

Rotational Spectra in Helium Clusters and Droplets

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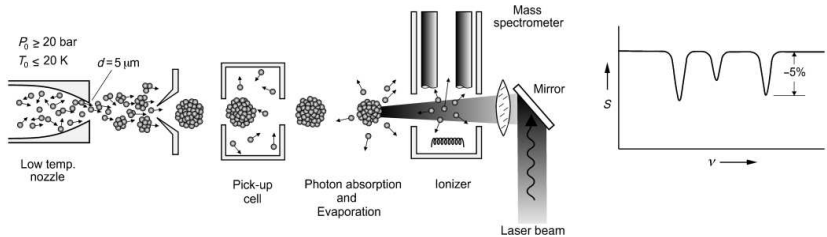
July 20, 2007

Outline

- 1 Introduction
 - Experiment
 - Hamiltonian
- 2 Molecule Dynamics and Collective excitations
 - Correlated Basis Function Theory
 - Linewidth of CO in He, bulk and droplet
- 3 Molecule Dynamics and Superfluidity
 - Path Integral Monte Carlo and Imaginary Time Correlation functions
 - Rotational dynamics of LiH in He clusters
 - OCS in He clusters and Rb-He exciplexes

Helium matrix isolation spectroscopy

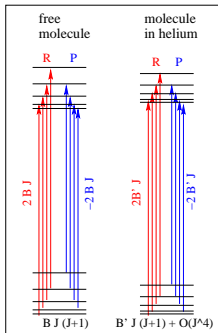
depletion spectroscopy: chromophore excitation detected by evaporating ^4He atoms.



from J. P. Toennies and A. F. Vilesov

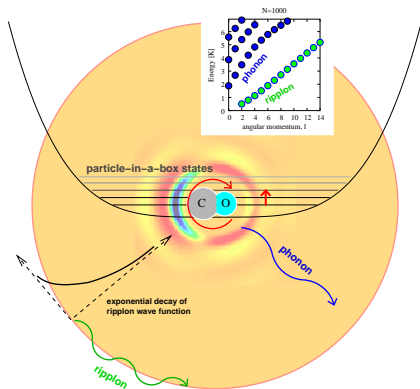
- measuring sharp rovib. spectra of *isolated* molecules at low T ;
- stabilizing transition states (conformations);
- assembly of small clusters in He?;
- probing ^4He : superfluidity on microscopic scale – microscopic Andronikashvili exp. (Grevenev et al., Science 1998)

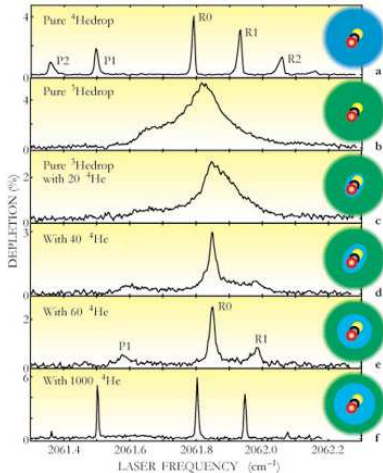
Dynamics of (linear) molecule in He droplet



- 1 sharp lines \Leftrightarrow long life-times
- 2 linear rotor spectrum, but B changes value: B_{eff}
 symmetry is preserved
 distortion constant is increased

$$E_J = B_{\text{eff}} J(J+1) - D_{\text{eff}} (J(J+1))^2$$



Experiment: spectrum of OCS in ^4He and ^3He 

OCS molecule in pure ^4He and ^4He - ^3He mixtures:

- 1 sharp lines for (bosonic) ^4He
- 2 collapsed spectrum for (fermionic) ^3He

→ temperature: 0.4K/0.15K

from: J. P. Toennies, A. F. Vilesov, and K. B. Whaley,
Physics Today **54**, 31 (2001)

Hamiltonian for spectroscopy

linear molecule (\mathbf{r}_0, Ω) + N helium atoms ($\{\mathbf{r}_i\}$):

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{H}_{\text{mol}} + \hat{V} \\ \hat{H}_0 &= -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i < j} v_{\text{He-He}}(|\mathbf{r}_i - \mathbf{r}_j|) \\ \hat{H}_{\text{mol}} &= -\frac{\hbar^2}{2M} \nabla_0^2 + B \hat{L}^2(\Omega) \\ \hat{V} &= \sum_{i=1}^N V(\mathbf{r}_i - \mathbf{r}_0, \Omega)\end{aligned}$$

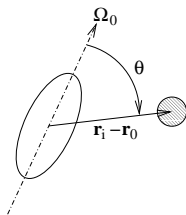
input:

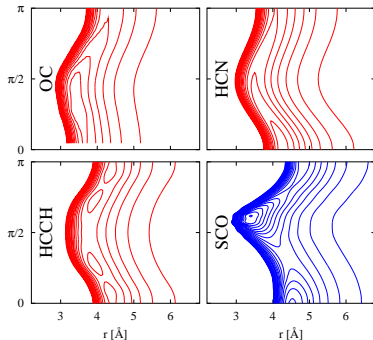
gas phase rotational constant B

molecule-helium interaction potential $V(r, \theta)$

output:

rotational spectrum $S_J(\omega)$ for $0 \rightarrow J$ transition ($J = 1$)



molecule-helium interaction $V(r, \theta)$ 

- “fast” rotors: $B \gtrsim 1\text{K}$
potential weakly anisotropic
 B_{eff}/B reduction 0.8 – 0.9
no adiabatic following, but coupling
to phonon-rotor spectrum (CBF)
- “slow” rotors: $B \lesssim 1\text{K}$
potential strongly anisotropic
 B_{eff}/B reduction 0.3 – 0.4
adiabatic following of ρ_n

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Correlated Basis Function (CBF) Theory

Given the ground state Φ_0 , make the following ansatz:

$$|\Phi(t)\rangle = \frac{e^{\delta U(t)}|\Phi_0\rangle}{\langle\Phi_0|e^{\Re\delta U(t)}|\Phi_0\rangle}$$

and determine $\delta U(t)$ using stationarity of action integral

$$\mathcal{L} = \int dt \langle\Phi(t)|H - i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle = \text{Min.}$$

by linearizing and solving the resulting Euler-Lagrange equations $\delta\mathcal{L} = 0$.
(Linear response approach)

Ground state Φ_0 obtained from diffusion Monte Carlo (DMC), using descendent weighting for sampling $\langle\hat{A}\rangle$ if $[H, \hat{A}] \neq 0$.

or get Φ_0 from anywhere else (e.g. HNC/EL), but must be optimized!

CBF = Time-dependent pair-density functional theory

Most important contributions to $\delta U(t)$ are from few-body correlations:

$$\begin{aligned}\delta U &= \delta U(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ &= \text{single particle excitations} + \text{pair excitations}\end{aligned}$$

(linearization not valid for e.g. vortices)

Specifically for molecule excitation in helium

$$\delta U = \delta u_1(\mathbf{r}_0, \Omega) + \sum_{i=1}^N \delta u_2(\mathbf{r}_0, \mathbf{r}_i, \Omega)$$

Rotation Spectrum of linear molecule in bulk He

Solution of Euler-Lagrange equations $\delta\mathcal{L} = 0$ leads to rotational spectrum “renormalized” by a self-energy. In *bulk* He:

$$E_J = BJ(J+1) + \Sigma_J(E_J)$$

and to corresponding absorption spectrum in frequency ω

$$S_J(\omega) = \Im m \left[\hbar\omega - BJ(J+1) - \Sigma_J(\hbar\omega) \right]^{-1}$$

\implies Lorentzian peaks at E_J of width $\Im m \Sigma(E_J)$ (if $\Im m \Sigma(E_J)$ small)

the self energy is given by

$$\begin{aligned} \Sigma_J(\hbar\omega) &= \Sigma_J \left[\text{ground state pair distribution } g(r, \theta) \right] \\ &= -\frac{B^2}{\pi} \frac{2\rho}{2J+1} \sum_{\ell} \int \frac{dp p^2}{S(p)} \frac{\sum_{\ell'} \tilde{L}(J, \ell', \ell) g_{\ell'}^2(p)}{B\ell(\ell+1) + \epsilon(p) + \hbar^2 p^2 / 2M - \hbar\omega} \end{aligned}$$

Results: CBF rotation spectra of molecules in bulk ^4He

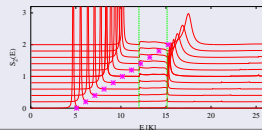
HCN (REZ, K. B. Whaley, PRB'04)

- exp: $B_{\text{eff}}/B = 0.814$; CBF: $B_{\text{eff}}/B = 0.85$
- confirmed also by PIMC
- increase of B_{eff}/B for DCN consistent with experiment

HCCH (REZ, Y. Kwon, K. B. Whaley, PRL 93, 250401 (2004))

- exp: $B_{\text{eff}}/B = 0.89$; CBF: $B_{\text{eff}}/B = 0.91$
- confirmed also by PIMC
- large centrifugal distortion constant
- rotation-rotor coupling for $J = 2$

Changing B (stars) $\in [0.5 \times B, 1.5 \times B]$:



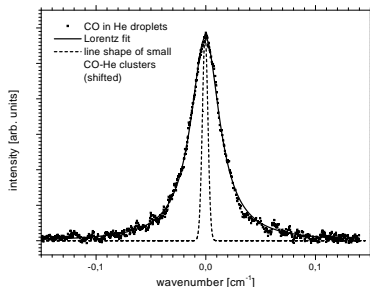
OCS

- CBF does not give accurate excitation energy. Why?...
- ... very strong ^4He density anisotropy around OCS \Rightarrow adiabatic following of normal fraction (\leftarrow **superfluidity**)

\Rightarrow correct and accurate description of rotational dynamics of **light linear molecules**

Experimental Rovibrational spectrum of CO in large He droplets

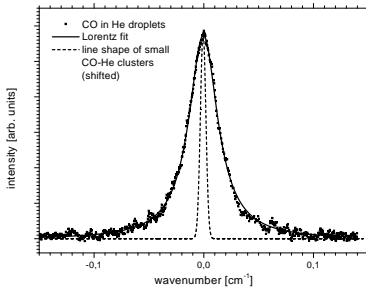
- larger reduction $B \rightarrow B_{\text{eff}}$ than other small molecules: 63%
- larger (rotational?) linewidth than other small molecules: 0.034cm^{-1} (FWHM)
- Lorentzian lineshape \Rightarrow homogeneous?
- isotope effect on B_{eff}
- simulations for small clusters give significantly higher $B \rightarrow B_{\text{eff}}$ of $\sim 78\%$



K. von Haeften et al., PRB **73**, 054502 (2006)

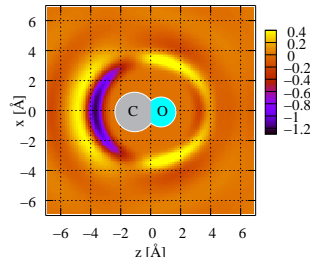
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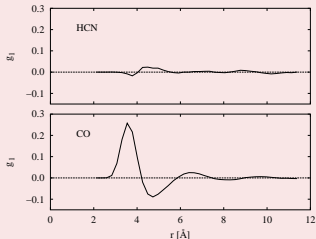
sample $g(r \cos \theta)$ by DMC



CBF results for rotational spectrum of CO in bulk He

CBF explanation of experimental findings:

- larger reduction $B \rightarrow B_{\text{eff}}$ than other small molecules: 63%.
strong asymmetry of potential ($\ell = 1$). exp: 63%, CBF: 67%

 $\ell = 1$ component of $g(r \cos \theta)$:

- larger (rotational?) linewidth than other small molecules: 0.034cm^{-1} (FWHM)
strong asymmetry of potential \Rightarrow coupling to long wavelength $\ell = 1$ -phonon and decay. CBF in qualitative agreement: 0.018cm^{-1} (FWHM).

CBF results for rotational spectrum of CO in bulk He

CBF explanation of experimental findings:

- Lorentzian lineshape \Rightarrow homogeneous?
CBF for bulk yields indeed Lorentzian shape due to homogeneous (lifetime) broadening. BUT: see next slide.
- isotope effect on B_{eff}
CBF yields correct isotope correction of B_{eff} due to center of mass shift of potential.

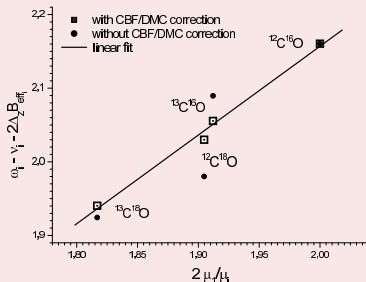
$$\text{expand: } B_{\text{eff}}^{(i)} = B_{\text{eff}}^{(1)} + \frac{\partial B_{\text{eff}}}{\partial B} \Delta B^{(i)} + \frac{\partial B_{\text{eff}}}{\partial \Delta z} \Delta z^{(i)}$$

$$\text{1st derivative: assume linear scaling } \frac{\partial B_{\text{eff}}}{\partial B} \approx \frac{B_{\text{eff}}^{(1)}}{B_0^{(1)}}$$

2nd derivative: correlated DMC sampling

$$\Rightarrow \omega^{(i)} = \nu^{(i)} + \alpha + 2 \cdot \frac{\mu^{(1)}}{\mu^{(i)}} B_{\text{eff}}^{(1)} + 2 \frac{\partial B_{\text{eff}}}{\partial \Delta z} \Delta z^{(i)}$$

\Rightarrow obtain vibrational shift α and $B_{\text{eff}}^{(1)}$ from linear fit:

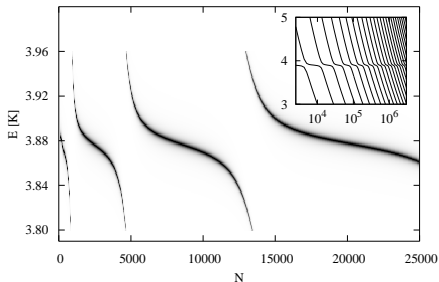


CBF: Rotational spectrum of CO in He *droplet* (with K. K. Lehmann)

what is minimum model, based on CBF, for CO in finite droplet of radius R / size N ?

simple model for finite droplets:

- discretize phonons such that they have a node at $r = R$
- no ripplons
- no realistic effective confinement potential for molecule



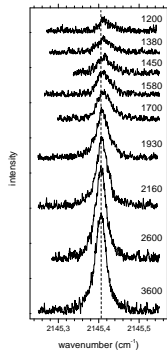
spectrum obtained as average
of individual spectra at size N
over log-normal size distribution
 $P(N)$ (average size \bar{N} , width d)
inhomogeneous broadening

Droplet size dependence of Rotational spectrum of CO in He

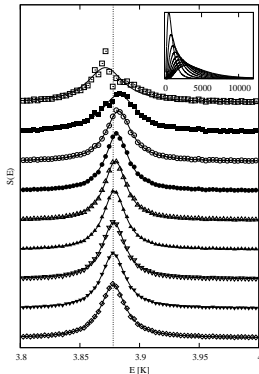
Result:

blue shift for decreasing \bar{N} , but near-perfect Lorentzian line shape

experiment:



CBF model:



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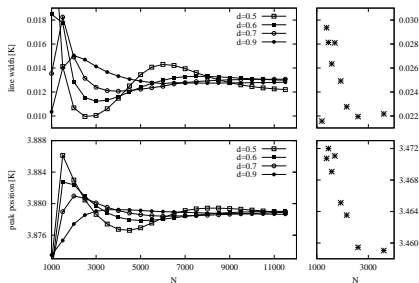
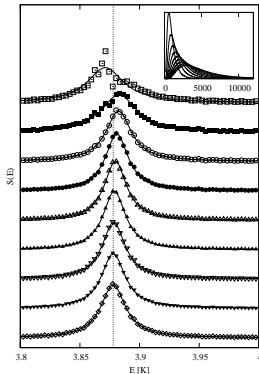
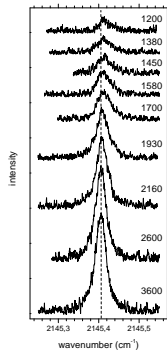
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experiment:

CBF model:

linewidth(\bar{N}), peak position(\bar{N}):



Droplet size dependence of Rotational spectrum of CO in He

- finite droplet CBF model reproduces \bar{N} dependence
- Lorentzian lineshape \Rightarrow homogeneous?
finite droplet model yields inhomogeneous Lorentzian shape due to size distribution.
- general statement:
single particle / localized excitation coupled to a collective excitation yields inhomogeneous Lorentzian lineshape, provided there is a sufficient spread of system sizes; equal to linewidth in bulk.

consistent with exactly solvable model of Lehmann (J. Chem. Phys.'07).

still to do:

full CBF theory of chromophore in finite ^4He droplet.

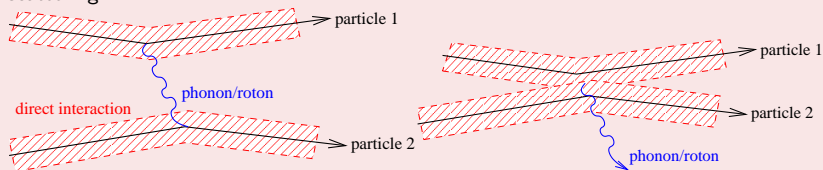
What's next after that?

molecules well understood: CO, HCN, HCCH, CH₄,...

CBF theory of (c.o.m. motion and) internal degrees of freedom = rotation.

“unbind” the molecules: > 1 atoms solvated in ⁴He

CBF theory of all internal degrees of freedom (rotation + relative distance) = scattering.



→ Elastic and **inelastic** scattering of particles in ⁴He:

- initial step for synthesis of small structures (e.g. Si clusters) in ⁴He clusters.
- dilute ³He-⁴He mixtures

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Path Integral Monte Carlo

for molecules in helium (primitive approximation + pair density approximation):

$$\rho(\tau) = \rho_{\text{trans}}(\{\mathbf{r}_i\}, \{\mathbf{r}'_i\}; \tau) \rho_{\text{rot}}(\Omega, \Omega'; \tau) \\ \times \exp \left[- \sum_{i>j} u(r_{ij}, r'_{ij}; \tau) - \frac{\tau}{2} \sum_i (V(r_i, \cos \theta_i) + V(r'_i, \cos \theta'_i)) \right]$$

\iff classical system of harmonic chains

Bose symmetry:

$$\rho(R, R'; \beta) \rightarrow \frac{1}{N!} \sum_P \rho(R, PR'; \beta)$$

\iff reconnecting chains

D. M. Ceperley, Rev. Mod. Phys. **67**, 279 (1995)
REZ, F. Paesani, Y. Kwon, K. B. Whaley, J. Chem. Phys. **123**, 114301 (2005)

Linear Response: Excitations from *Imaginary* Time Correlation functions

The **imaginary** time **orientational correlation function**

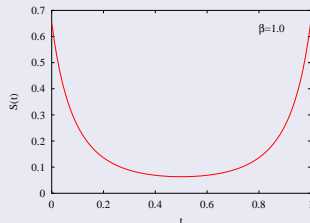
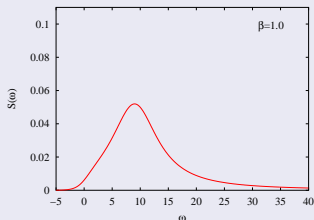
$$S_J(\tau) = \sum_M \text{Tr}\{\rho Y_{JM}(\Omega(\tau))Y_{JM}(\Omega(0))\}$$

is the **Laplace** transform of the rotational spectrum $S_J(\omega)$

$$S_J(\tau) = \int d\omega e^{-\omega\tau} S_J(\omega)$$

$S_J(\tau)$ easy to calculate by PIMC

example:



Linear Response: Excitations from *Imaginary* Time Correlation functions

The **imaginary** time **orientational correlation function**

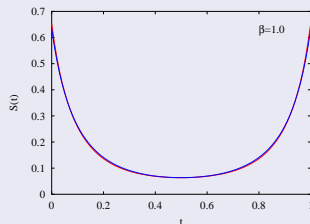
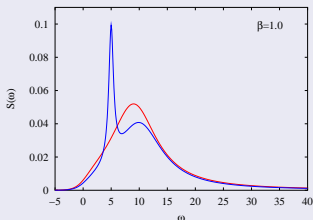
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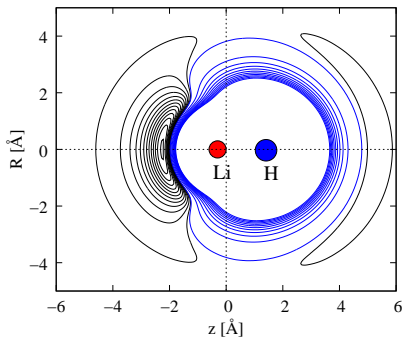


⇒ Laplace-transform is hard to invert, law of “conservation of difficulty”

LiH-He interaction potential

unlikely combination:

- strongly anisotropic LiH-He interaction $V(r, \theta)$
- gas phase rotational constant of LiH: $B = 10.8\text{K}$



Taylor, Hinde, JCP **122**, 074308 (2005)

What is structure and dynamics of LiH-He_N?

LiH inside droplet or floating on surface?

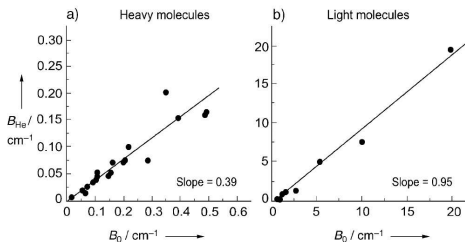


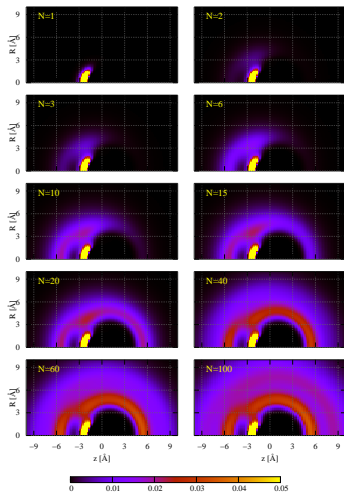
Figure 13. The experimentally available rotational constants in helium droplets (B_{He}) and the gas-phase (B_0) for heavy molecules (a) and light molecules (b).^[134]

J. P. Toennies, A. Vilesov, *Ang. Chem.* **43**, 2622 (2004)

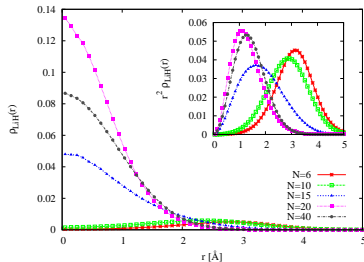
is classification only according to B_0 meaningful?

Structure: pair density and confinement

He-LiH pair density:



LiH density w/resp to center of mass:



conclusion

⇒ LiH is *inside* droplet

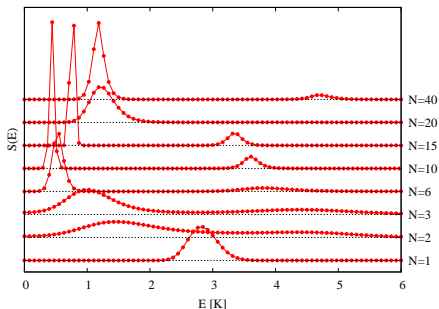
REZ, K. B. Whaley, in press J. Chem. Phys (2007)

Dynamics: rotational spectrum

maximum entropy inversion

$$S_J(\tau) \rightarrow S_J(E)$$

yields rotational spectrum ($J = 1$):

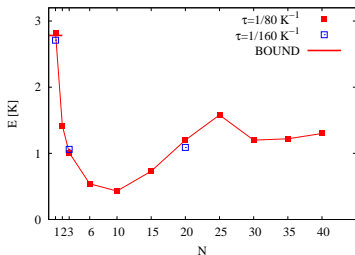


- similar to other molecules (OCS, CO_2 , N_2O ,...): gradual transition from full adiabatic following of ^4He to partial adiabatic following (of superfluid fraction)
- higher transitions with smaller weight (required by sum rule $\int d\omega \omega S(\omega) = 2B_0$)
- rotational linewidth is artefact from entropy smoothing

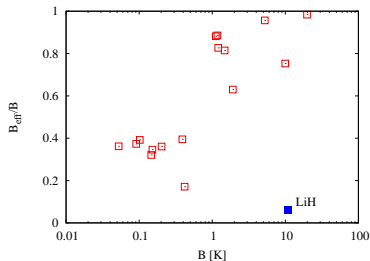
Dynamics: rotational excitation energies

⇒ associate maximum of peak with excitation energy:

(lowest) $J = 0 \rightarrow 1$ excitation energies
as function of N :



relative reduction, B_{eff}/B , of molecules
in large He droplets (exp.) compared to
 $\text{LiH-}^4\text{He}_{40}$:



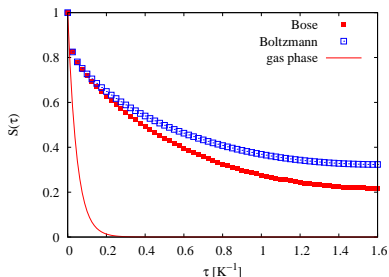
conclusion

classification according to B alone not meaningful (consistent with isotope effect for CO in He).

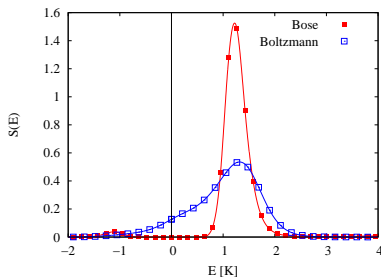
Dynamics: influence of Bose symmetry

PIMC simulation with Boltzmann and Bose helium:

$S_{J=1}(\tau)$:



$S_{J=1}(E)$:



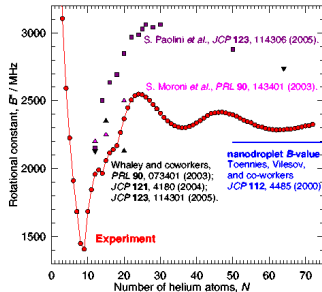
- single(?) excitation at $E = 2B_{\text{eff}}$ in Bose case in the shown energy window
- additional lower energy excitations in Boltzmann case

OCS- ${}^4\text{He}_N$ re-re-...-visited: B_{eff} for large N

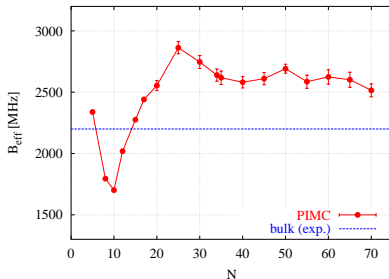
typical experimental observation for molecule in ${}^4\text{He}_N$ clusters:

- B_{eff} does not converge quickly to large droplet (i.e. bulk) limit with growing N
- B_{eff} oscillates as function of N

W. Jaeger et al., PRL'06:



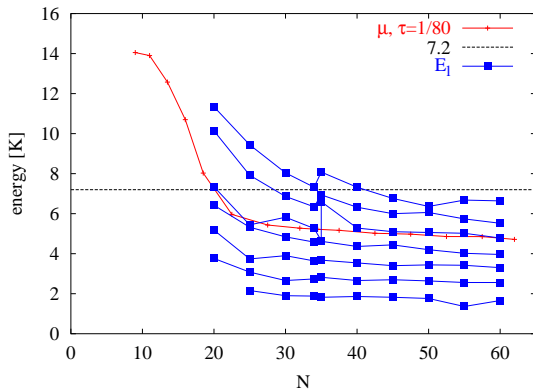
PIMC (fitting B_{eff} to imag. time correlation):



Reason for oscillations, slow convergence to bulk? Magic numbers?

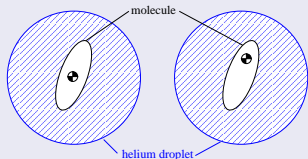
OCS- ${}^4\text{He}_N$ re-re-...-visited: B_{eff} for large N

lowest ${}^4\text{He}$ excitations ω_ℓ for $\ell = 2, \text{dots}, 8$:



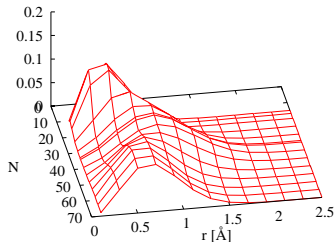
no crossing of μ and ω_ℓ .

OCS- ${}^4\text{He}_N$ re-re-...-visited: B_{eff} for large N



center of mass \neq "center" of potential (isotopic substitution)

probability density
 $r^2\rho(r)$ for OCS w/resp.
to ${}^4\text{He}$ center of mass:

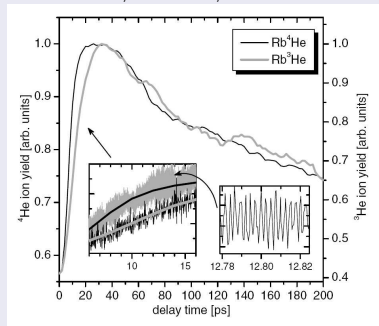
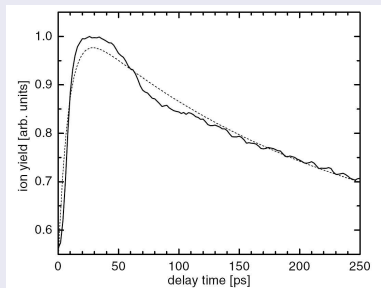


oscillation, but not
same periodicity as
 B_{eff} oscillation

Rb*He exciplex formation on ^4He and ^3He droplets

Bielefeld experiment:

Pump-probe spectrum for excitation of Rb from g.s. to $\Pi_{1/2}$ and $\Pi_{3/2}$:



G. Droppelmann et al. PRL **93**, 023402 (2004)

- phenomenological tunnelling model ambiguous.
- why formation of Rb^4He faster than Rb^3He ?
- vibrational relaxation mechanism?

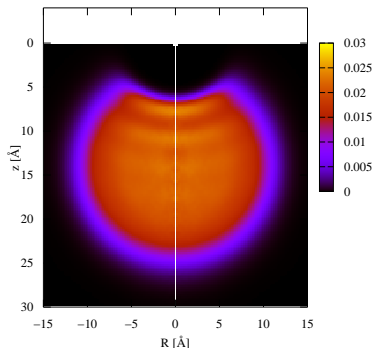
Equilibrium of Rb-⁴He₁₀₀

electronic ground state:

Rb sits in dimple

→ probe pulse excites Rb to $\Pi_{3/2}$

$E_B = -11\text{K}$



measured Rb*He formation time = 8.5ps → MCTDH of very small clusters

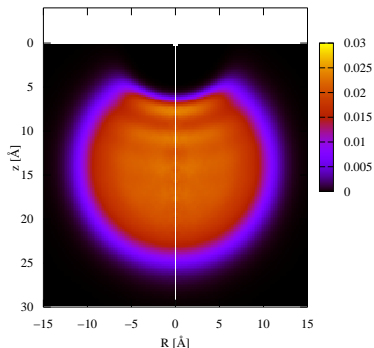
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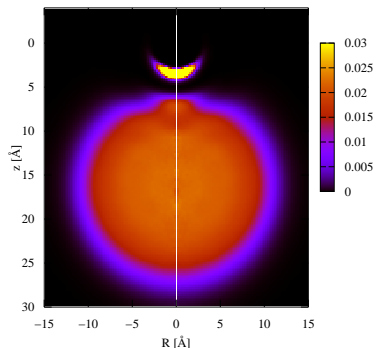


electronic excited state $\Pi_{3/2}$:

none-pairwise additive DIM potential

Rb*He₁ exciplex formation

$E_B \approx -11\text{K}$



measured Rb*He formation time = 8.5ps → MCTDH of very small clusters

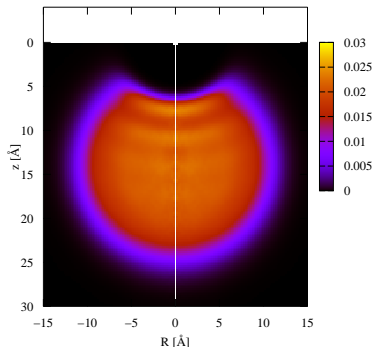
Equilibrium of Rb-⁴He₁₀₀

electronic ground state:

Rb sits in dimple

→ probe pulse excites Rb to $\Pi_{3/2}$

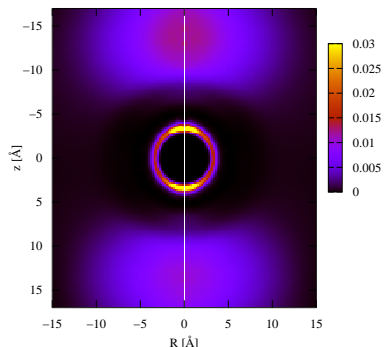
$E_B = -11\text{K}$



electronic excited state $\Pi_{3/2}$:

Rb in *center* of He₆₄ droplet

Rb*He₂ exciplex formation



measured Rb*He formation time = 8.5ps → MCTDH of very small clusters

Summary

- 1 CBF theory can reproduce and explain rotational spectra of molecules in superfluid He
 - renormalized excitation energy ($\rightarrow B_{\text{eff}}$) by coupling to collective excitations of He
 - Linewidth by coupling to long wavelength phonon
 - phenomenological model of finite size effects \rightarrow full CBF implementation
- 2 equilibrium PIMC allows calculation of rotational spectra (sometimes completely, sometimes effective constants)
 - N dependence
 - T dependence
 - sharp rotational spectra due to superfluidity of He

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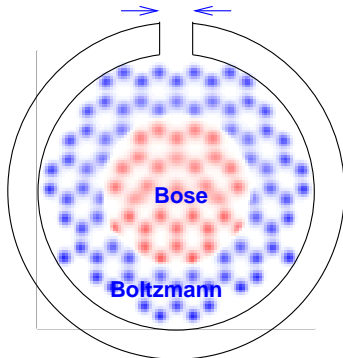
NSF CHE-0107541;

NPACI NSF 930004 grant with San Diego Supercomputing center

Solid He with Dislocation

Perfect hcp helium probably not superfluid. hcp helium with defects?

construction of boundary condition for edge dislocation:



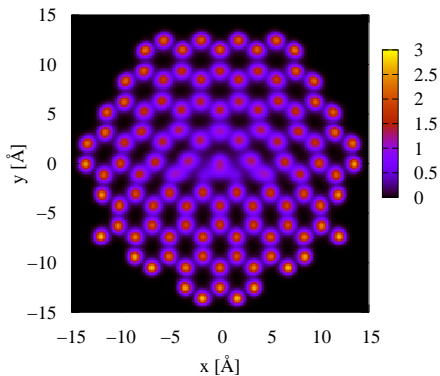
6 crystal layers high: a b a b a b ($\approx 17.4\text{\AA}$)

3 concentric cylinders:

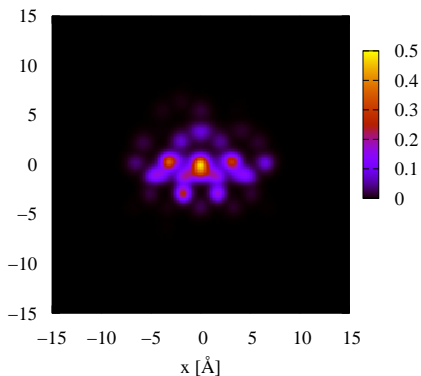
- ① inner: ${}^4\text{He}$ with Bose exchange ($N = 102$)
- ② middle: ${}^4\text{He}$ w/o exchange ($N = 228$)
- ③ outer: rigid ${}^4\text{He}$ models far field displacement of dislocation ($N = 306$)

Solid He with Dislocation

total density:



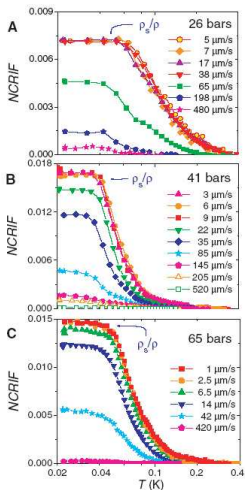
winding-paths-density ($\neq \rho_s$):



rigid system \Rightarrow very inefficient sampling of exchange

Solid He with Dislocation

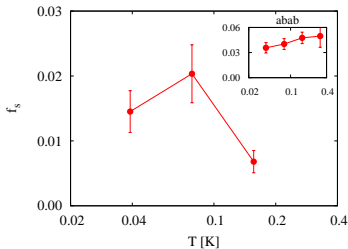
Kim & Chan, Science (2004):



Dislocation w/PIMC:
linear response to translation \Rightarrow winding path estimator:

$$f_s \equiv \frac{\rho_s}{\rho} = \frac{m}{\hbar^2} \frac{\langle W^2 \rangle}{N\beta}$$

E. L. Pollock, D. M. Ceperley, PRB **36**, 8343 (1987)
w/resp to inner cylinder ($N = 102$) \Leftrightarrow 1 dislocation / 200\AA^2 !



finite size effect? $f_s(\text{PIMC}) > f_s(\text{real})$