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ICTP 40th Anniversary

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Joint DEMOCRITOS - ICTP School on

CONTINUUM QUANTUM MONTE CARLO METHODS

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PATH INTEGRALS FOR T = O SIMULATIONS

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These are preliminary lecture notes, intended only for distribution to participants.

Path Integrals for $T = 0$ simulations

- Variational–Projector Approach

$$\Psi(\beta) = e^{-\beta H/2}\Psi \rightarrow \Phi_0 \text{ (large } \beta)$$

- Various algorithms:

  Variational Path Integral (VPI)
  Path Integral Ground State (PIGS)
  Reptation quantum Monte Carlo (RQMC)
  ...
  Pure Diffusion Monte Carlo (PDMC)

- Comparison with Diffusion Monte Carlo

  population control, mixed estimators
  correlated sampling
  imaginary time correlations
  branching vs. Metropolis algorithm

- Applications

Monte Carlo calculation

Trotter's theorem, $\tau = \beta/p$

$$Z(\beta) = \langle \Psi \mathrm{e}^{-\beta H} \Psi \rangle \approx \int dR_0 \ldots dR_p$$

$$\times \Psi(R_p) \langle R_p \mathrm{e}^{-\tau H} R_{p-1} \rangle \ldots \langle R_1 \mathrm{e}^{-\tau H} R_0 \rangle \Psi(R_0)$$

Energy

$$E(\beta) = \langle \Psi(\beta) H \Psi(\beta) \rangle / \langle \Psi(\beta) \Psi(\beta) \rangle$$

$$= \int dX E_L(R_p) \pi(X) / \int dX \pi(X) = \langle E_L(R_p) \rangle_\beta$$

Use Metropolis algorithm to sample

$$\pi(X) = \frac{\Psi(R_p) \langle R_p \mathrm{e}^{-\tau H} R_{p-1} \rangle \ldots \langle R_1 \mathrm{e}^{-\tau H} R_0 \rangle \Psi(R_0)}{Z(\beta)}$$

where X is a discretized path

$$X = \{R_0, R_1, \ldots, R_p\}$$

(for Fermions use TE or Fixed Node)

Variational–Projector Approach

$$\Psi(\beta) = \mathrm{e}^{-\beta H/2}\Psi$$

$$Z(\beta) = \langle \Psi(\beta)\Psi(\beta)\rangle = \langle \Psi \mathrm{e}^{-\beta H}\Psi\rangle$$

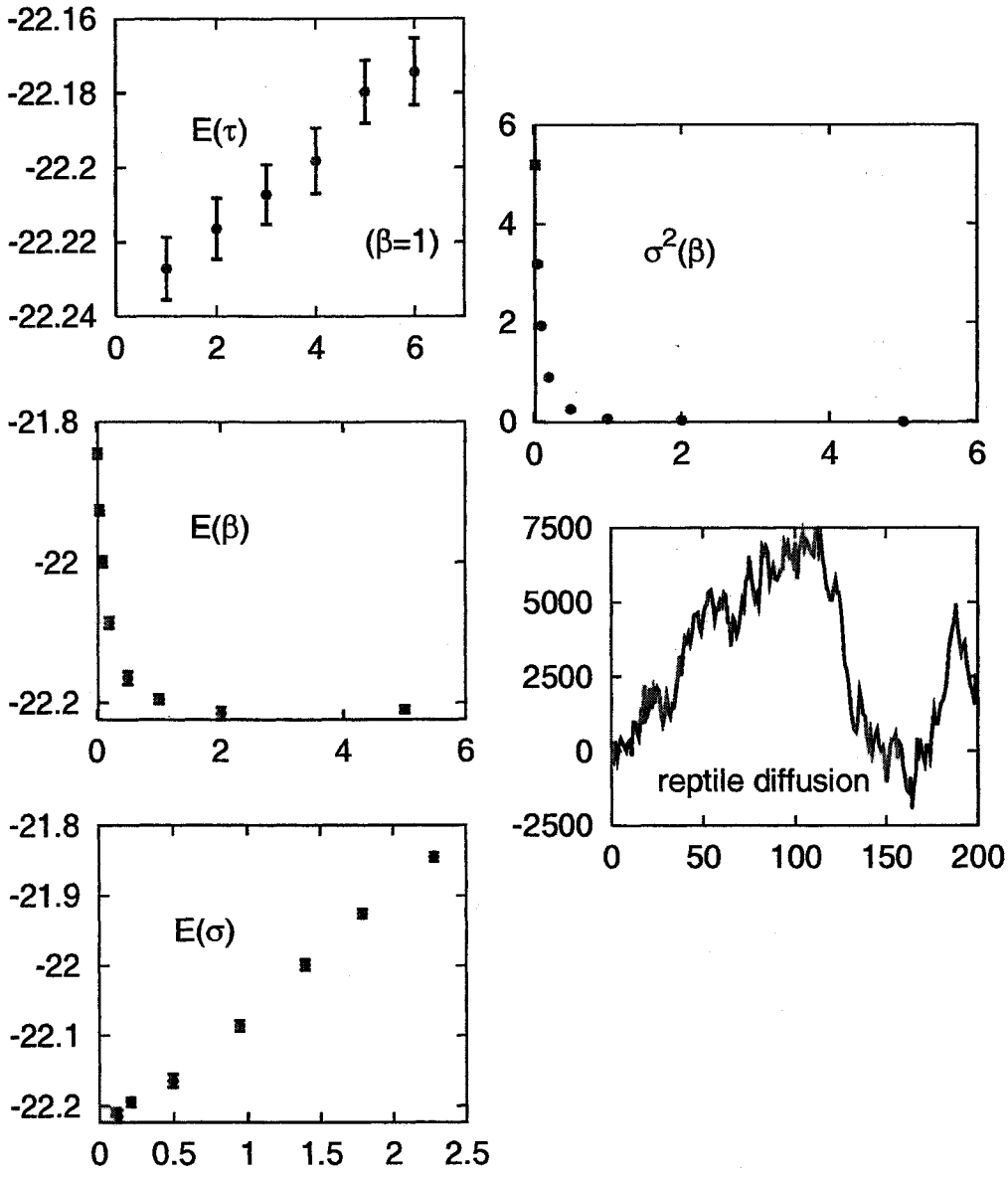
Energy

$$E(\beta) = -\frac{d\ln Z}{d\beta} = \frac{\langle \Psi(\beta) H \Psi(\beta)\rangle}{\langle \Psi(\beta)\Psi(\beta)\rangle} = \langle E_L(R_p)\rangle_\beta$$

$E(\beta)$ converges to the exact ground–state energy E_0 monotonically since

$$\begin{aligned} -\frac{dE(\beta)}{d\beta} &= \sigma^2(\beta) = \frac{\langle \Psi(\beta)[H - E(\beta)]^2\Psi(\beta)\rangle}{Z(\beta)} \\ &= \langle E_L(R_0)E_L(R_p)\rangle_\beta - E(\beta)^2 > 0 \end{aligned}$$

Convergence parameters, $^4He_3$–CO_2 cluster



Other observables

Probability distribution of individual slices:

Φ_0^2 in the inner ($j = p/2$) slices

$$P(R_j) = \int dR_0 \dots dR_{j-1} dR_{j+1} \dots dR_p \pi(X)$$
$$\approx \Phi_0(R_j)^2$$

mixed distribution in the border slices

$$P(R_0) = \int dR_1 \dots dR_p \pi(X) \approx \Phi_0(R_0)\Psi(R_0)$$

Pure estimators:

$$\mathcal{O} = \int dX \mathcal{O}(R_j)\pi(X)$$

Imaginary time correlations:

$$C_{\mathcal{O}}(n\tau) = \int dX \mathcal{O}(R_j)\mathcal{O}(R_{j+n})\pi(X)$$

Correlated sampling:

$$\mathcal{O}' = \frac{\sum_\alpha \mathcal{O}'(R_{j,\alpha})\pi'(X_\alpha)/\pi(X_\alpha)}{\sum_\alpha \pi'(X_\alpha)/\pi(X_\alpha)}$$

(assuming $\langle R'\mathcal{O}R\rangle = \mathcal{O}(R)\delta(R - R')$)

Algorithms: VPI/PIGS

- Use the pair product approx. to $\langle R' \mathrm{e}^{-\tau H} R \rangle$

- Use multilevel Metropolis + bisection to sample X from $\pi(X)$

Variational Path Integral
D.M. Ceperley, RMP 67, 279 (1995).

- Application to bulk ^{4}He (liquid and solid) and He_2Cl_2 complex.

Path Integral Ground State
A. Sarsa, K.E. Schmidt, W.R.Magro,
JCP 113, 1366 (2000).

Algorithms: Reptation

- Approximation to $G(R, R'; \tau) = \langle R' \mathrm{e}^{-\tau H} R \rangle$

Importance–sampled Green's function

$$\begin{aligned} \tilde{G}(R, R'; \tau) &= \Psi(R') G(R, R'; \tau) / \Psi(R) \\ &\approx \mathrm{e}^{-(R' - R - 2\lambda\tau \nabla \log \Psi(R))^2 / 4\lambda\tau} \\ &\times \mathrm{e}^{-\tau[(E_L(R) + E_L(R')]/2} \end{aligned}$$

$$\pi(X) \to \tilde{\pi}_+(X)$$
$$= \tilde{G}(R_{p-1}, R_p) \ldots \tilde{G}(R_0, R_1) \Psi^2(R_0)$$

use a symmetrized form, e.g.

$$\tilde{\pi}(X) = [\tilde{\pi}_+(X) \tilde{\pi}_-(X)]^{1/2}$$

where

$$\tilde{\pi}_-(X) = \Psi^2(R_p) \tilde{G}(R_p, R_{p-1}) \ldots \tilde{G}(R_1, R_0)$$

Algorithms: Reptation

- Moving the path around:
  - choose randomly one of the two ends
  - grow the chosen end by adding a slice
  - if the move is accepted, discard tail slice

Metropolis algorithm: given $\tilde{\pi}(X)$, choose the a–priori transition probability $T(X \to X')$ and calculate the acceptance rate

$$T = \tfrac{1}{2}(T_{+1} + T_{-1})$$

$$T_{+1} = \mathrm{e}^{-(R' - R_p - 2\lambda\tau\nabla \log \Psi(R_p))^2/4\lambda\tau}$$

$$T_{-1} = \mathrm{e}^{-(R' - R_0 - 2\lambda\tau\nabla \log \Psi(R_0))^2/4\lambda\tau}$$

$$A_d(X \to X') = \min\left[\frac{\tilde{\pi}(X')T_{-d}(X' \to X)}{\tilde{\pi}(X)T_d(X \to X')}, 1\right]$$

Large acceptance when $E_L(R)$ is smooth

Algorithms: Reptation

How long does it take to refresh all slices?

A random walk with step 1 takes $\approx p^2$ moves to cover a distance p.
(one–way moves don't work)

Consider "block moves" of k slices.

We need $\approx (p/k)^2$ (accepted) block moves.
The computational effort per block move is k times larger so gain is $\approx k \times$ acc. rate.

Choose k to optimize efficiency
(cfr. Δ in simple Metropolis).

Algorithms: Reptation

Automatic optimization: bounce algorithm
(D. Ceperley)

- Move one slice at a time

- Keep moving in the same direction until rejection occurs

The bounce algorithm does not satisfy detailed balance. However $\tilde{\pi}(X)$ and the transition probability $P(X, d \to X', d')$ do satisfy the equation

$$\sum_{X,d} \tilde{\pi}(X) P(X, d \to X', d') = \tilde{\pi}(X')$$

in the enlarged space (X, d)
(d is the direction)

RQMC and classical diffusion

Importance–sampled Green's function for $\mathcal{H}$:

$$\mathcal{G}(R', R, \tau) = \mathrm{e}^{-[R'-R-2\lambda\tau\nabla \log \Psi(R)]^2/4\lambda\tau}$$

The true Hamiltonian is $H = \mathcal{H} + E_L(R)$

$\rightarrow$ Trotter breakup

$$\tilde{G}(R', R, \tau) = \mathcal{G}(R', R, \tau)\mathrm{e}^{-\tau(E_L(R)+E_L(R'))/2}$$

Apply to all slices in the path:

$$\tilde{\pi}_+(X) =$$
$$\mathcal{G}(R_{p-1}, R_p) \ldots \mathcal{G}(R_0, R_1)\Psi^2(R_0)\mathrm{e}^{-S(X)}$$

$$S(X) = \frac{\tau}{2}\sum_{i=1}^{p}[E_L(R_i) + E_L(R_{i-1})]$$

Generalized Feynman–Kac's formula

$$\langle \Psi(\beta)\Psi(\beta)\rangle = \langle \mathrm{e}^{-S(X)}\rangle_{DRW}$$

RQMC and classical diffusion

Classical–quantum mapping:

- $\Psi(R) = \mathrm{e}^{-v(R)/2} = P_s(R)^{1/2}$
- $\Phi(R,t)\Psi(R) = P(R,t)$

Replace in the Fokker–Planck equation:

$$\rightarrow \quad \frac{\partial \Phi(R,t)}{\partial t} = -\mathcal{H}\Phi(R,t)$$

Imaginary–time Schrödinger equation, with

$$\mathcal{H} = -\lambda\nabla^2 + \mathcal{V}(R), \quad \mathcal{V}(R) = \frac{\lambda}{\Psi(R)}\nabla^2\Psi(R)$$

- $\Psi(R)$ is the ground state of $\mathcal{H}$:

  $\rightarrow$ can do VMC with Langevin (with time step bias)

- keep path in memory:

  $\rightarrow$ exact imaginary–time dynamics for a fictitious system

Can we fix the variational bias?

RQMC and classical diffusion

Langevin dynamics:

$$R_{k+1} = R_k + \tau F(R_k) + \xi_k$$

- $F(R) = -2\lambda\nabla v(R)$ force
- ξ_k gaussian rnd with variance $2\lambda\tau$
- τ time step.

Asymptotically samples the stationary solution $P_s(R) \propto \mathrm{e}^{-v(R)}$ of the Fokker–Planck equation

$$\frac{\partial P(R,t)}{\partial t} = \nabla^2 P(R,t) - \nabla[F(R)P(R,t)]$$

Keep in memory a sequence of $p+1$ points $R_k \ldots R_{k+p}$ (discretized path)

$\rightarrow$ Dynamical properties of classical system

PDMC

Pure Diffusion Monte Carlo
(Caffarel, Claverie 1988)

- Sample path with Langevin dynamics
- fix the VMC bias using $e^{-S(X)}$ as a weight

$$E = \frac{\langle E_L(R_0) e^{-S(X)} \rangle_{DRW}}{\langle e^{-S(X)} \rangle_{DRW}}$$

Advantage: one–way moves
Drawback: weights fluctuations

Useful for relatively simple systems

RQMC or VPI?

RQMC

- Move not bounded to end in given place
- All–particle moves

VPI

- Reconstruct inner parts of the path
- One– or few–particle moves

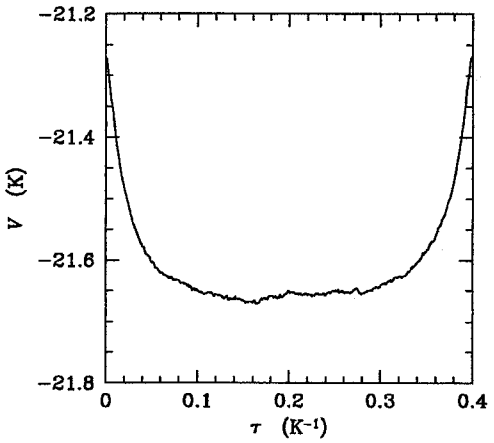
Best to have both moves in the code

Most of the applications use RQMC. For the one–body density matrix only VPI did work.

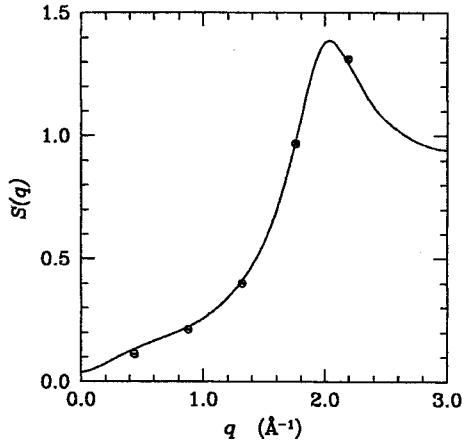
A case study of ^{4}He

- Pure estimators:

$\rightarrow$ Potential energy



$\rightarrow$ Static structure factor



average on middle slices is unbiased

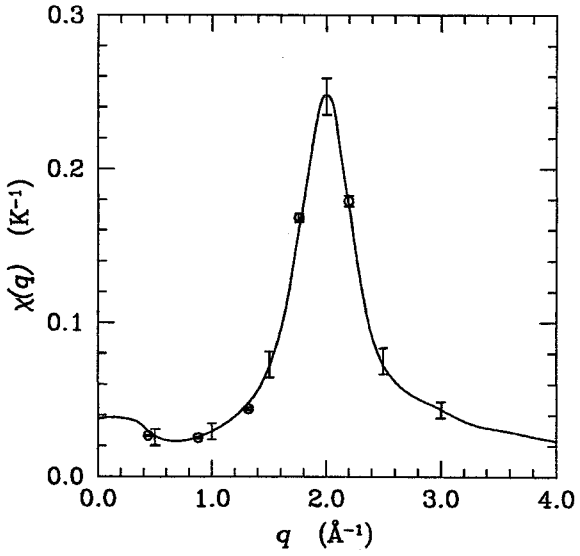
A case study of ^{4}He

- Imaginary–time correlations of the density fluctuation operator $\rho_q = \sum_i \exp(-i\mathbf{q}\cdot\mathbf{r}_i)$

$$F(q,t) = \frac{1}{N}\langle \rho_q(t)\rho_{-q}(0)\rangle_\beta$$

$\rightarrow$ static susceptibility*

$$\chi(q) = -2\int_0^\infty d\omega\ S(q,\omega)/\omega, = -2\int_0^\infty dt\ F(q,t)$$



$\rightarrow$ dynamical structure factor

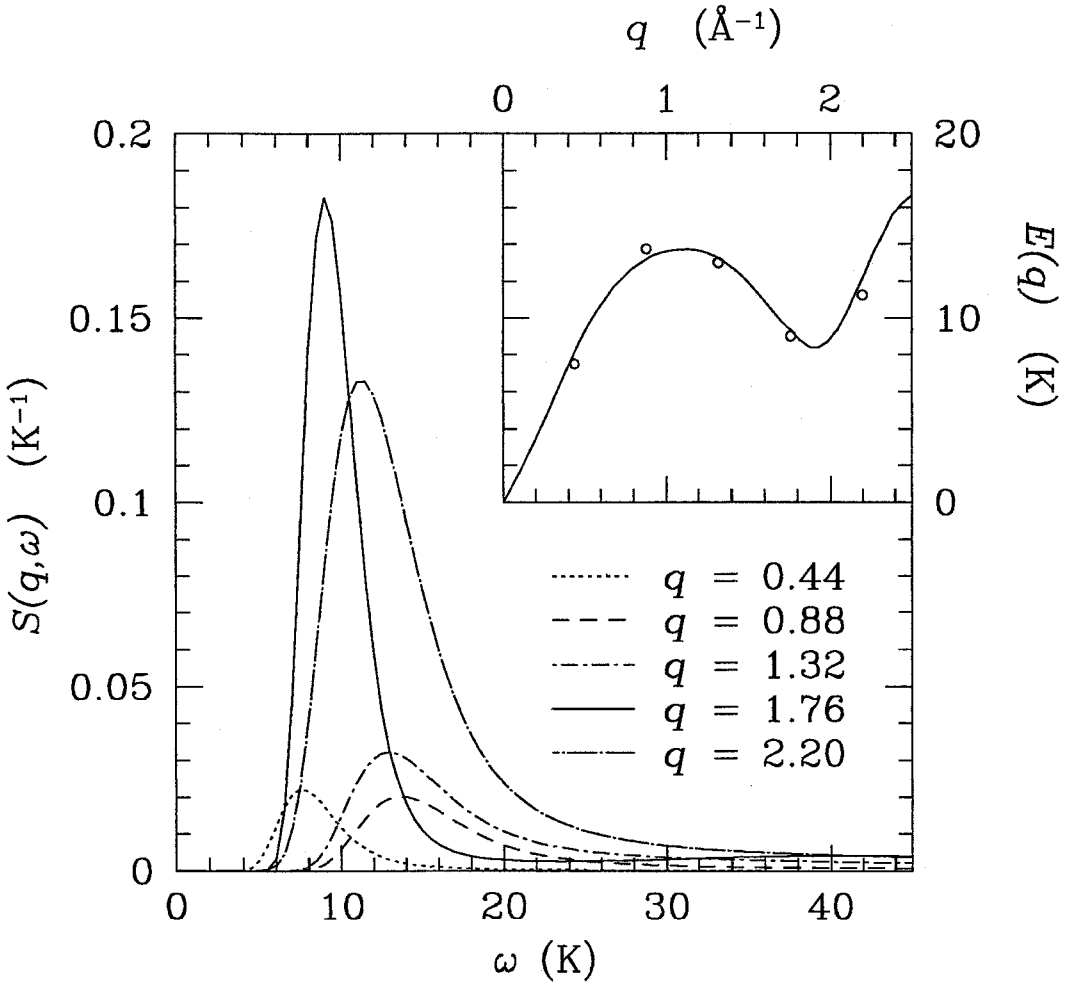
$$F(q,t) = \int_0^\infty d\omega\ \mathrm{e}^{-\omega t}\ S(q,\omega)$$

*Also as second derivative of energy wrt external cosine potential

A case study of ^{4}He

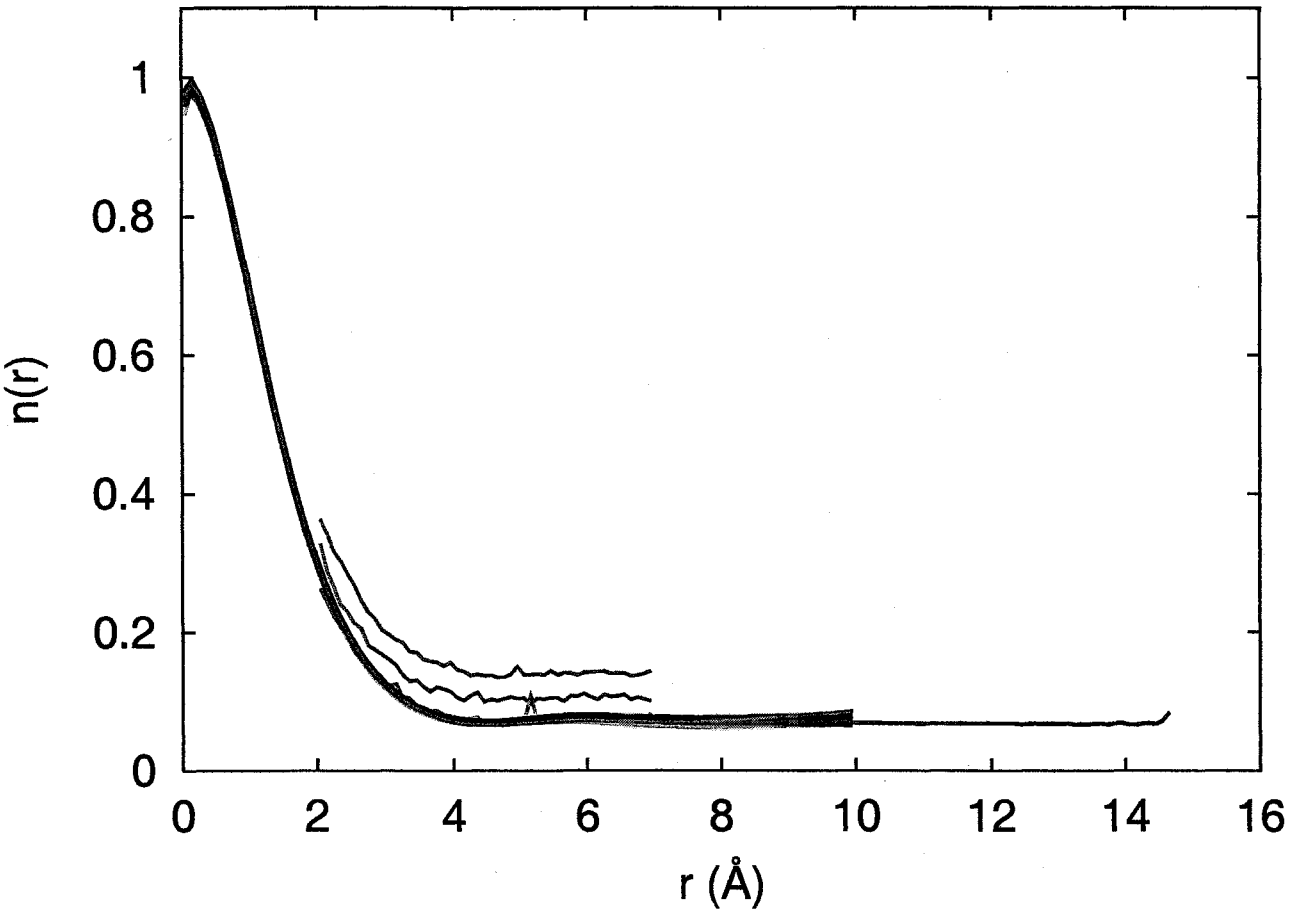
→ (limited) dynamical information

Spectral reconstruction with Maxent:



Condensate fraction of superfluid ^{4}He

- end–to–end distribution of an open polymer



VPI: $n_0 = 0.069(3)$

experiment*: $n_0 = 0.06(1)$

extrapolated estimates: $n_0 = 0.07 \div 0.09$

*Glyde, Azuah, Stirling (2000)

Doped Helium clusters

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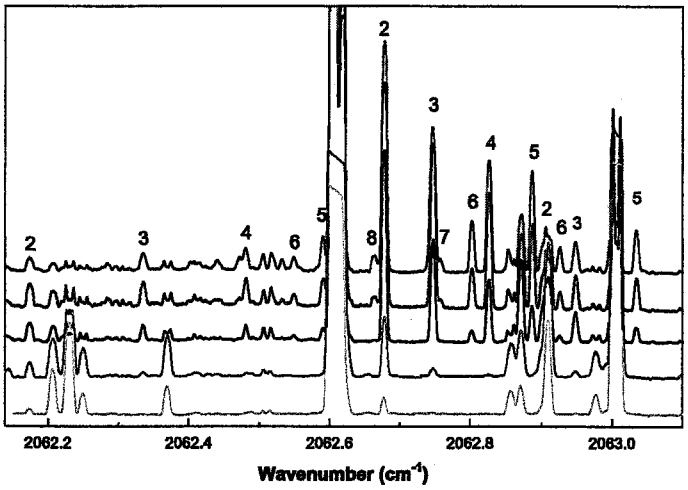

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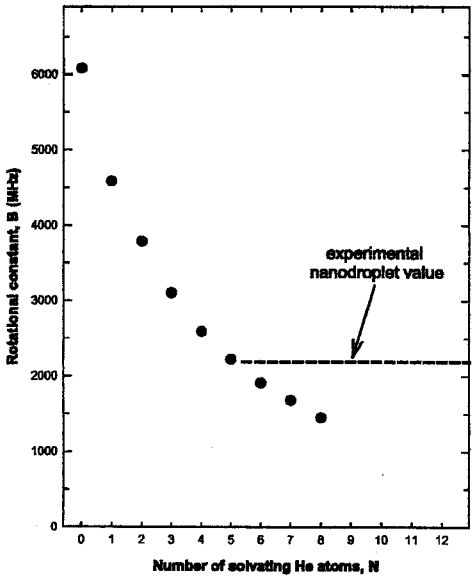
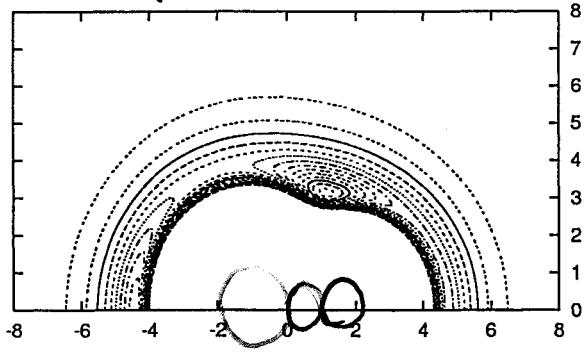


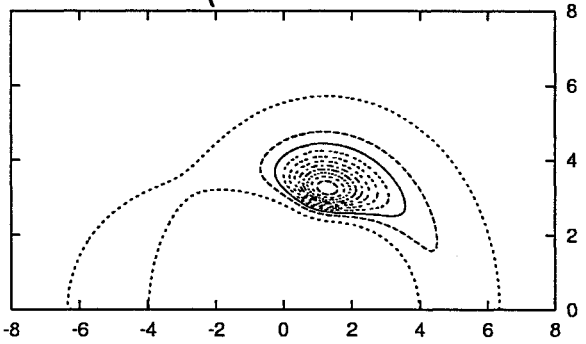
IR/MW expt. on He_N-OCS, selective on N

Tang, Xu, McKellar, Jaeger 2002

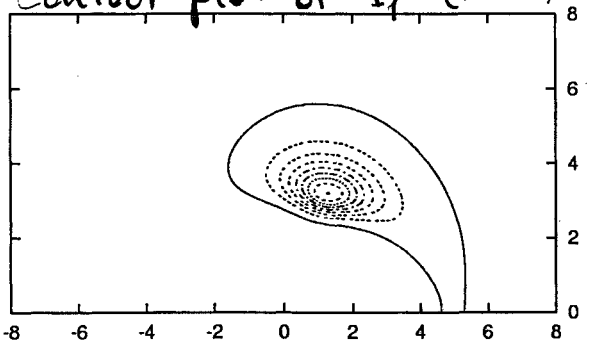
contour plot of He-OCS pot.



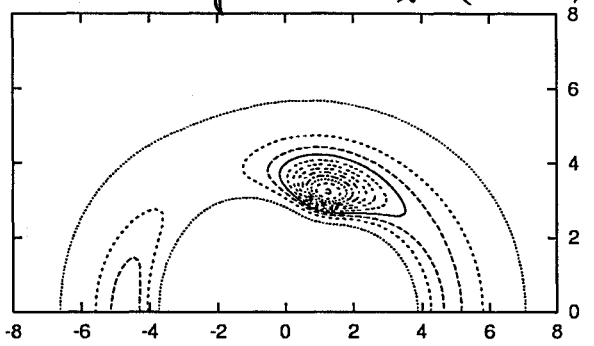
contour plot of f_1 (N=6)



contour plot of f_1 (N=3)



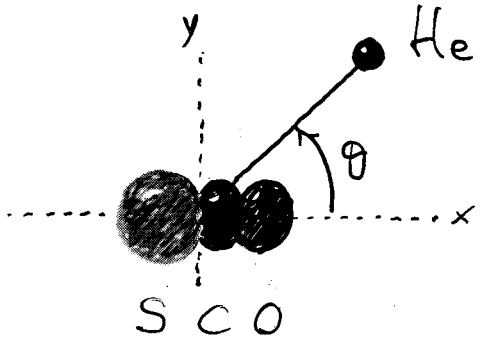
contour plot of f_1 (N=9)



TRIAL FUNCTION

$$\Psi = \prod_{i<j} f_2(r_{ij}) \prod_i f_1(r_i - \rho)$$

$$f_1(r) = e^{-\sum_L u_L(r) P_L(\cos\theta)}$$



V_{He-He} : Korona et al. JCP 106 5109(97)

V_{He-OCS}: Howson et al. JCP 115 5059(01)

~30 variational parameters

Rotational dynamics

- Compute the imaginary–time correlations $C_J(t) = \langle P_J(\hat{\mathbf{n}}(0) \cdot \hat{\mathbf{n}}(t)) \rangle_\beta = \sum_i c_{i,J} \mathrm{e}^{-tE_{i,J}}$ ($\hat{\mathbf{n}}$ is the versor of the molecule)

- Fit the c's and E's to the computed C's. Very few will contribute if rotation is nearly free –use Maxent or multiexp.

- The spectrum of a linear rotor $E_J = BJ(J+1) - D[J(J+1)]^2$ (only one eigenvalue for given J). Fit the rotational constant B and centrifugal distortion D to the fitted E's.

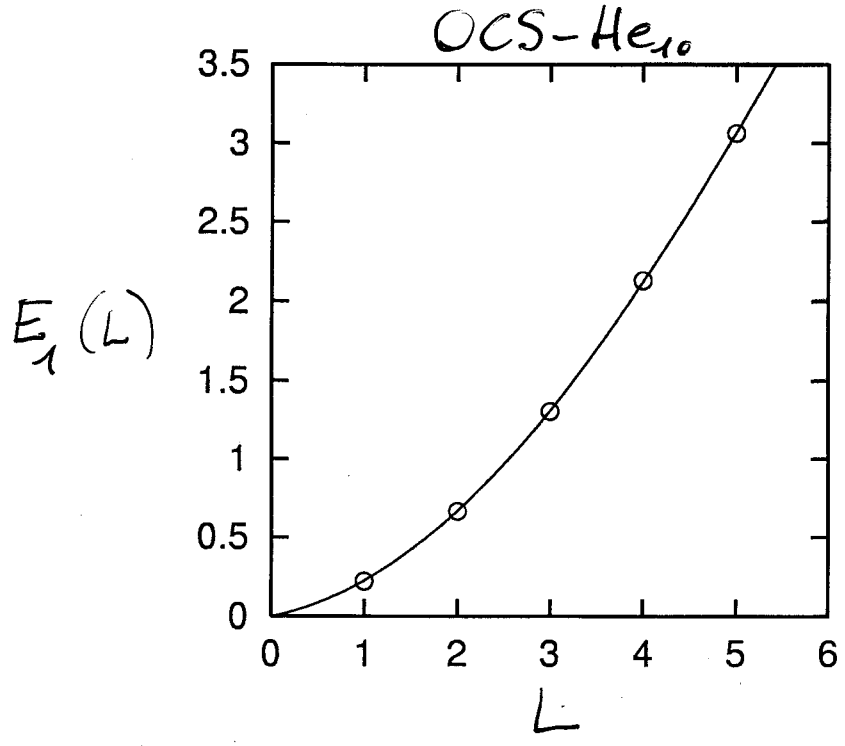
- The effective moment of inertia is $I = 1/2B$.

From angular correlation functions to rotational constants:

$$C_L(t) = \sum_i a_{L,i} \exp(-E_i(L)t) \qquad (E_1 < E_2 < \dots)$$

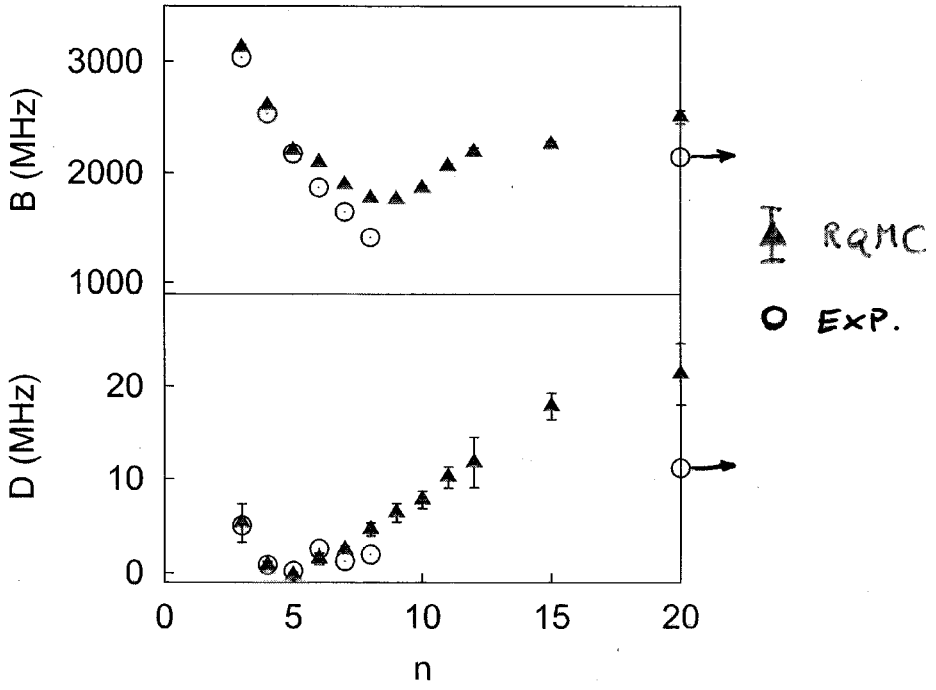
Fit to the rotational spectrum of a linear molecule

$$E_1(L) = \underbrace{B\,L(L+1)}_{\text{rigid rotator}} - \underbrace{D\,L^2(L+1)^2}_{\text{centrifugal distortion}}$$



ROTATIONAL CONSTANT

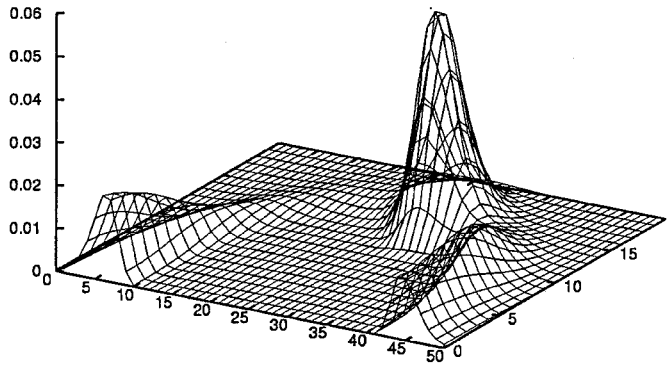
CENTRIFUGAL DISTORTION

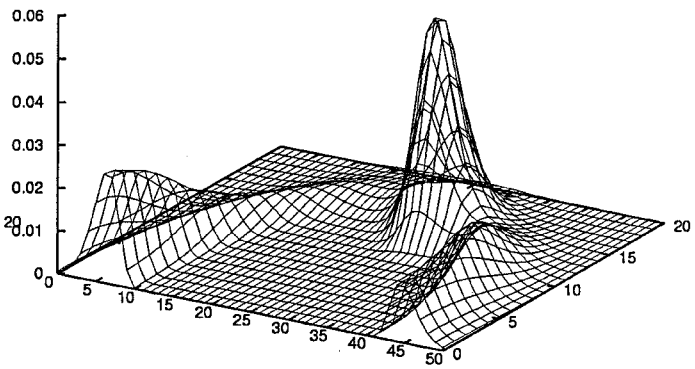


N = 8

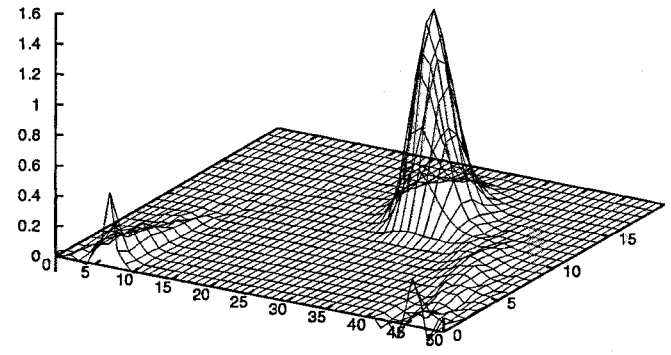
N = 9

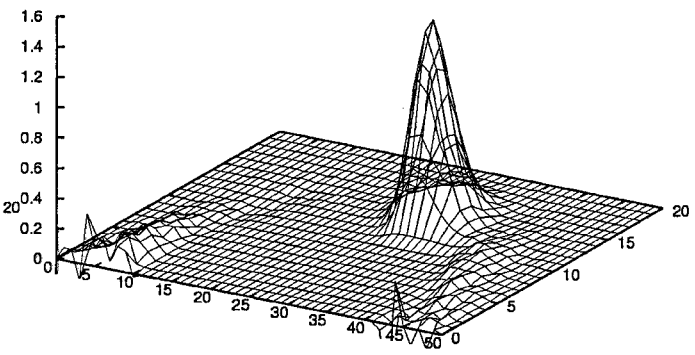
4He density

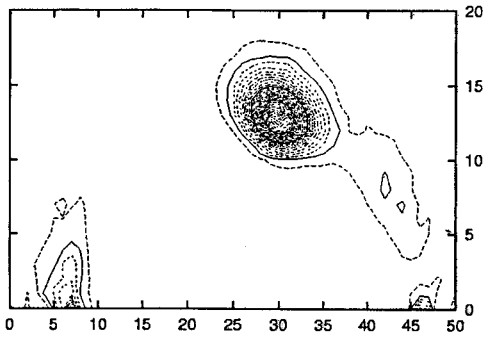


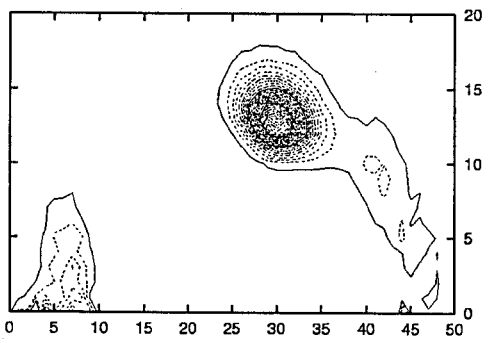


angular momentum correlation



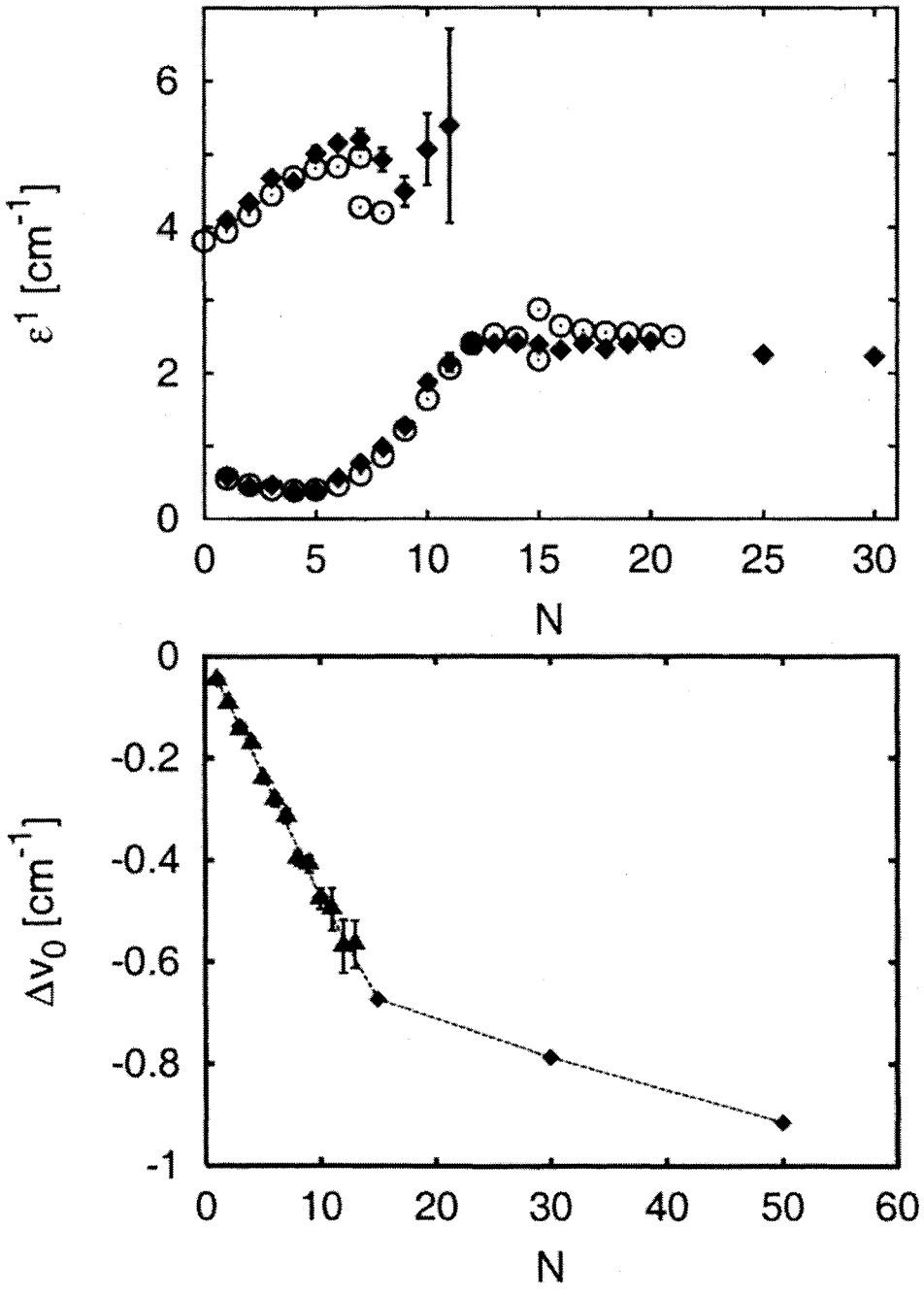






Rotational dynamics

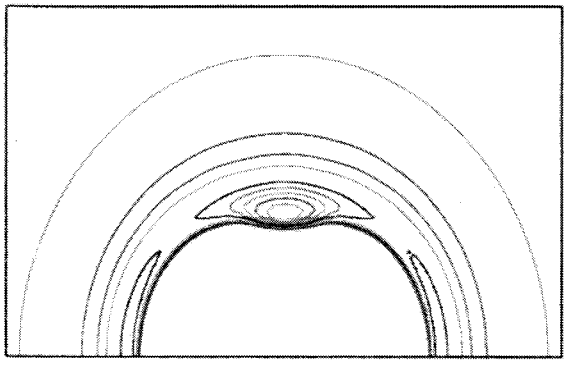
A case with two relevant lines: He_N–CO



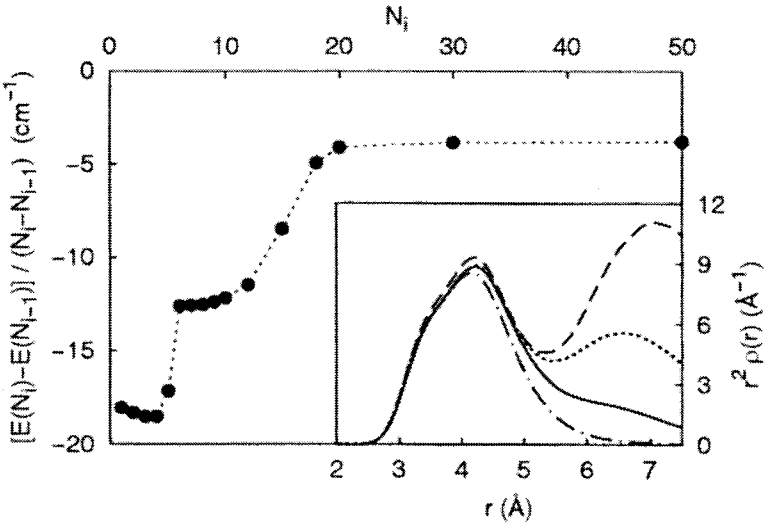
IR experiment by Tang and McKellar, 2002

He_N–CO_2 clusters

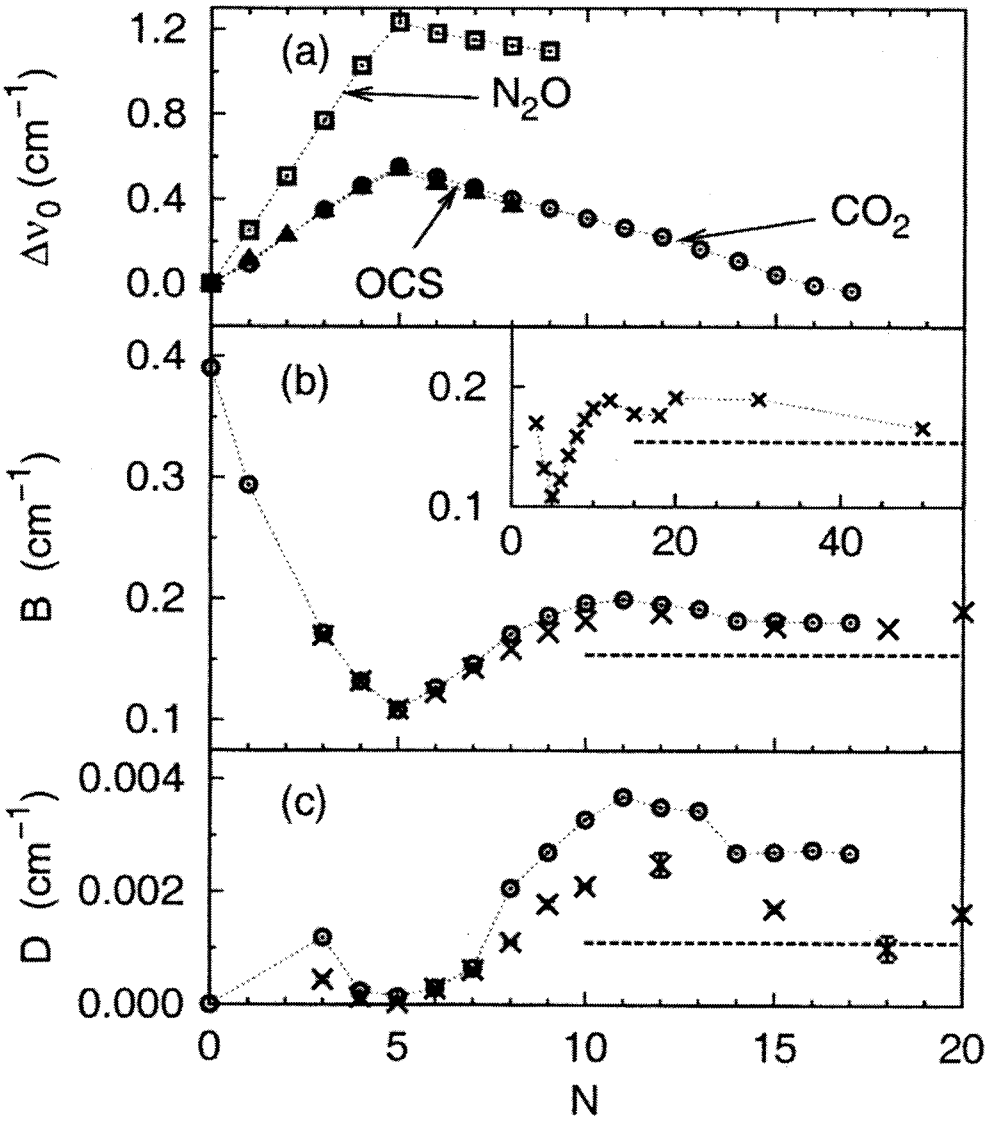
He–CO_2 potential (Moszynski et al., 2001)



Structural information: Chemical potential (left) and density distribution



He_N–CO_2 clusters

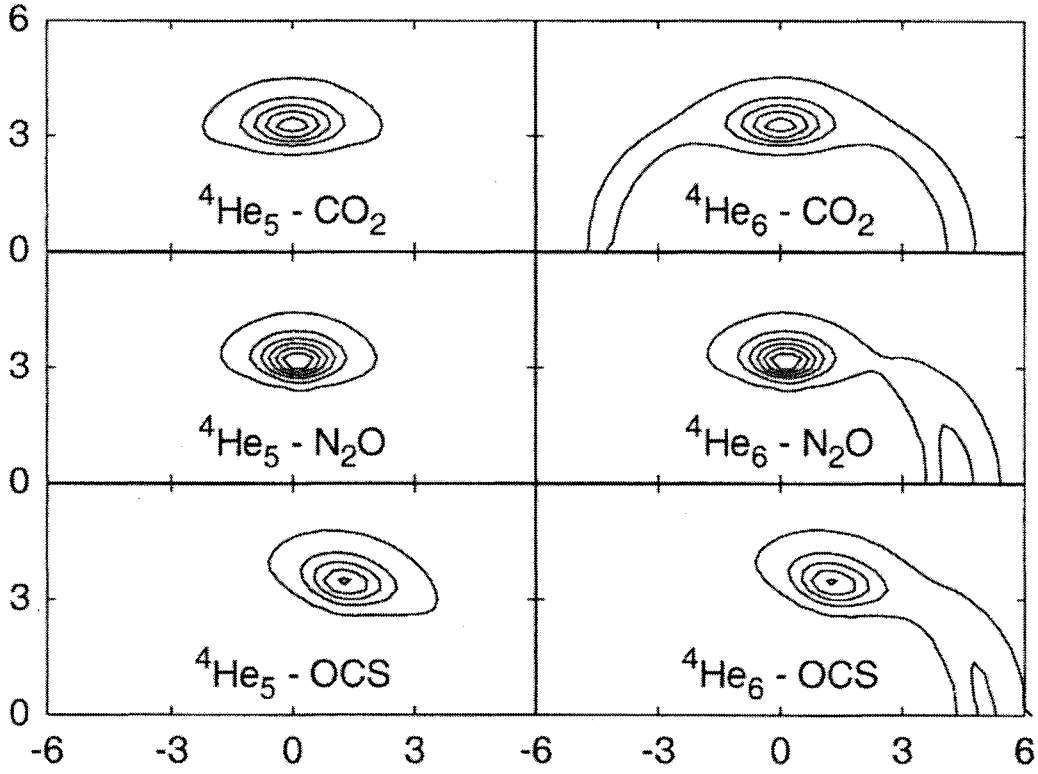


Crosses, RQMC

Circles, IR (Tang and McKellar, 2004)

He_N–CO_2 clusters

He density profiles



Relating structural and dynamical info:

Why does the min. of B occur at 5?

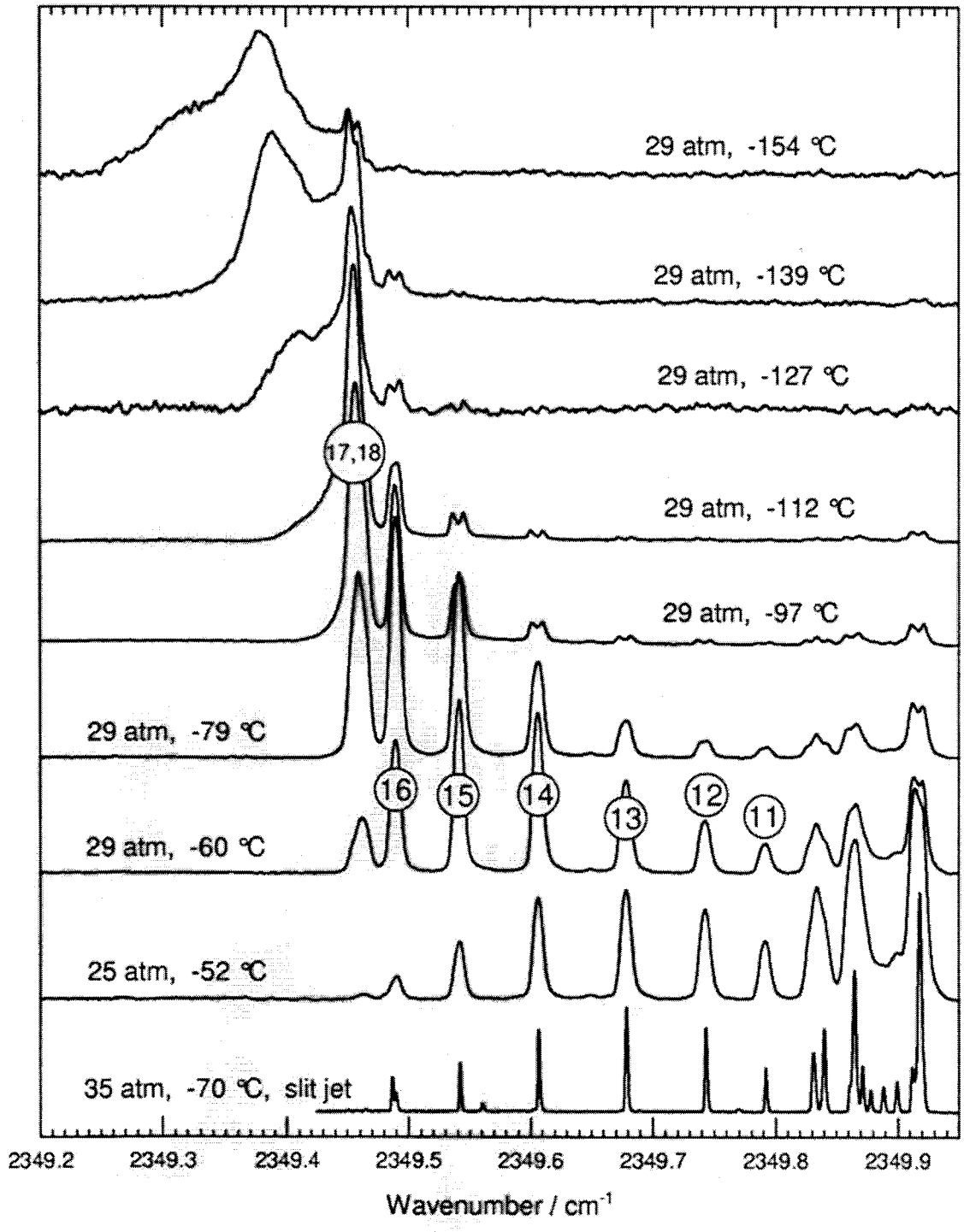

29 atm, -154 °C
29 atm, -139 °C
29 atm, -127 °C
17,18
29 atm, -112 °C
29 atm, -97 °C
29 atm, -79 °C
16
15
14
13
12
11
29 atm, -60 °C
25 atm, -52 °C
35 atm, -70 °C, slit jet
2349.2
2349.3
2349.4
2349.5
2349.6
2349.7
2349.8
2349.9
Wavenumber / cm-1

Figure 3.