

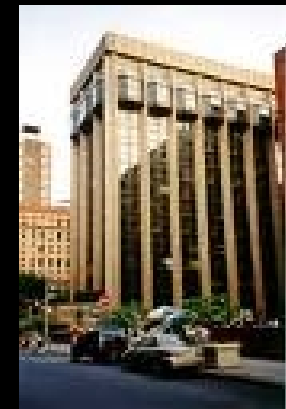
# The interatomic potential of helium atoms in the condensed phases and the multi-weight diffusion Monte Carlo method

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# The Multi-weight Extension to The Diffusion Monte Carlo Method

- Correlated results associated to small changes of the interparticle interacting potential can be obtained in a single run
- Almost a single set of walkers is used to compute the properties of a system described by different potentials
  - Allows straightforward calculations of the energies associated with the potentials and their difference without any approximation
  - Accurate calculations of small energies differences
- This is an extension easy to implement and test

# Applications in Systems of Helium Atoms

- Selection of the best two-body component of the interatomic potential
- Analysis of three-body contributions to the interatomic potential
- Choice of a damping factor for the Axilrod-Teller Muto triple-dipole term
- Change of the amplitude of a three-body exchange potential

# Motivations

- Results for the EOS for the solid phase were not satisfactory as those for the liquid phase where at all densities values of the energy per atom were in agreement with experiment
- The role of individual contributions of the three-body components in the interatomic potential in the description of some properties of a system of helium atoms were not known
  - “Ab initio” exchange calculations that differ by an order of magnitude
  - Enhance the physical content of the analytical functions use to fit the three-body contributions

# Example of an application of the MW-DMC method:

Three-body contributions  
in the description of the  
condensed phases of  $^4\text{He}$

- In order to investigate these contributions we have considered three different Hamiltonians

# A system with only two-body interactions

$$H_2 = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2 + V_2(R), \text{ where } R \equiv \{\mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_N\}$$

- $V_2$  is the *ab initio* potential of Korona and collaborators where retardation effects have been introduced by Janzen and Aziz



# The Axilrod-Teller Muto triple-dipole three-body term

$$H_{2\text{ddd}} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2 + \underbrace{V_{2\text{ddd}}(R)}_{V_2 + V_{\text{ddd}}}$$

- $V_{\text{ddd}}$  is the damped Axilrod-Teller Muto triple-dipole potential  $V_{\text{DDD}}$

$$V_{\text{ddd}} = V_{\text{DDD}} f_3(r_{ij}, \delta) f_3(r_{ik}, \delta) f_3(r_{jk}, \delta)$$

- Damping factors of the Tang-Toennies form

$$f_3(r_{ij}, \delta) = 1 - \sum_{k=0}^3 e^{-\delta r} (\delta r)^k / k!$$

- $\delta$  is a parameter determined using the MW-DMC

# The exchange term in the three-body interatomic potential

$$H_3 = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2 + \underbrace{V_3(R)}_{V_2 + V_{ddd} + V_{ex}}$$

- $V_{ex} = AV_{CM}$  is the exchange potential of Cohen and Murrell times an amplitude  $A$ 
  - The amplitude  $A$  was determined as well employing the MW-DMC

# Some technical details

- A single guiding function is used for all the Hamiltonians we consider
- Standard diffusion and weight update
- Each walker carries more than one weight
  - One for each potential we want to consider
- Slight generalization of the branching rules

# The guiding functions

- **The liquid phase:** a function of the Jastrow form

$$\psi_G(R) = \prod_{i < j} f_{ij} \quad \text{where} \quad f_{ij} = \exp \left[ \left( \frac{b}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^5 \right]$$

- **The solid phase:** a function of the Nosanow-Jastrow form

$$\psi_G(R) = \prod_{i < j} f_{ij} \prod_i \exp \left[ -\frac{C}{2} |\mathbf{r}_i - \mathbf{l}_i|^2 \right]$$

- Certainly more accurate guiding functions could be used as well

# Diffusion

- The sampling of a new walker  $R' \rightarrow R$  is standard, *i. e.*,

$$G_d(R, R') = (4\pi D \Delta\tau)^{-3N/2} \exp\left[-\frac{(R - R' - 4D \Delta\tau v_D(R'))^2}{4D \Delta\tau}\right]$$

- where  $v_D = 2 \nabla \ln \psi_G$  is the drift force  
 $D = \hbar^2 / 2m$  the diffusion coefficient  
 $\Delta\tau$  the time step

# Weights update

- For each of the Hamiltonians  $m=\{2, 2\text{ddd}, 3\}$  we are considering the weight update  $w'^{(m)} \rightarrow w^{(m)}$  is standart

$$w^{(m)} = w'^{(m)} G_b^{(m)}(R, R')$$

$$G_b^{(m)}(R, R') = \exp \left[ -\frac{\Delta \tau}{2} (E_L^{(m)}(R) + E_L^{(m)}(R')) + \Delta \tau E_T^{(m)} \right]$$

$$E_L^{(m)}(R) = \frac{H_m \Psi_G}{\Psi_G}$$

- $E_T^{(m)}$  is a parameter changed during the simulation so that  $w^{(m)} \approx 1$

# Branching

- If walker  $i$  has  $\min(w_i^{(2)}, w_i^{(2\text{ddd})}, w_i^{(3)}) \geq 2$  then it is split in two
  - each one with weights  $(w^{(2)}/2, w^{(2\text{ddd})}/2, w^{(3)}/2)$
- If a walker  $j$  has  $\max(w_j^{(2)}, w_j^{(2\text{ddd})}, w_j^{(3)}) < 0.3$  then it is put aside

# Combining walkers

- If we have two walkers  $j$  and  $k$  with all their weights less than 0.3 they are combined according to the following rules

- with probability 
$$r^{(m)} = \frac{w_j^{(m)}}{w_j^{(m)} + w_k^{(m)}}$$

ascribe to walker  $j$  the sum of weights associated with Hamiltonian  $m = \{2, 2\text{ddd}, 3\}$ , otherwise assign the value 0

- if **all weights** of a walker are zero, delete this walker
- otherwise both walkers are kept



# Comments about the combination of walkers

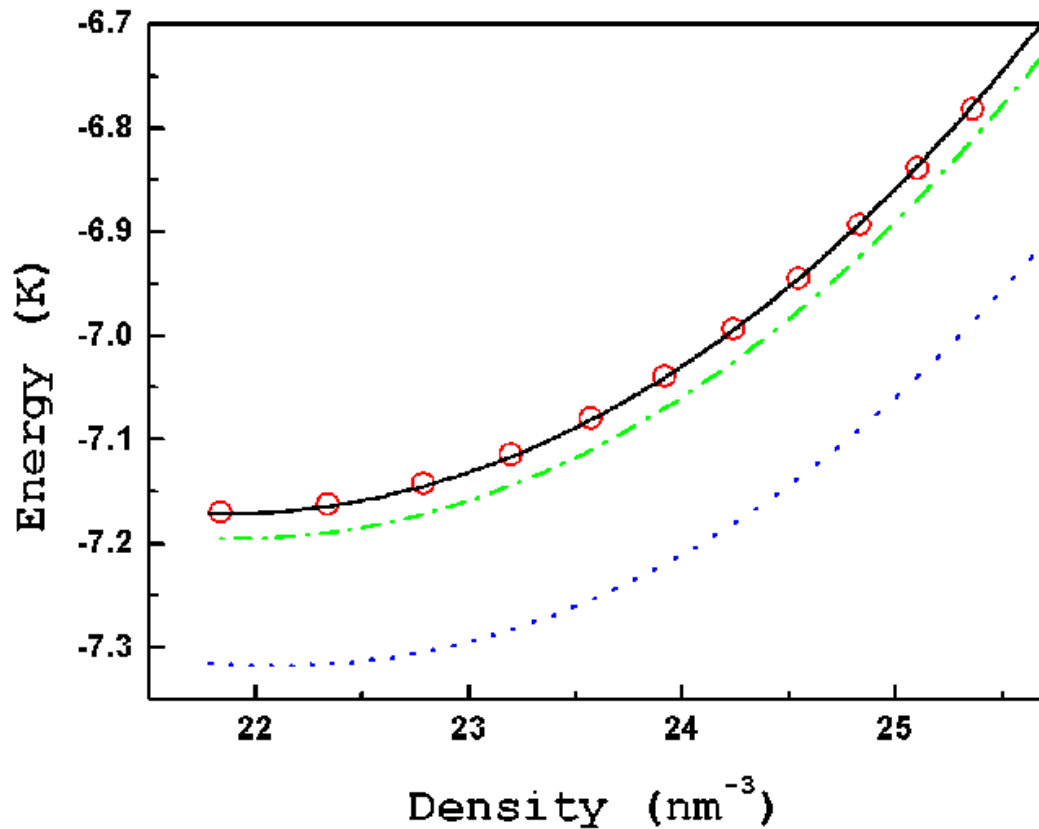
- Worst case: walkers  $i$  and  $j$  will finish with weights given say by
  - $(w_j^{(2)} + w_k^{(2)}, 0, 0)$  and  $(0, w_j^{(2ddd)} + w_k^{(2ddd)}, w_j^{(3)} + w_k^{(3)})$
- In principle we do not have any problem in considering both walkers in the weighted averages used in the calculations of the energies  $E_m$ 
  - However we are destroying the correlations among the results we want to build
  - Fortunately the number of such walkers can be minimized by the choice of the threshold for walkers recombination
    - For a threshold of 0.3, less than 5% of the walkers carry one of their weights equal to zero

# Estimation of the energies

- At every evaluation of the energy cycle through  $m=\{2, 2\text{ddd}, 3\}$

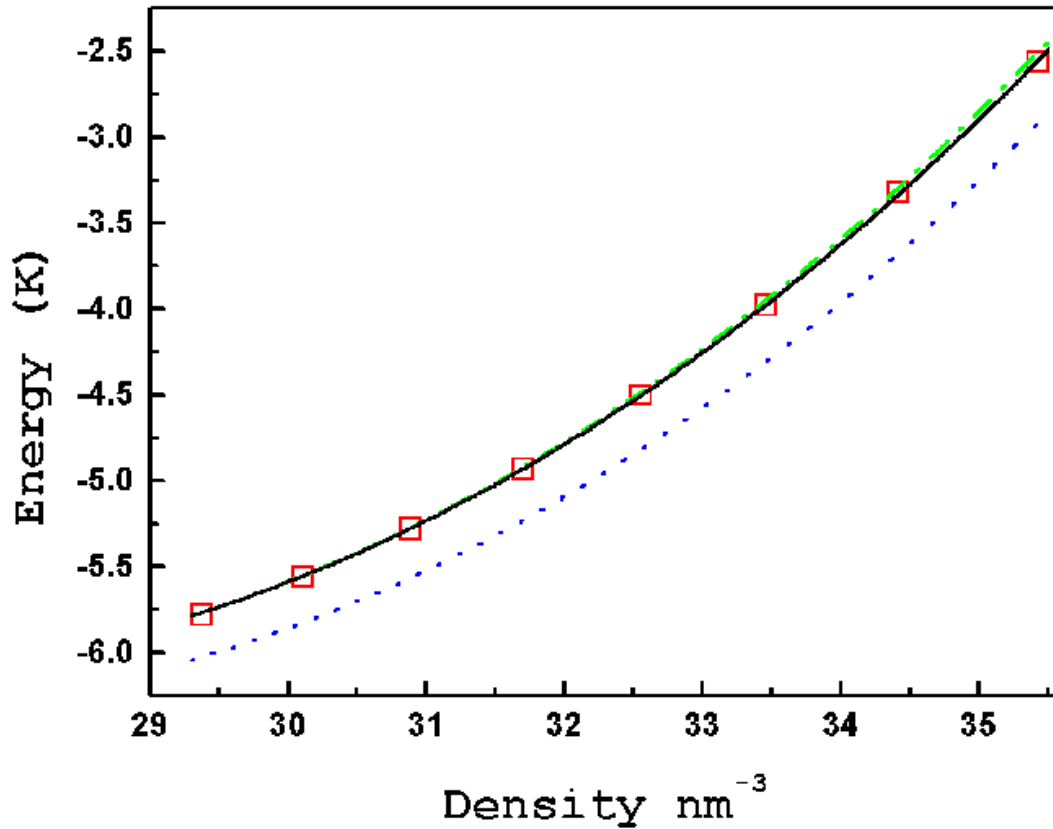
$$E_m = \frac{\sum_i w^{(m)}(R_i) E_L^{(m)}(R_i)}{\sum_i w^{(m)}(R_i)}$$

# EOS for the liquid phase



	Energy at $\rho_0$
$E_2$	$-7.316 \pm 0.008$
$E_{2\text{ddd}}$	$-7.195 \pm 0.008$
$E_3$	$-7.171 \pm 0.008$
<b>Exp</b>	<b>-7.170</b>

# EOS for the solid phase



Energy at  $\rho^* = 32.55$

$E_2$   $-4.822 \pm 0.009$

$E_{2\text{ddd}}$   $-4.491 \pm 0.009$

$E_3$   $-4.509 \pm 0.009$

Exp  $-4.50$

# Comments

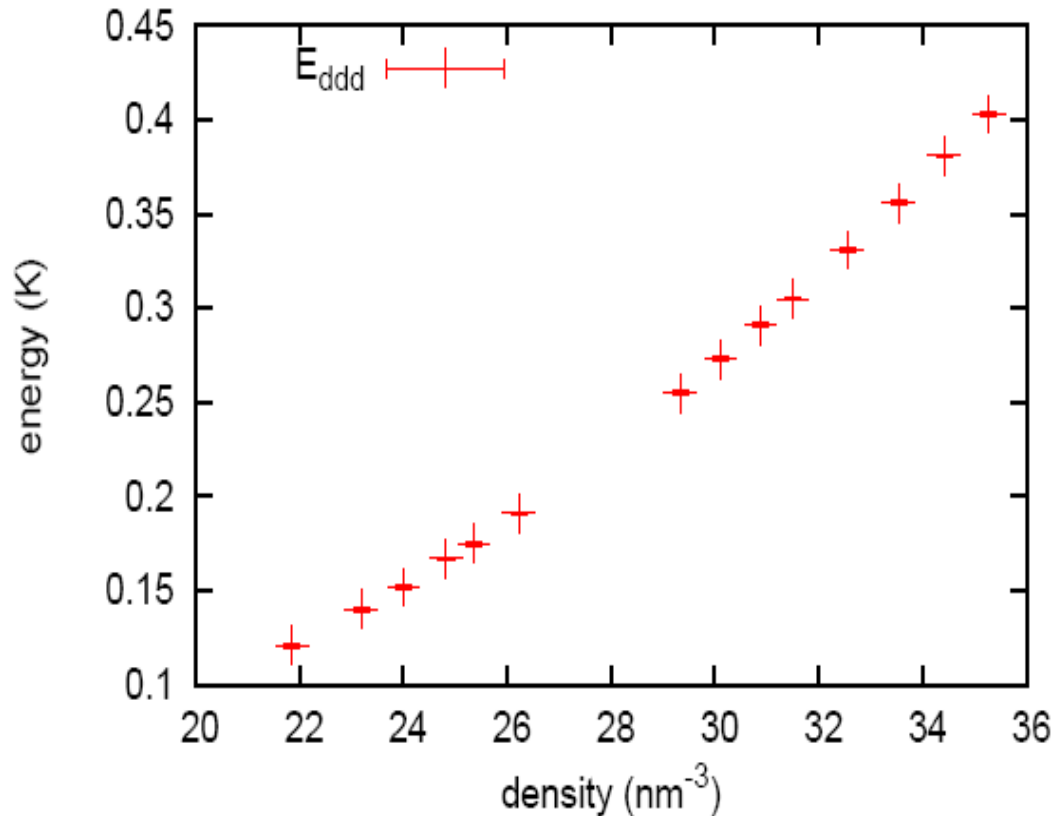
- In the interatomic potential we have introduced two adjustable parameters
  - $\delta=20.35 \text{ nm}^{-1}$   $\Rightarrow$  The parameter  $\delta$  of the Tang-Toennies damping function  $f_3(r, \delta)$  in the triple-dipole term
  - $A=4.0$   $\Rightarrow$  The amplitude  $A$  of the Cohen and Murrell exchange term
- At all densities in both the solid and liquid phases we are able to get energies per atom in agreement with experiment

# $\rho_{\text{melting}}$ , $\rho_{\text{freezing}}$ and $\rho_0$ Densities

Potential	$\rho_m$	$\rho_f$	$\rho_0$
$V_2$	$29.07 \pm 0.32$	$26.05 \pm 0.32$	$22.10 \pm 0.13$
$V_{2\text{ddd}}$	$29.04 \pm 0.31$	$26.09 \pm 0.31$	$21.87 \pm 0.14$
$V_3$	$28.93 \pm 0.31$	$25.95 \pm 0.31$	$21.82 \pm 0.14$
Exp	28.568	$25.970 \pm 0.005$	21.834

# $E_{\text{ddd}}$ the energy associated to the triple-dipole term

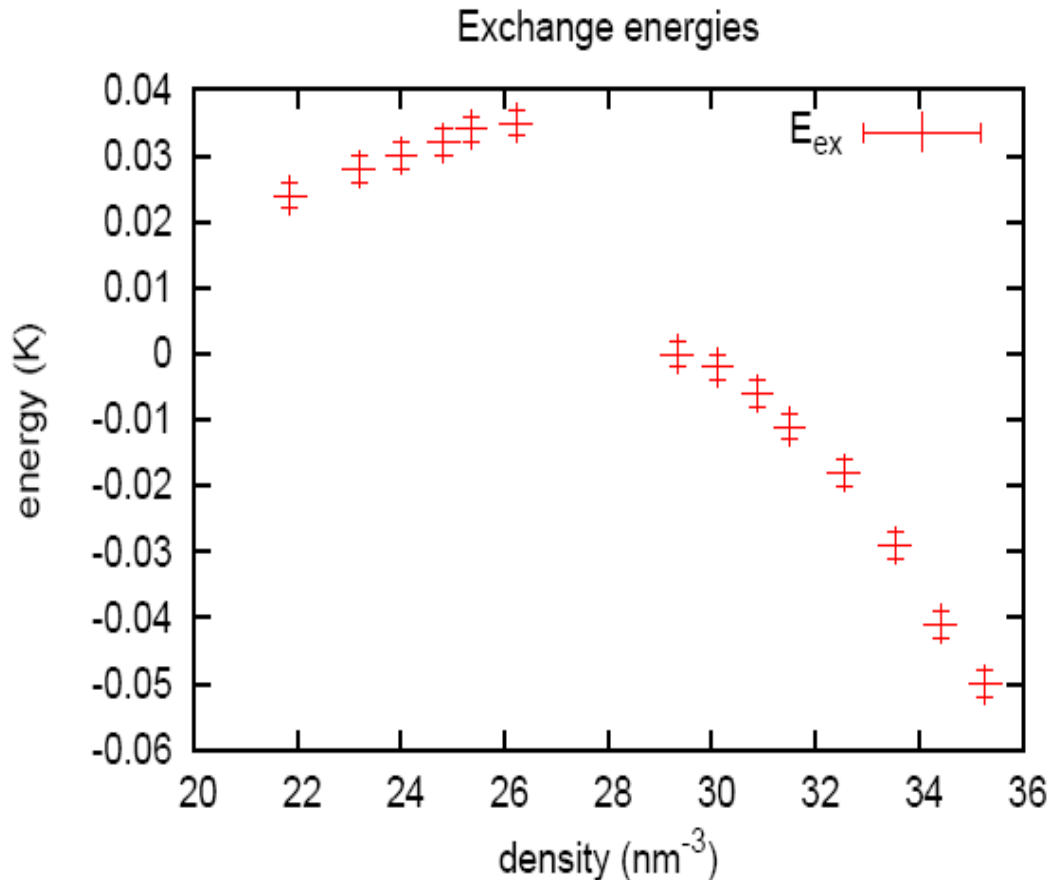
Energies of the triple-dipole interaction



$E_{\text{ddd}}$  is computed without any approximation from the correlated energies  $E_{2\text{ddd}}$  and  $E_2$  at each time they are evaluated

$$E_{\text{ddd}} = E_{2\text{ddd}} - E_2$$

$E_{\text{ex}}$  the energy associated to the exchange term



Similarly,  $E_{\text{ex}}$  is computed without any approximation from the correlated energies  $E_3$  and  $E_{2\text{ddd}}$  at each time they are estimated

$$E_{\text{ex}} = E_3 - E_{2\text{ddd}}$$



# Final Comments

- In despite of its small contribution to the total energy,  $V_{\text{ex}}$  can not be neglected if agreement with experiment is wanted in both phases of the system
- The need of an amplitude factor  $A=4.0$  in the “*ab initio*” exchange term is more than an indication that this component of our interatomic potential might have some problems
- The MW extension to the DMC method is a reliable tool to compare results obtained with similar potentials and a way to choose the best description of the system
  - Application to study bound states of some molecular systems