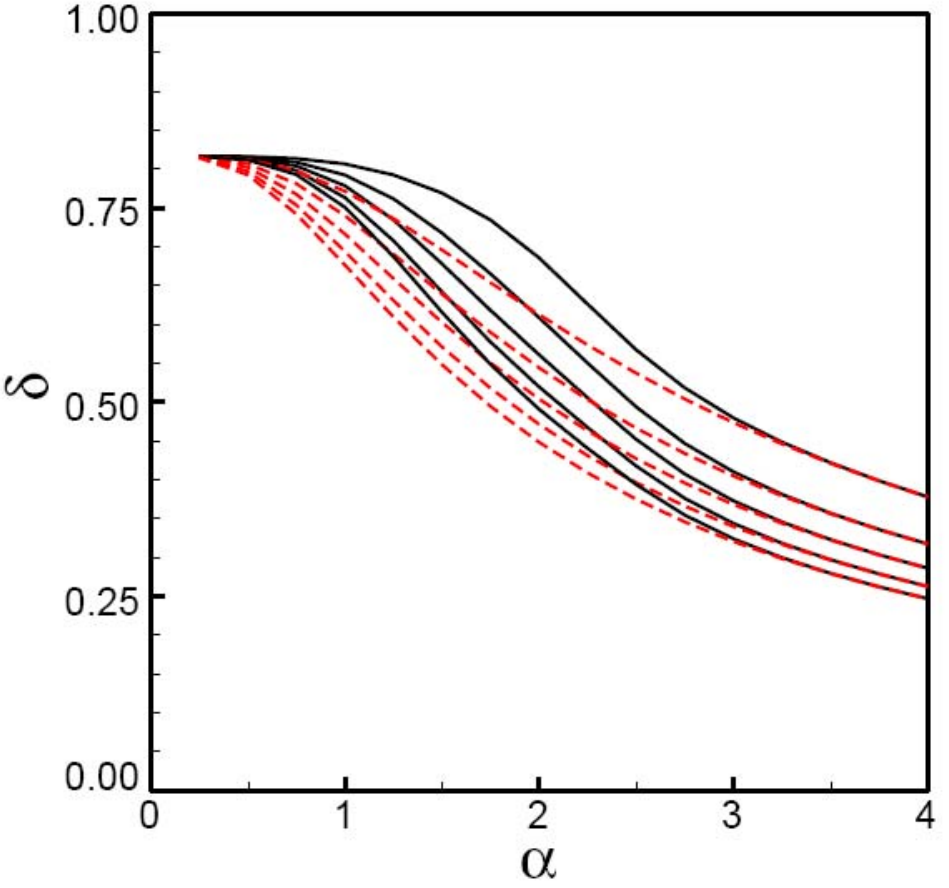
Solid:

□>3.2 □<0.30

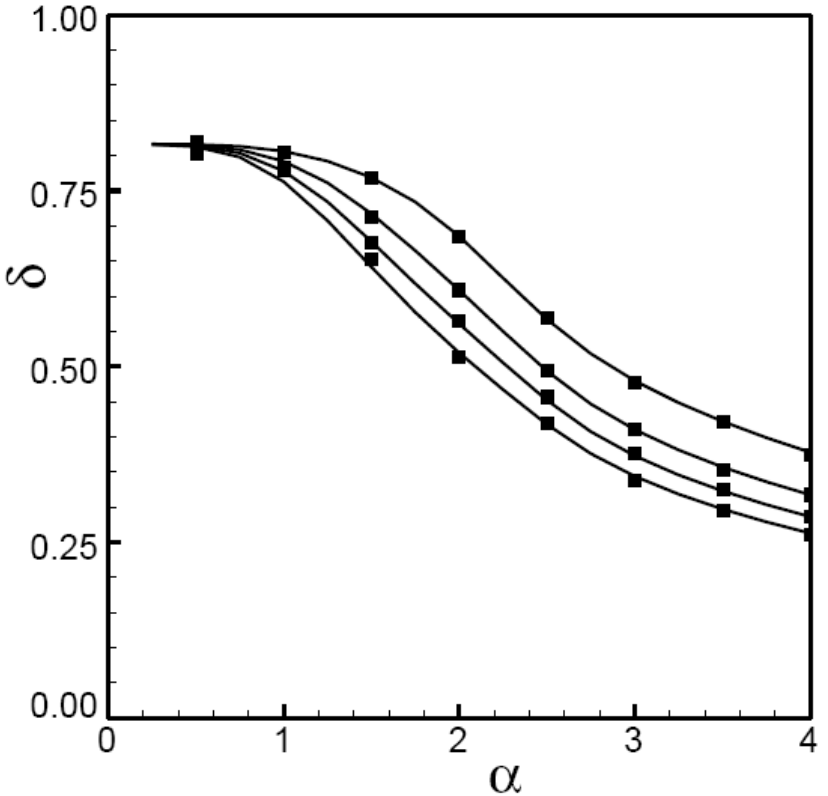
Liquid:

□<2.4 □>0.45

Role of Bose symmetry



Monte Carlo Metropolis calculation



Metropolis sampling adequate when Bose correlations are important.

Troubles with PIMC (no importance sampling wave function) ?

Lennard-Jones clusters

Reduced units hamiltonian

$$h = -\frac{\Lambda^2}{2}\sum_i \nabla_i^2 + \sum_{i<j} v(r_{ij})$$

De Boer parameter

$$\Lambda = \frac{\hbar}{\sigma\sqrt{m\epsilon}}$$

Noble gasses

Atom	σ(Å)	$\epsilon(K)$	m(amu)	Λ
^{4}He	2.56	10.212	4.003	0.426
Ne	2.75	35.365	20.18	0.094
Ar	3.40	123.13	39.95	0.029
Kr	3.68	166.59	83.80	0.016
Xe	4.07	224.53	131.29	0.010

para-Hydrogen: 0.30

ortho-Deuterium = 0.20

Variational calculation: trial function

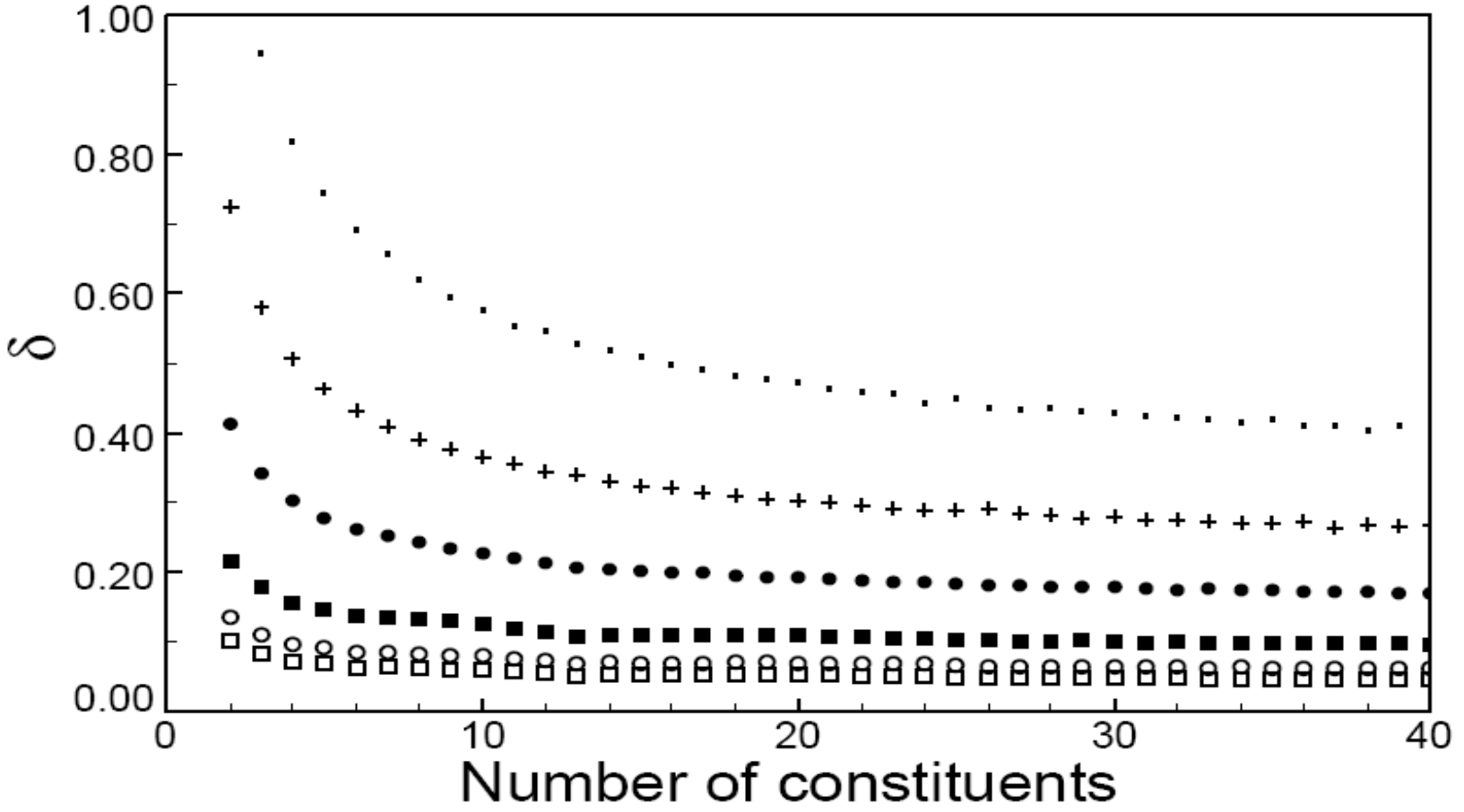
$$\Psi = \prod_{i<j} \exp(u_J(r_{ij})$$

$$u_J(r) = -\frac{1}{2}\frac{b^5}{r^5} - ar$$

$$b = \left(\frac{16}{25\Lambda^2}\right)^{1/10}$$

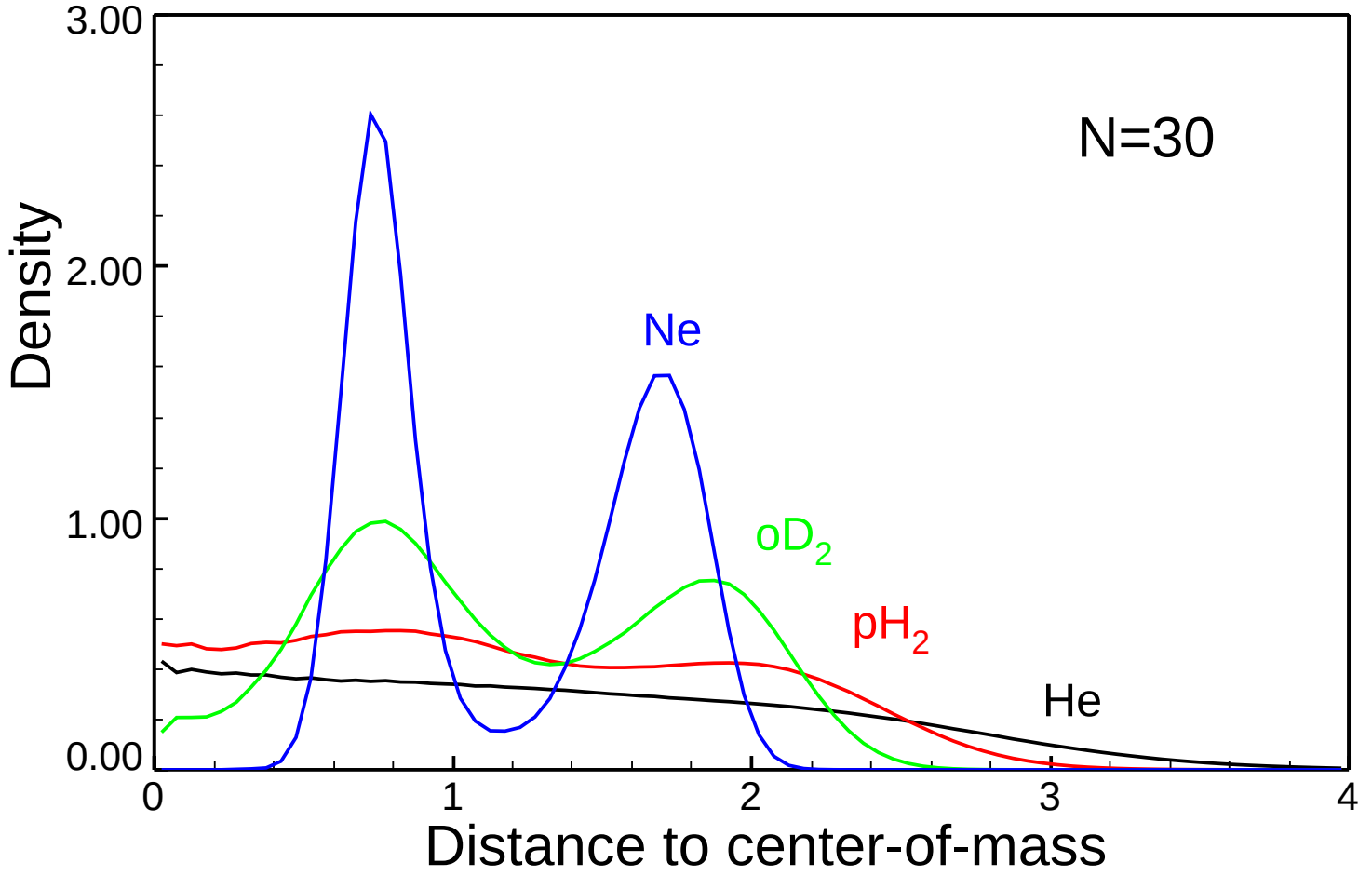
a = is the only variational parameter

New Lindemann parameter LJ



From bottom to top: L = 0.03(Ar), 0.05, 0.10(Ne), 0.20(o-D), 0.30(p-H), 0.40(He)

Radial distributions (variational)



Perhaps limits to be revised (pH seems more liquid than solid)

Conclusions

- New Lindemann parameter based on quantum uncertainty
- Fuzzy limits: above 0.42 is a liquid

  below 0.30 a solid

Limits to be revised (DMC calculation required)

Dear Siu,