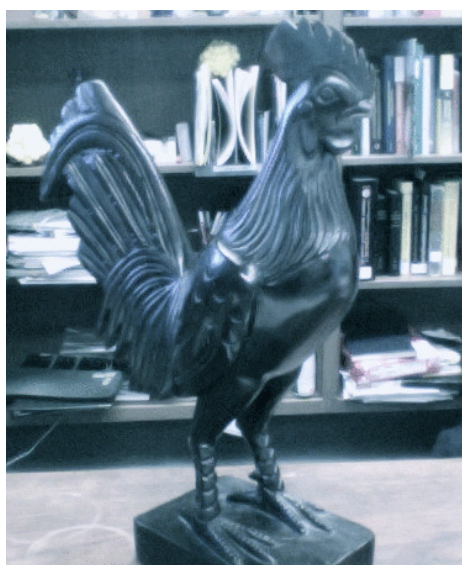


Quantum clusters: finite temperature variational quantum hydrodynamics

Eric R. Bittner--Dept. of Chemistry/University of Houston



John Simon Guggenheim Memorial Foundation
Fellowships to Assist Research and Artistic Creation

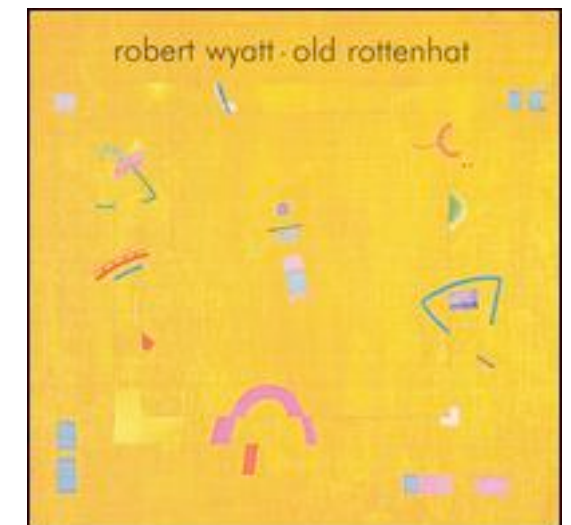
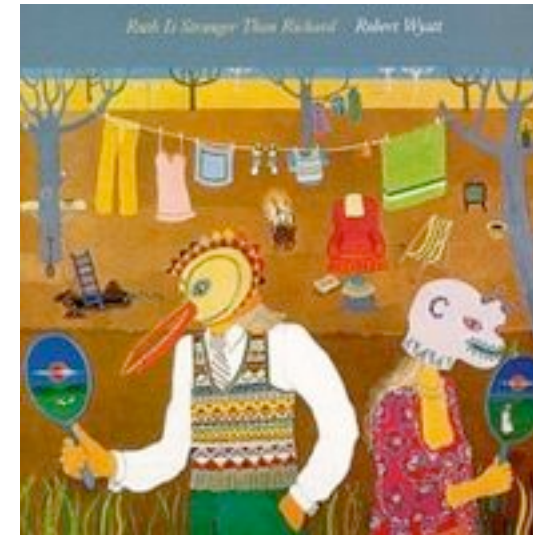
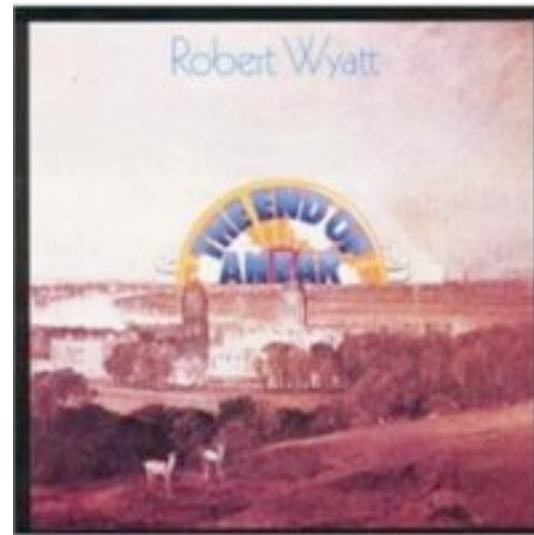


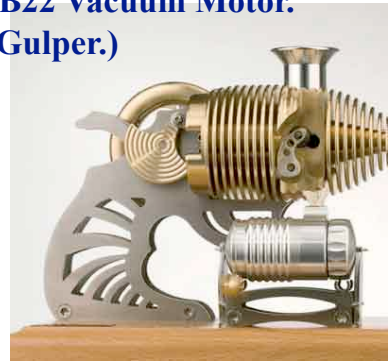
National Science Foundation
WHERE DISCOVERIES BEGIN

Texas: Lone Star State



the other Robert Wyatt:





Problem: how to use Bohm-inspired ideas?

- We've heard plenty about attempts to use Bohm trajectories for doing quantum dynamical calculations.

- Mostly model, 1D (or few D) problems that can be approached more efficiently using “standard” methods

- **PROBLEM:** Quantum potential becomes singular.

$$Q(x) \propto \frac{1}{\psi(x)} \psi''(x)$$

- **WANTED:** a problem that is difficult to solve using “traditional” methods and one in which “Bohm-inspired” methods *offer a solution in an efficient way.*
- **WANTED:** flexibility to use the approach for a wide range of problems.
- Karl Freed (U. Chicago) “Too much rigor makes for rigor mortis.”

#1: Let's forget about real-time dynamics

- For stationary states. Do not have to worry about the “node problem”

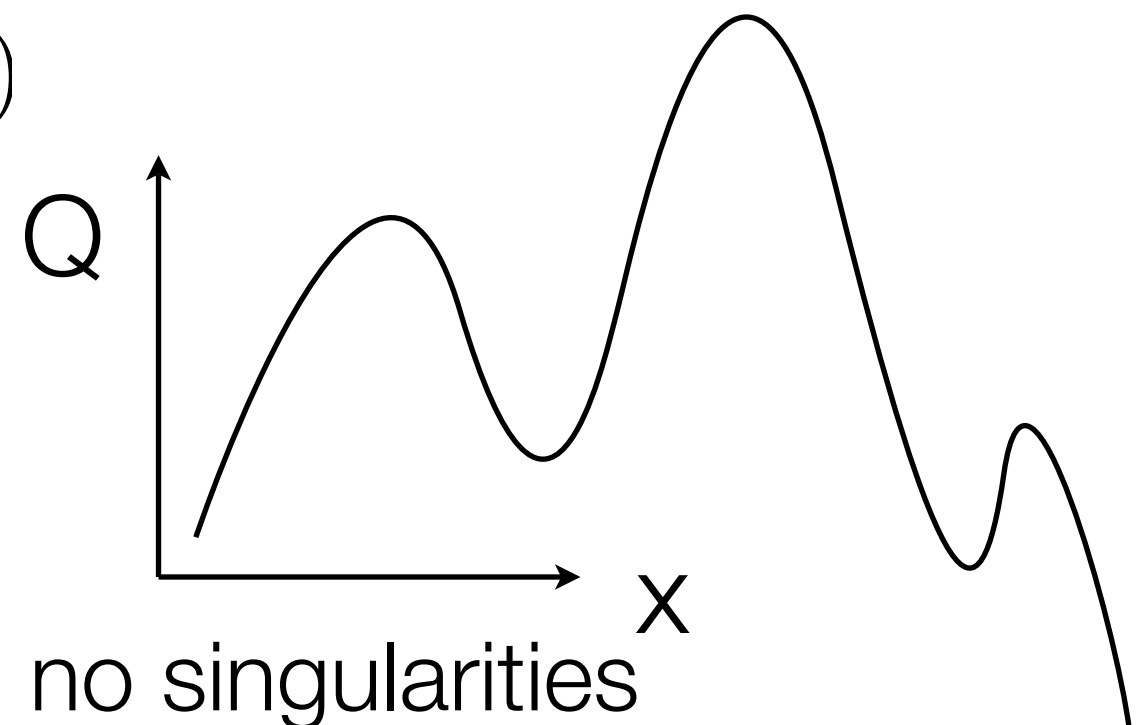
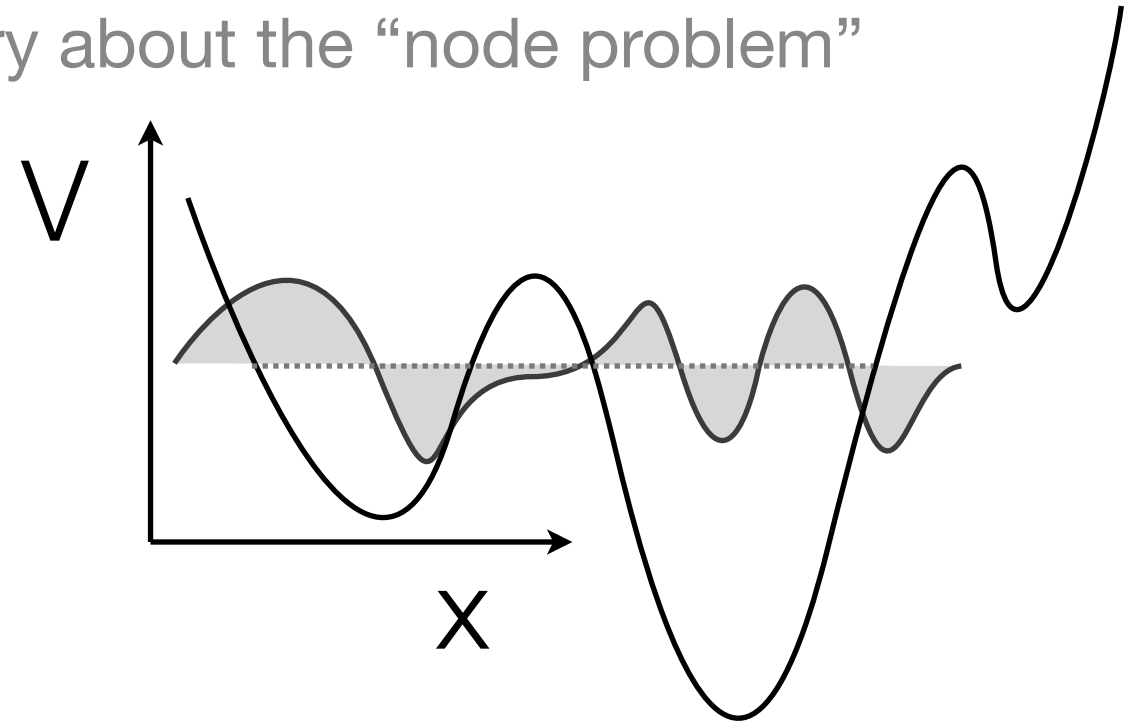
$$E\psi = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

$$E = -\frac{\hbar^2}{2m}\frac{1}{\psi}\nabla^2\psi + V$$

$$Q(x) = -\frac{\hbar^2}{2m}\frac{1}{\psi}\nabla^2\psi = E - V(x)$$

$$Q(x) = E - V(x)$$

no “node problem” for all
stationary states!!



Bohm/Monte Carlo idea.

- Basic Idea (Jeremy Maddox's PhD Thesis).
 - Sample the quantum density using Monte Carlo.
 - Use “maximal entropy” method to get $n(x)$
 - Use $n(x)$ to obtain quantum potential.
$$Q[n] = \frac{-\hbar^2}{2m} \frac{1}{\sqrt{n}} \nabla^2 \sqrt{n}$$
 - Move sample points along *conjugate gradient* of $E[n] = Q[n] + V[n]$ so that $\partial E = 0$
- At true ground state: sample points are stationary!
- Thermal effects can be included by performing calculations in a statistical ensemble (Mermin).

Mixture model

$$n(r) = \sum_m^M p(r, \{c_m\})$$

$p(r, \{c_m\})$ = prob. that a randomly chosen member of ensemble will have configuration r and is a variant of the m th approximate designated by $\{c_m\}$ (Joint probability)

$$p(r, \{c_m\}) = p(\{c_m\}) p(r \mid \{c_m\}) = n(r) p(\{c_m\} \mid r)$$

$p(r \mid \{c_m\})$ = prob. that a randomly chosen variant of $\{c_m\}$ has config. r

$p(\{c_m\} \mid r)$ = prob. that r is a variant of $\{c_m\}$

Bayes' Equation:

$$p(c_m \mid r_n) = \frac{p(\{c_m\}) p(r \mid \{c_m\})}{\sum_m p(\{c_m\}) p(r_n \mid \{c_m\})}$$

Note: Can choose approximates $p(r \mid \{c_m\})$ in a variety of ways.
 Easiest = gaussian with sparse covariance. (e.g. factored between different d.o.f.
 More exact: choose covariance perhaps correlating multiple atoms, d.o.f, etc.

Estimating density using n-Gaussian approximates

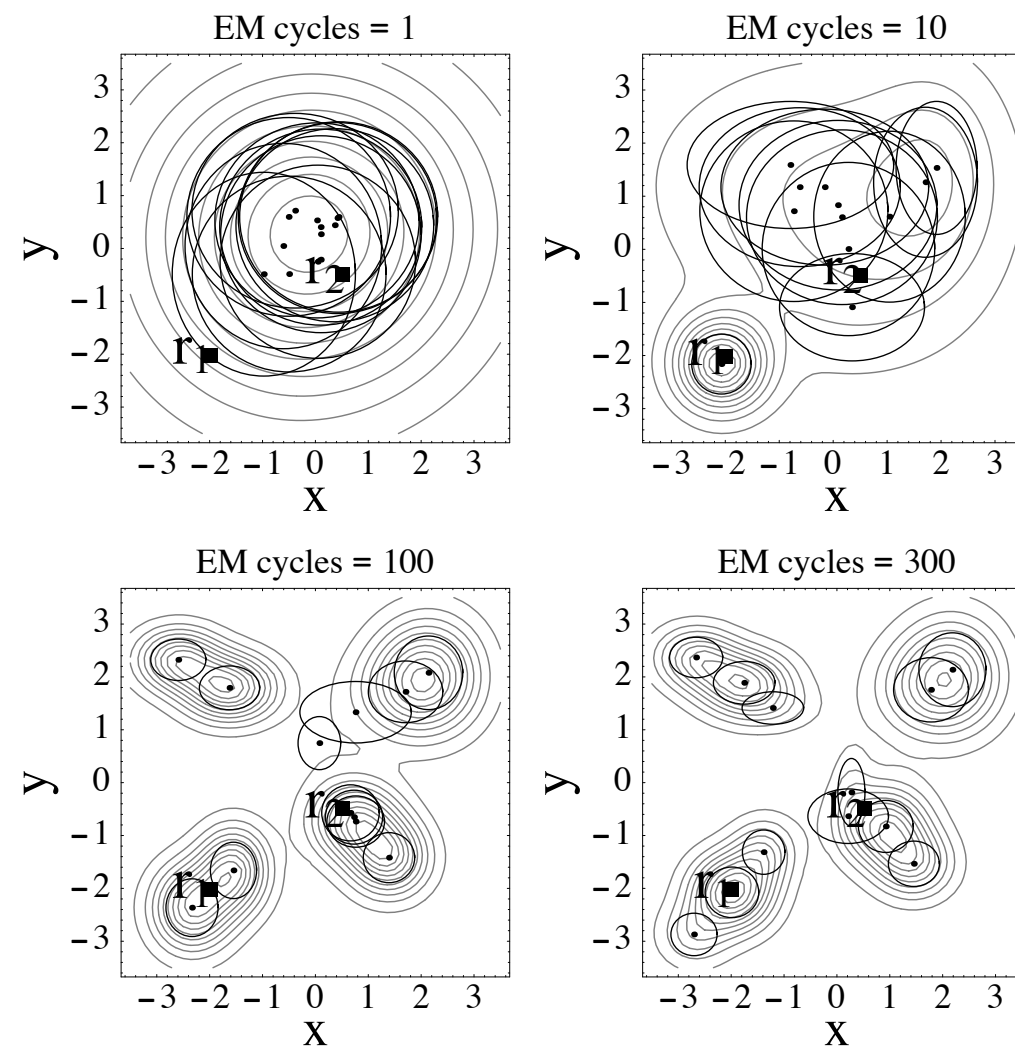
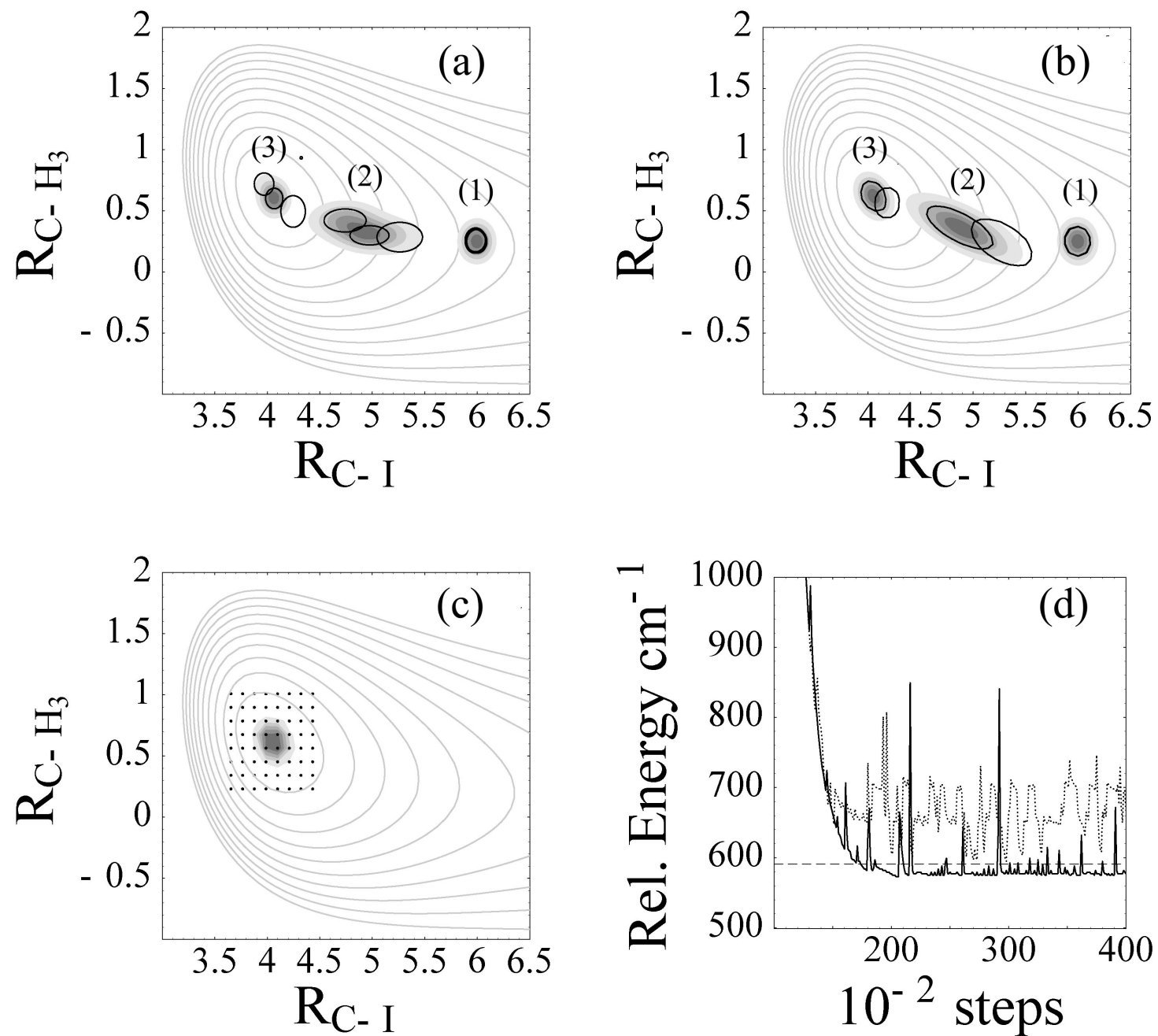


FIG. 2: This figure illustrates the EM algorithm for the data pictured in Fig. 1 using 16 separable Gaussian clusters. The contours reflect the approximated probability density during the course of the EM fitting routine. The black dots correspond to the average position of the Gaussian cluster, and the solid black ellipses represents the Gaussian half-width contours.

- [*Estimating Bohm's quantum force using Bayesian statistics*](#),
Jeremy Maddox and Eric R. Bittner, *J. Chem. Phys.* **119**, 6465 (2003).

Relaxation on a model Potential Surface (MeI)



- [Estimating Bohm's quantum force using Bayesian statistics](#),
Jeremy Maddox and Eric R. Bittner, J. Chem. Phys. **119**, 6465 (2003).

#2: Ask: When are QM effects important?

- DeBoer Ratio: ratio of de Broglie wavelength to range of potential

$$\Lambda = \frac{\lambda(T^*)}{\sigma} = \frac{\hbar}{\sigma \sqrt{m\epsilon}}$$

$T^* = \epsilon/\hbar$ effective T in terms of well-depth

Classical limit $\Lambda \rightarrow 0$

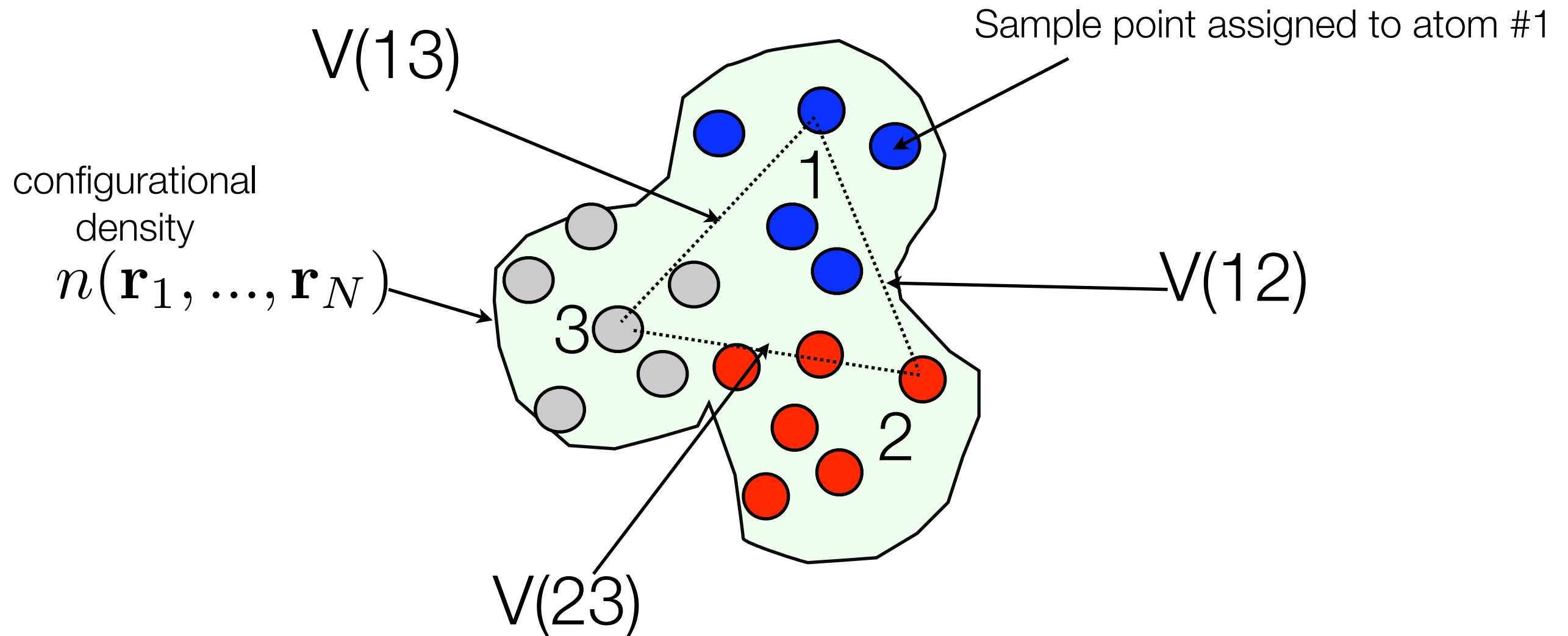
“Strongly QM” $\Lambda > 0.3$ (Liq. He)

Liquid Ne: $\Lambda_{Ne} > 0.1$



Physical Question: Are there appreciable quantum contributions to structure/thermodynamics of clusters?

System: Quantum rare-gas clusters



Energy density functional: $E[n(\mathbf{r}_1, \dots, \mathbf{r}_N)] = T[n] + V[n]$

T = 0K theory

$$H = - \sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i \neq j} V(ij),$$

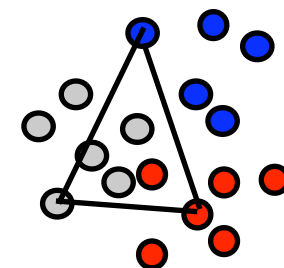
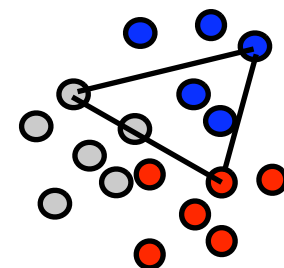
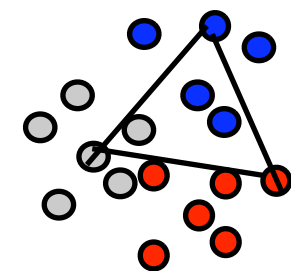
Energy is a functional of the
configurational density $n(\mathbf{r}_1, \dots, \mathbf{r}_N)$

$$E[n(\mathbf{r}_1, \dots, \mathbf{r}_N)] = T[n] + V[n]$$

Ground state: $\frac{\delta E[n]}{\delta n} = 0$

$$\Psi(\mathbf{r}) = \sqrt{n(\mathbf{r})} e^{i\phi}$$

$$\phi(r) = \text{const.}$$



Density factorization (mean field approx)

Configurational Density $n(12345)$

q.m. prob. for finding system in a given atomic configuration

Approx: full config. density as a sum over “statistical approximates”

$$n(\mathbf{r}_1, \dots, \mathbf{r}_N) \approx \sum_m p(\mathbf{r}_1, \dots, \mathbf{r}_N, c_m)$$

Hartree-factorization:

$$n(r_1, r_2, \dots, r_N) = \sum_m^N p(r_m, c_m)$$

variational
parameters



Variational equation

interactions

$$V[n] = \sum_{i>j} \int \int n_i(r_i) n_j(r_j) V(ij) dr_i dr_j$$

Kinetic energy functional = integral over quantum potential

$$T[n] = \int n(r) Q[n(r)] dr$$

Weissacker functional

$$T[n] = -\frac{\hbar^2}{2m} \sum_i \int \sqrt{n_i} \nabla_i^2 \sqrt{n_i} dr_i = \sum_i T_W[n_i]$$

variation of total energy: “orbital free” version of DFT

$$\delta \left\{ \sum_{i=1}^N \left(\overset{\text{kinetic energy}}{T_W[n_i(\mathbf{r}_i)]} + \overset{\text{interactions}}{\sum_{j \neq i} \int \int n_i(\mathbf{r}_i) n_j(\mathbf{r}_j) V(ij) d\mathbf{r}_i d\mathbf{r}_j} - \overset{\text{constraint}}{\mu \left(\int n_i(\mathbf{r}_i) d\mathbf{r}_i - 1 \right)} \right) \right\} = 0$$

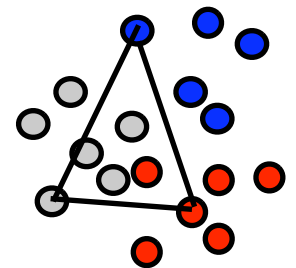
can include exchange/correlation for boson or fermion systems using approx. XC functionals

Euler Lagrange EOM

$$\frac{\delta T_W[n_i(\mathbf{r}_i)]}{\delta n_i(\mathbf{r}_i)} + \sum_{j \neq i} \int V(ij) n_j(\mathbf{r}_j) d\mathbf{r}_j - \mu = 0.$$

Effective (statistical) potential for atom i

$$V_i^e = Q(\mathbf{r}_i) + V_e(\mathbf{r}_i) + \sum_{j=1}^N V_p(\mathbf{r}_i, \mathbf{r}_j).$$



Sample each atomic density using points, move each sample point along gradient of total quantum energy

$$\nabla_i E = - \sum_{j \neq i} \int (\nabla_i V(ij)) n_j(r_j) dr_j - \nabla_i Q[n_i(r_j)]$$

Ne_n and Ar_n (n=4,13,19)

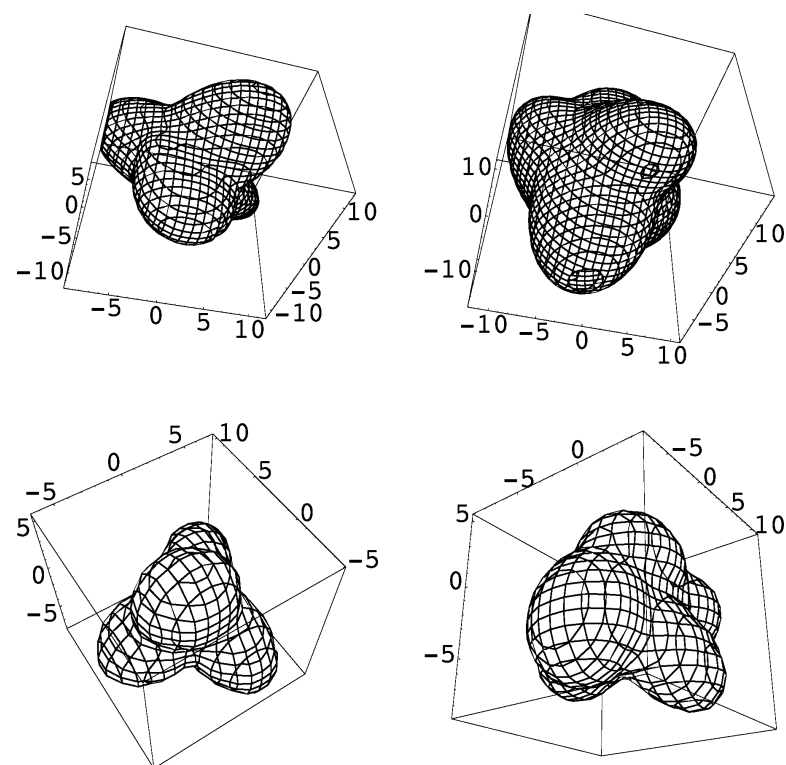
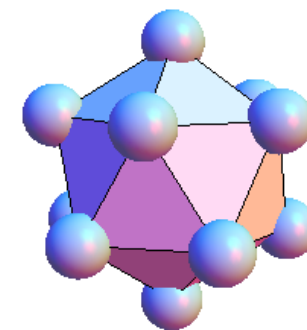


Figure 1. The isodensity contour plots of the clusters at a value of 0.006. In the upper left is the Ar₄ cluster, in the upper right is the Ne₄, lower left has the Ar₅, and then bottom right is Ne₅. The axes are listed in atomic units.

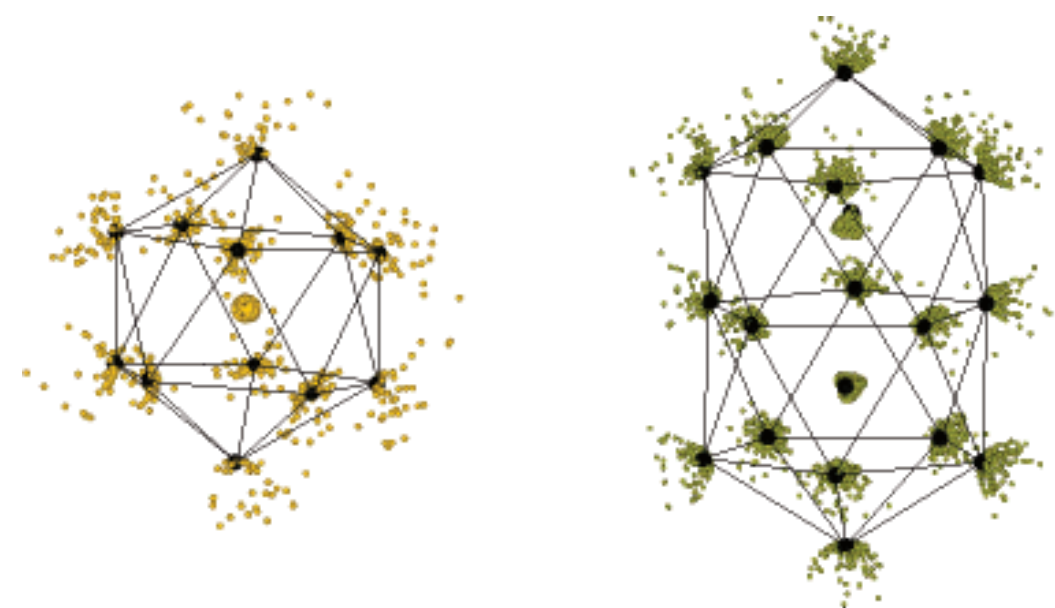


Figure 4. Thirteen and 19-atom clusters with the quantum sample points in yellow overlaid on the classical equilibrium positions in black.

Quantum Hydrodynamic Approach for Molecular Clusters

J. Phys. Chem. A, Vol. 110, No. 16, 2006 **5339**

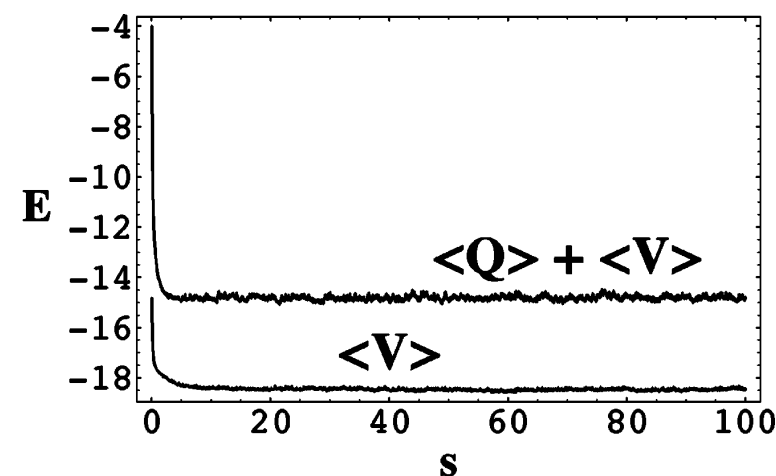
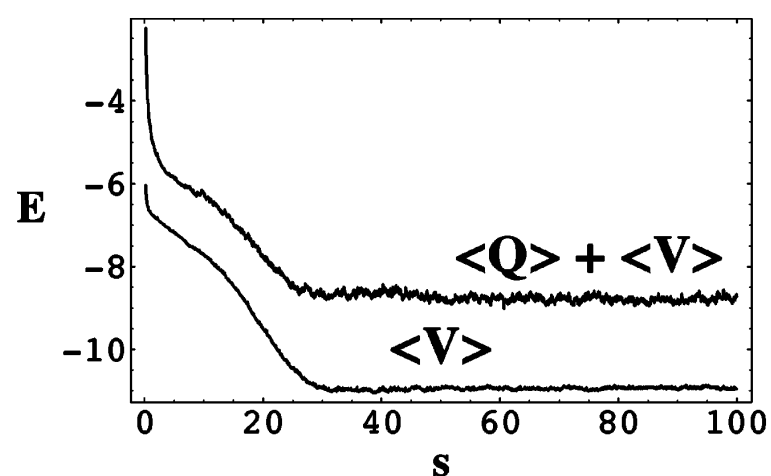
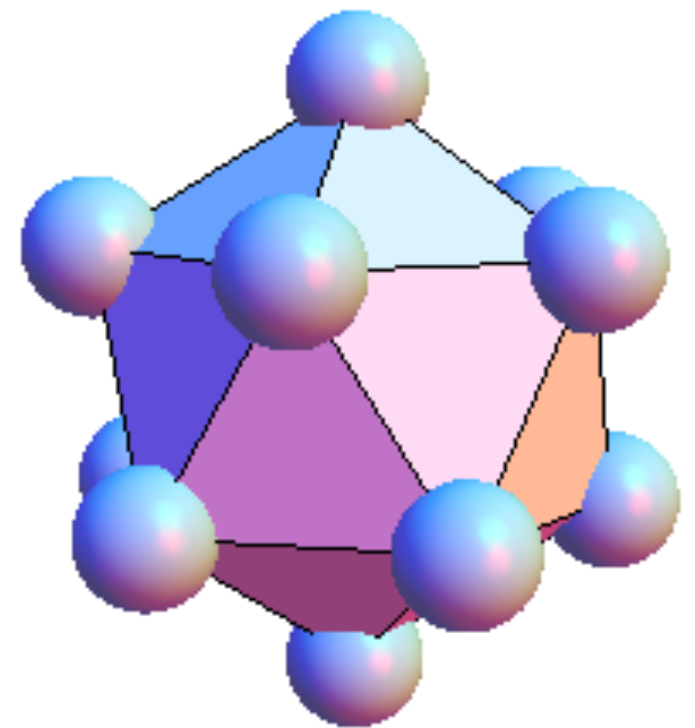
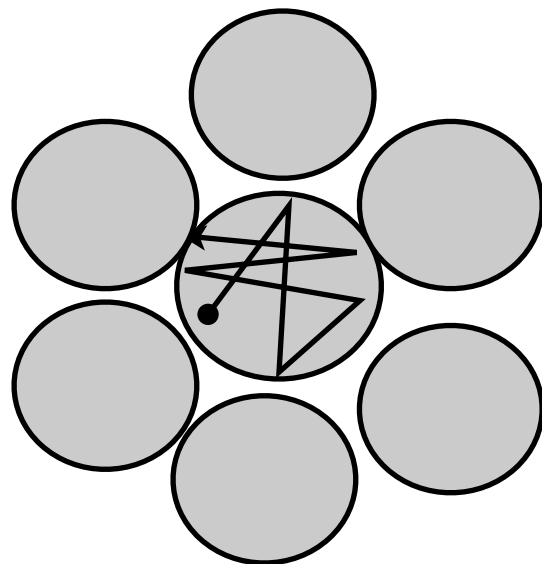


Figure 3. Convergence of the 13- and 19-atom clusters of neon. The energy is in kJ/mol and the steps are given in millions.

$$V_{\text{quantum}} > V_{\text{classical}}$$

- for 13 atom cluster: mean radius of quantum cluster about 3% > than classical
- 20% increase in volume.
- “spread of atoms due to uncertainty principle.
- internal quantum “pressure” of interior-most atom causes entire cluster to slightly swell for smaller closed (complete) shell clusters



Finite temperature theory $\delta\Omega = 0$

grand ensemble $Z(T, V, \mu) = \text{Tr}(e^{-\beta(H - \mu N)})$

$$\Omega = -\frac{1}{\beta} \log(\text{Tr}[e^{-\beta(H - \mu N)}])$$

Mermin: finite temperature DFT

$$\Omega[\hat{\rho}_T] = \text{Tr}[\hat{\rho}_T(K + V - \mu N + \frac{1}{\beta} \log \hat{\rho}_T)]$$

for any trial density: $\Omega[\hat{\rho}_T] \geq \Omega[\hat{\rho}]$

Entropy functional

$$\Omega[n(r)] = F[n(r)] - \mu \int n(r) dr$$

$$F[n(r)] = T_w[n(r)] + V[n(r)] + \frac{1}{\beta} S[n(r)]$$

Micro-canonical entropy: $S = k_B \log \Omega_{mc}$

$$S = -k_B Tr[\hat{\rho} \log \hat{\rho}]$$

$$\mu = \frac{1}{\beta} \frac{\delta S}{\delta n} + Q(r) + V_{mf}(r)$$

$$S[n(r)] = \frac{1}{\beta} \sum_i \int n_i(r_i) \log(n_i(r_i)) dr_i = \sum_i S[n_i]$$

Entropic
“force”

$$\frac{\delta S}{\delta n_i} = \frac{1}{\beta} (\log(n_i(r_i)) + 1)$$

Ground state energy vs. size.

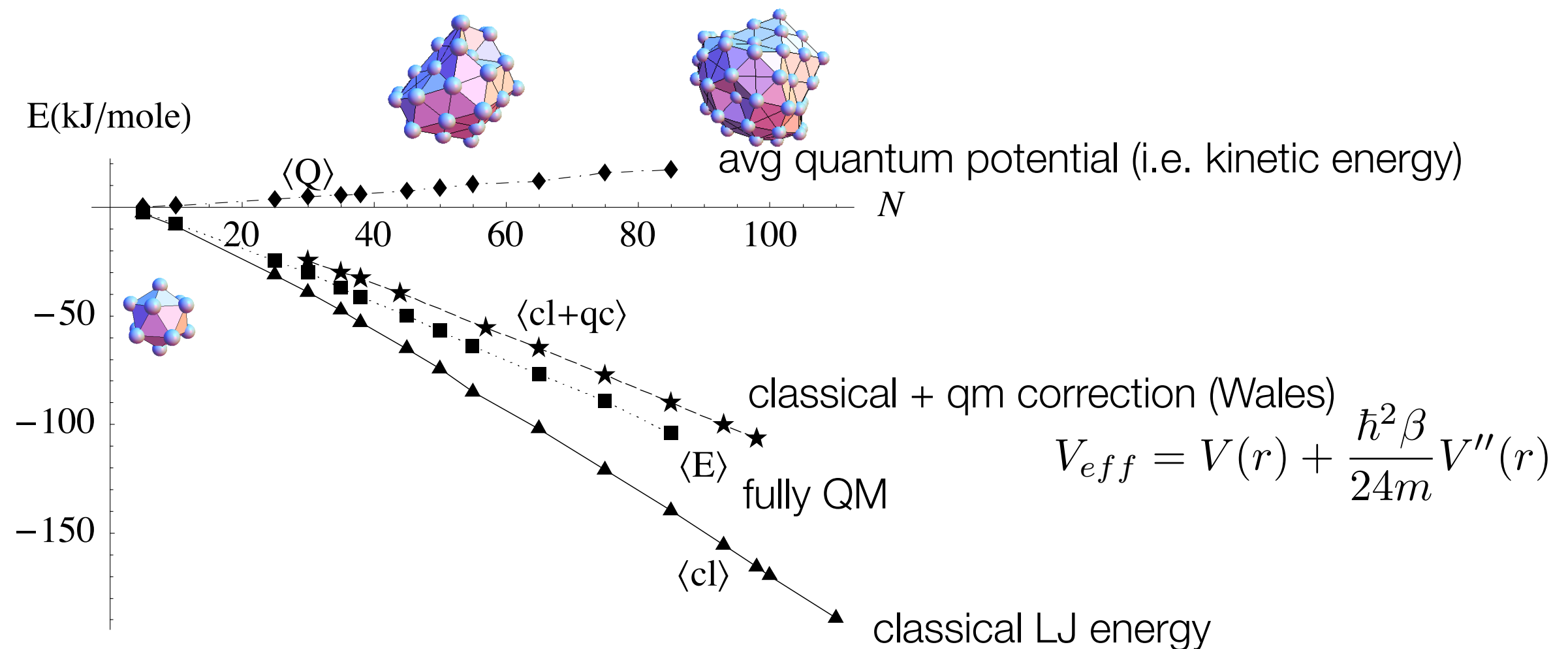


FIG. 2: Various energetic contributions for quantum and classical Neon clusters versus cluster size, N . Key: $\langle \text{cl} \rangle$ = classical global potential minimum energy, $\langle \text{cl} + \text{qc} \rangle$ = zero-point energy corrections from Ref. [6], $\langle \text{E} \rangle$ = total energy, $\langle \text{Q} \rangle$ = quantum kinetic energy (from quantum potential).

Fully QM vs. Q/C Corrected Energies.

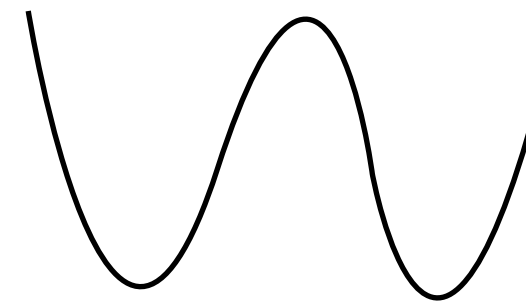
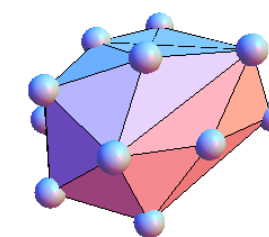
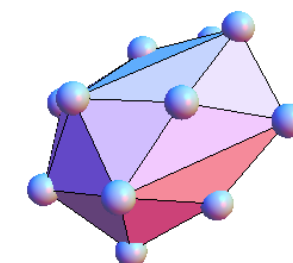


TABLE I: Ground state vibrational energies for Ne_n clusters for our results compared to the results tabulated by Calvo *et al.* Ref. [6]

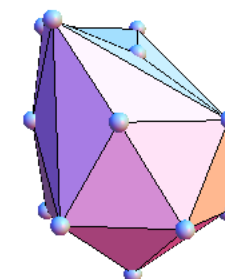
Cluster	order	Energy (From Ref. [6])	order	This work.
17C	(1)	-11.0853 kJ/mol	(2)	-16.6336
17B	(2)	-11.0814	(3)	-16.3188
17A	(3)	-11.0633	(1)	-16.6699
27B	(1)	-21.5483	(2)	-27.6994
27A	(2)	-21.5099	(1)	-28.2823
28B	(1)	-22.5892	(2)	-28.7459
28A	(2)	-22.5496	(1)	-29.3524



17c



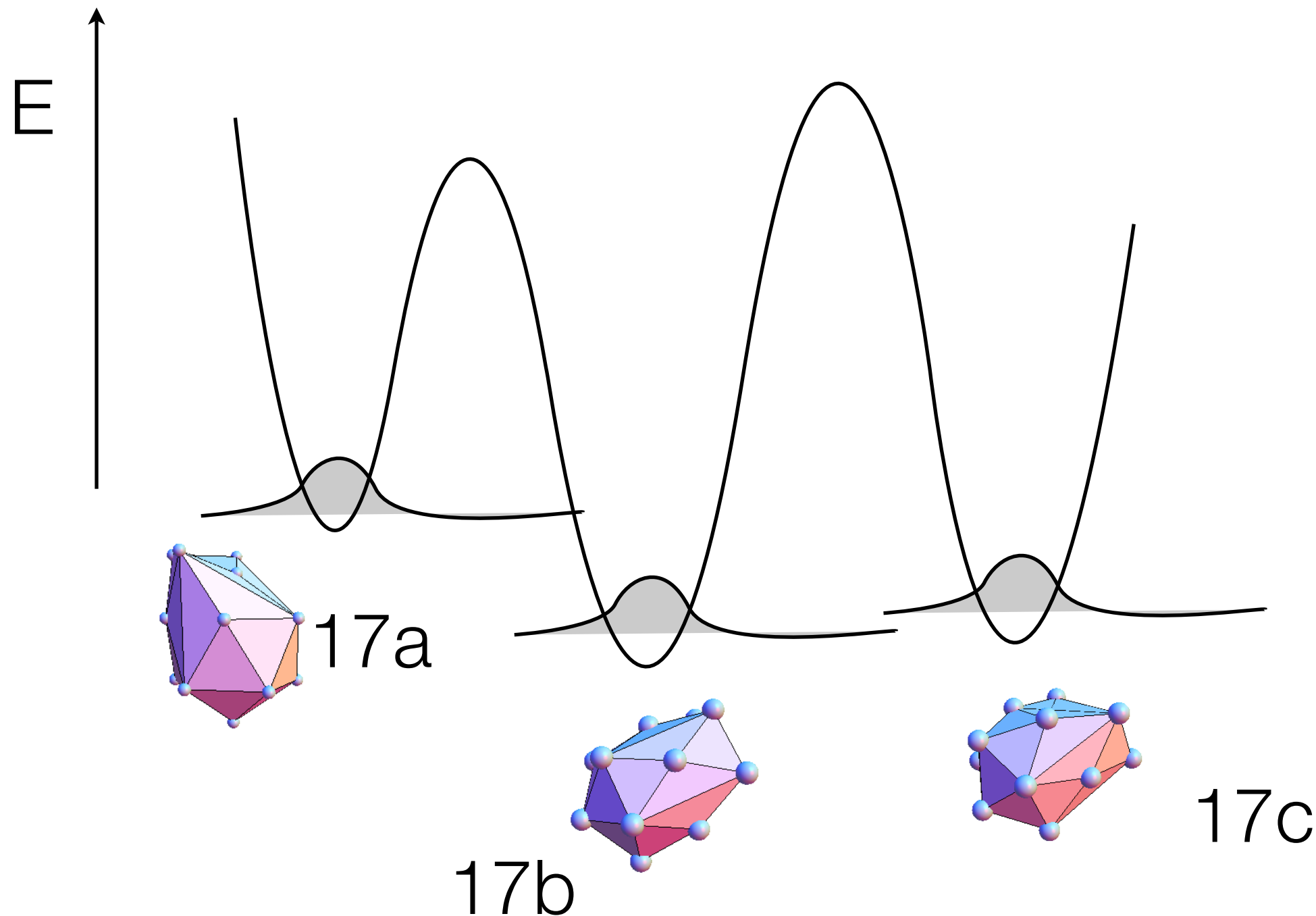
17b



17a

Multiple “minima” separated by high barriers

approach and effectively sample a high-dimensional potential energy landscape



Free energy vs. T for various small clusters

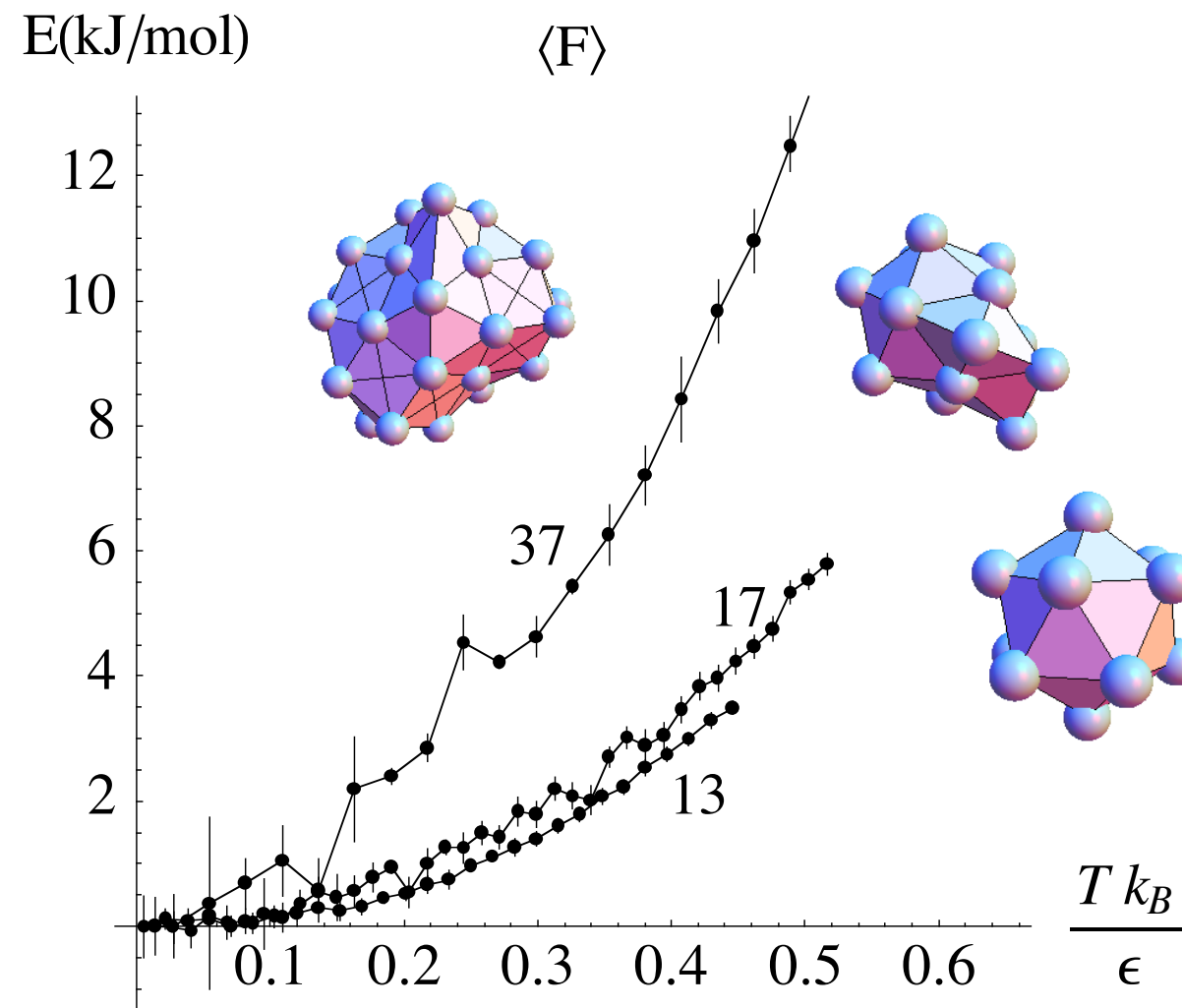


FIG. 3: The free energy of the different clusters vs. temperature. Error bars indicate numerical/statistical precision of each computed free energy value. Note the $T = 0$ values are offset to a common origin for comparison. The energies at $T = 0\text{K}$ for the three clusters are as follows: $F_0^{13} = -11.21$ kJ/mol, $F_0^{17} = -15.216$ kJ/mol, and $F_0^{37} = -39.03$ kJ/mol.

Ne₁₃

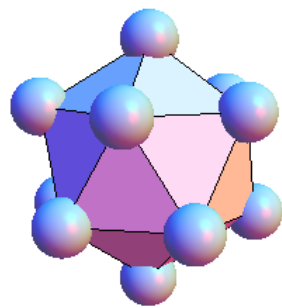
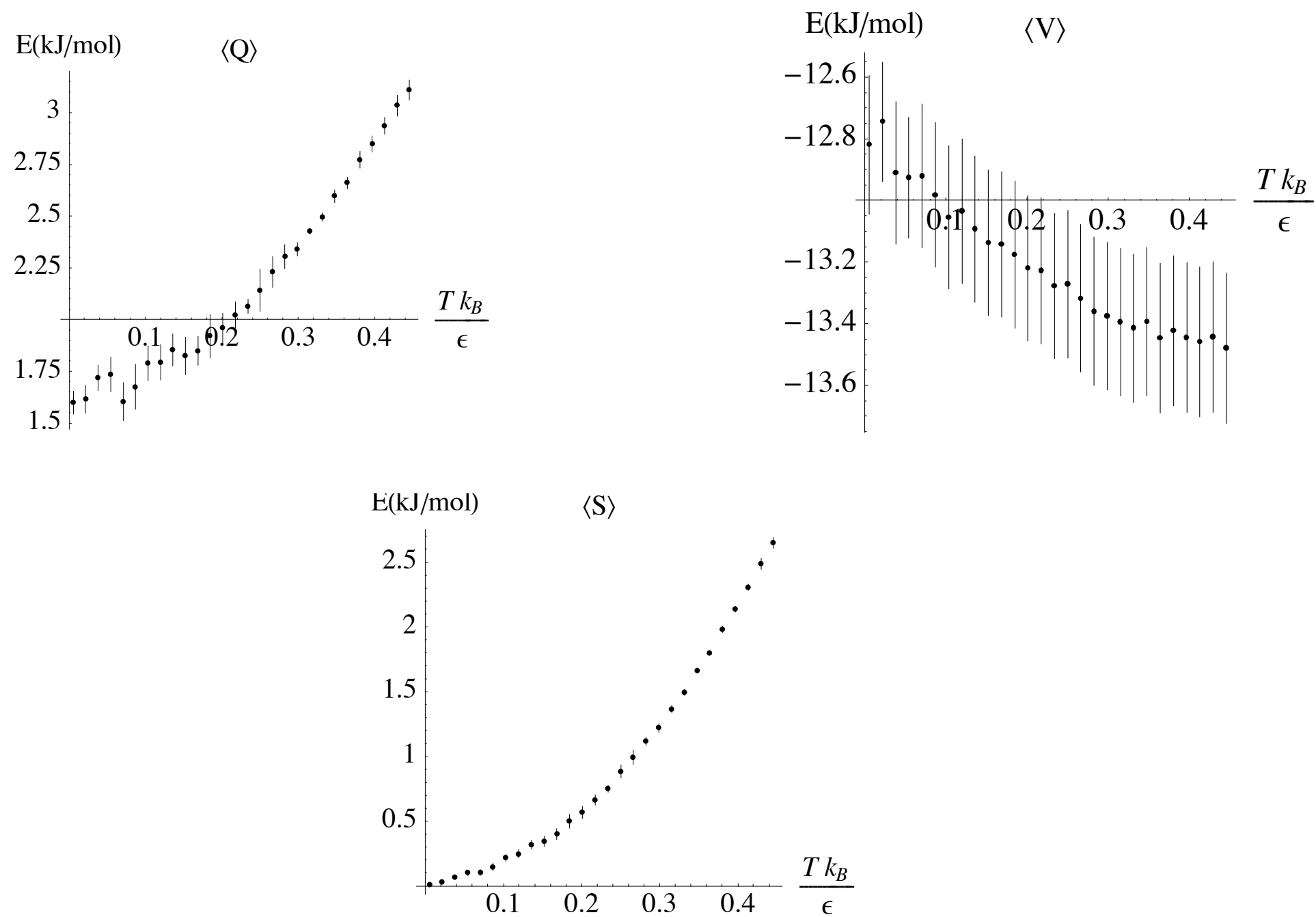


FIG. 4: Plots of the quantum, total potential, and entropic contributions to the total free energy vs. temperature for Ne₁₃.



Debye model:
$$U = 9Nk_B T \left(\frac{T}{T_D} \right)^3 \int_0^{T/T_D} \frac{x^3}{e^x - 1} dx$$

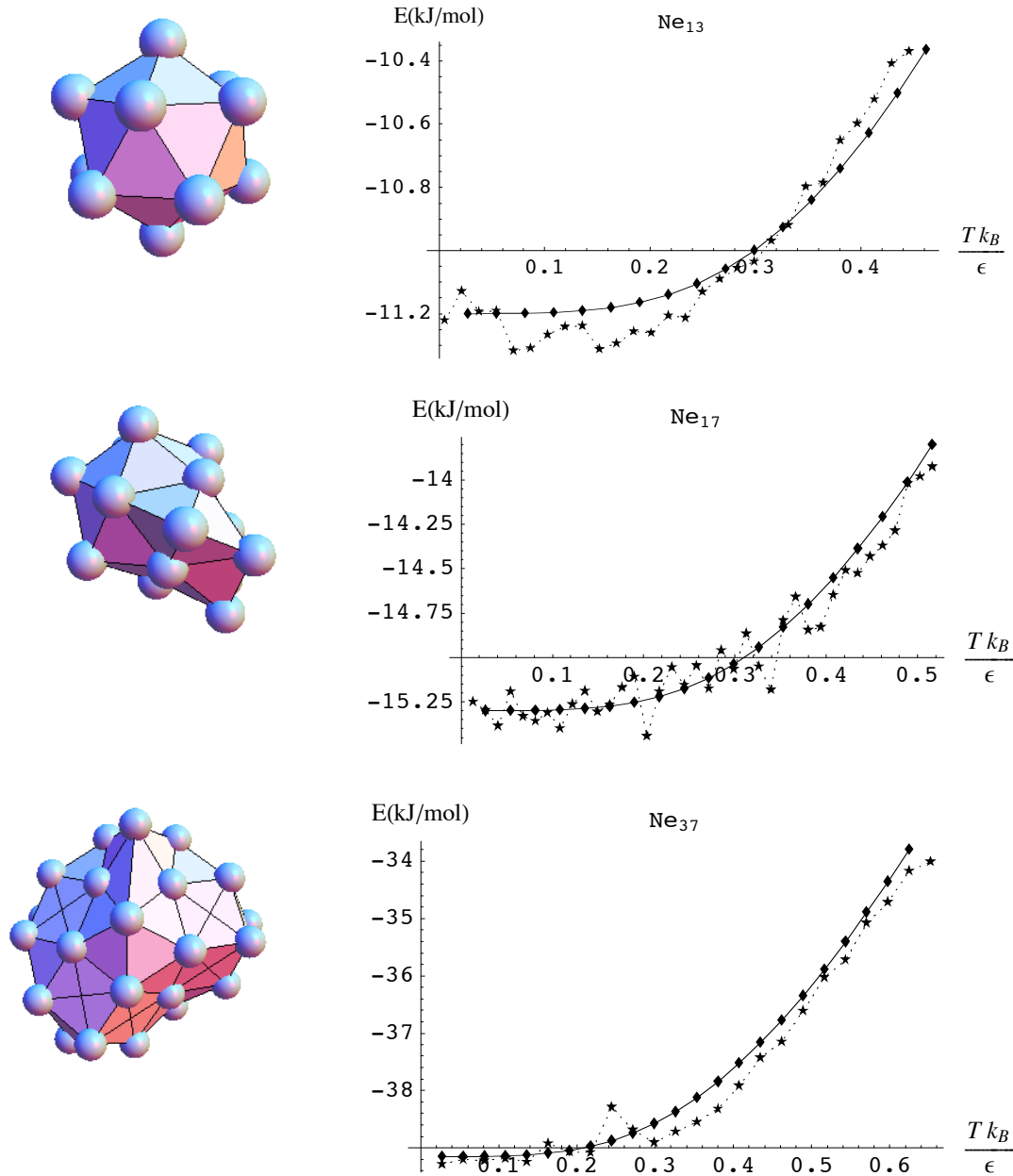


FIG. 5: Internal energy comparison of the current results ($\cdots \star \cdots$) with the Debye model ($-$).

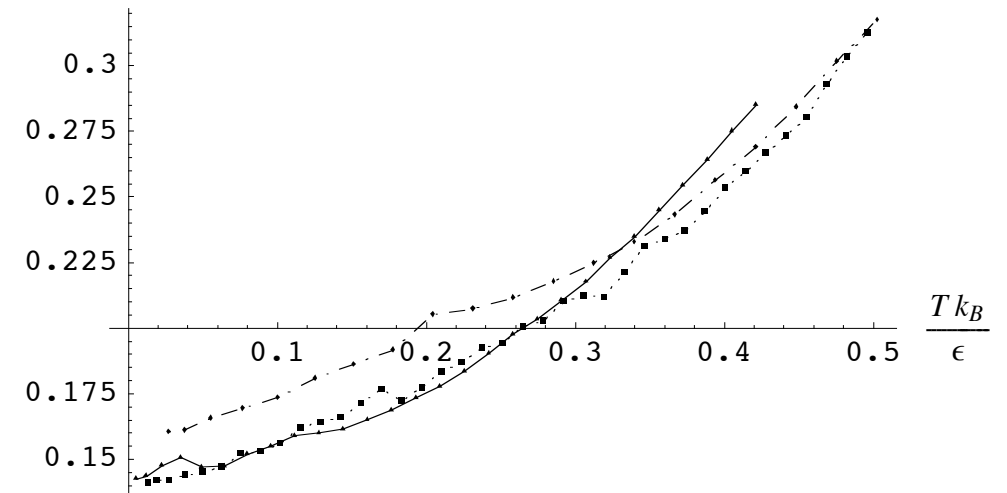


FIG. 6: $(\langle Q \rangle / \langle U \rangle)$ vs. T . (Key: $-$: 13 atoms, \cdots : 17 atoms, $- \cdot -$: 37 atoms).

$$T_D = \frac{hc_s}{2k_B} \left(6N\pi V \right)^{-3}$$

$$T_D(\text{Ne}) = 75\text{K}$$

Negative heat capacity?

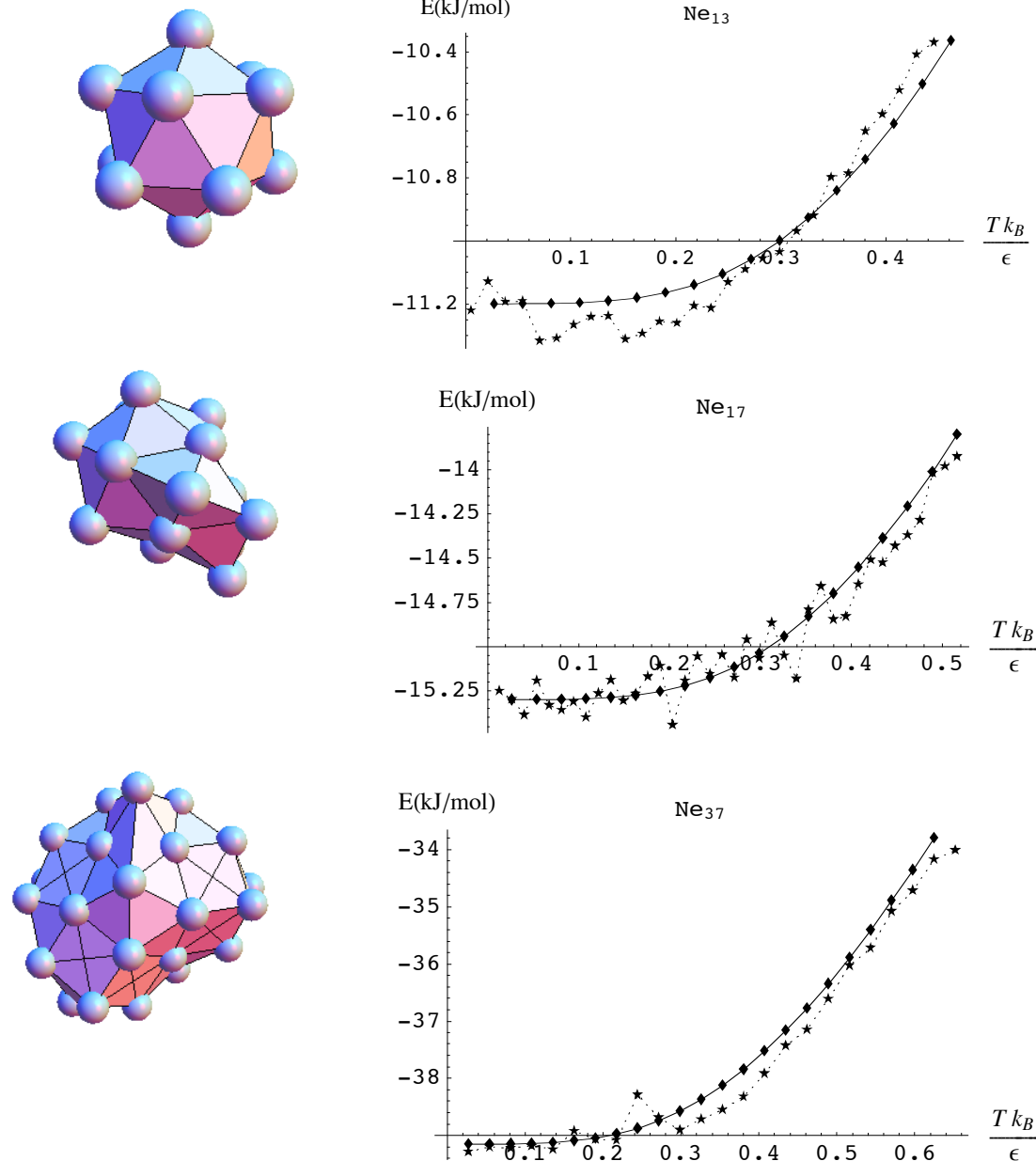


FIG. 5: Internal energy comparison of the current results ($\cdots \star \cdots$) with the Debye model ($-$).

- **Numerical/Systematic Error?:**

$C_p < 0$ reported by D. Wales on the Ne_{13} cluster...not by Mandelshtam (filter diagonalization methods)

- **Physical Grounds:** $C_p < 0$ has been reported for Na_{147} clusters and possibly neutron stars, certain types of blackholes, etc..

Schmidt, et al Phys.Rev Lett. **86**, 1191 (2001).

Can show $C_p < 0$ analytically for centrosymmetric potentials

Review: D. Lynden-Bell *Physica A* **263**, 293 (1999)

virial ratio: $\langle Q \rangle / \langle U \rangle$

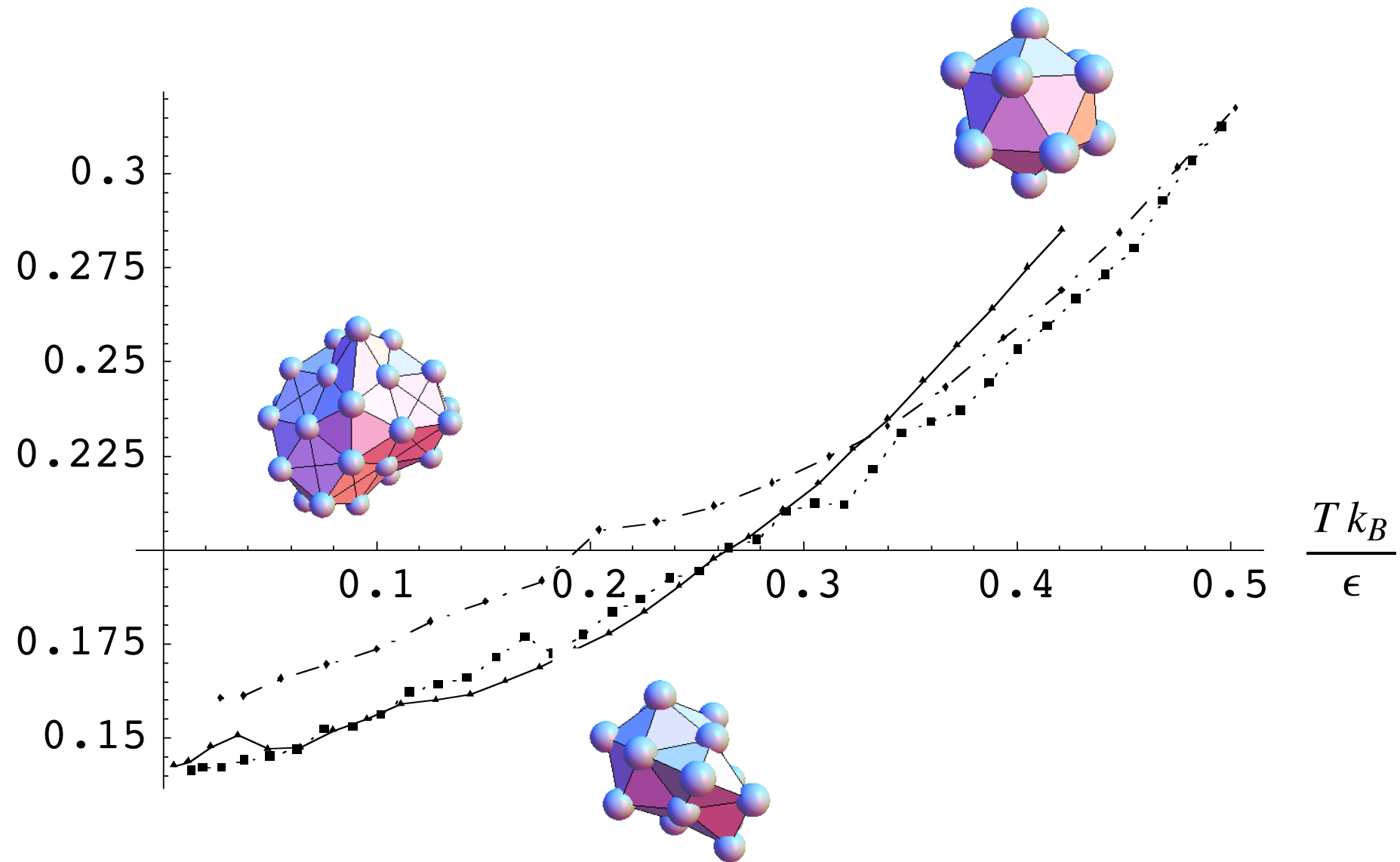


FIG. 6: $(\langle Q \rangle / \langle U \rangle)$ vs. T . (Key: —: 13 atoms, \cdots : 17 atoms, $- \cdot -$: 37 atoms) .

Conclusions

- “Bohm-inspired” approach for including quantum effects into a many-body system.
- **To date this is the ONLY** application of the Bohm/Hydrodynamic approach in a non-trivial system.
- Molecular dynamics “flavor” allows one to easily choose certain degrees of freedom to be described with varying degrees of “quantum” character. Much like path-integral MC or path-integral centroid dynamics.
- Finite temperature results: structural predictions and thermodynamics for rare-gas clusters are at least consistent with more standard approaches.
- Do not see “pre-melting” or “surface melting” (consistent w/Mandelshtam (PIMC)--different from classical simulation)
- Not restricted to magic number or closed shell clusters.

Group Publications/References

- *Estimating Bohm's quantum force using Bayesian statistics*,
Jeremy Maddox and Eric R. Bittner, J. Chem. Phys. **119**, 6465 (2003).
- *A self-consistent field quantum hydrodynamic approach for molecular clusters*,
Sean Derrickson and Eric R. Bittner, J. Phys. Chem A **110**, 5333 (2006).
Note Invited article for John C. Light Festschrift issue
- *Thermodynamics of mesoscopic atomic clusters using variational quantum hydrodynamics*,
Sean W. Derrickson and Eric R. Bittner, J. Phys. Chem. A **111**, 10345 (2007).
Note Invited article for Robert E. Wyatt Festschrift issue.

Thanks

- Bob Wyatt--inspiration and introduction to the topic.
- Jeremy Maddox, Sean Derrickson--2 PhD students crazy enough to pickup on this idea.
- Funding: National Science Foundation, Robert A Welch Foundation, TLC²
- J.S. Guggenheim Foundation (Fellow: 2007).
- Thanks: Irene Burghardt (ENS/Paris), David Wales (Cambridge).

“Entropic force” $\frac{\delta S}{\delta n_i} = \frac{1}{\beta} (\log(n_i(r_i)) + 1)$

Gaussian trial density: $n(x) = \sqrt{\frac{1}{2\pi\langle x^2 \rangle}} e^{-x^2/2\langle x^2 \rangle}$

Harmonic osc:

$$\langle F \rangle = \frac{1}{8m\langle x^2 \rangle} + \frac{m\omega^2}{2} \langle x^2 \rangle - \frac{1}{2\beta} (\log(2\pi\langle x^2 \rangle) + 1)$$

$$\delta \langle F \rangle = 0$$

$$\langle x^2 \rangle_{opt} = \frac{kT}{2m\omega^2} \left(1 + \sqrt{1 + (\hbar\omega/kT)^2} \right)$$

$$\langle x^2 \rangle_{exact} = \frac{\hbar}{2m\omega} \coth \left(\frac{\Theta_v}{2T} \right)$$

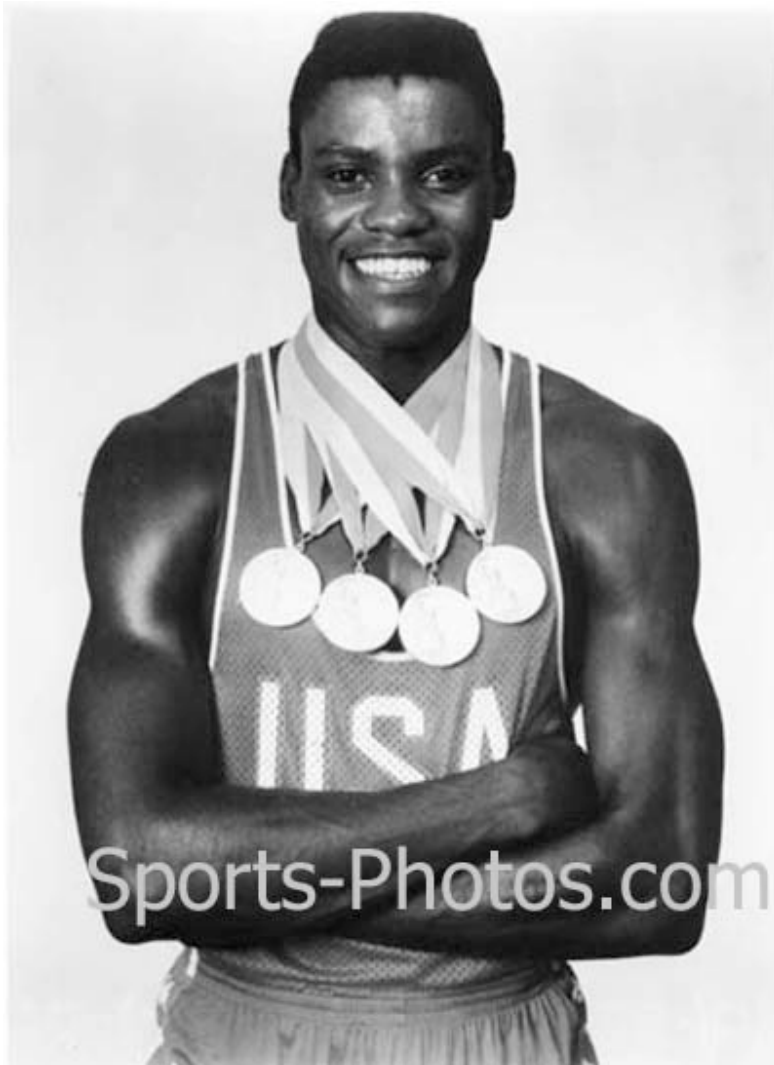
OK at high and low temperature--error is small

Univ. of Houston

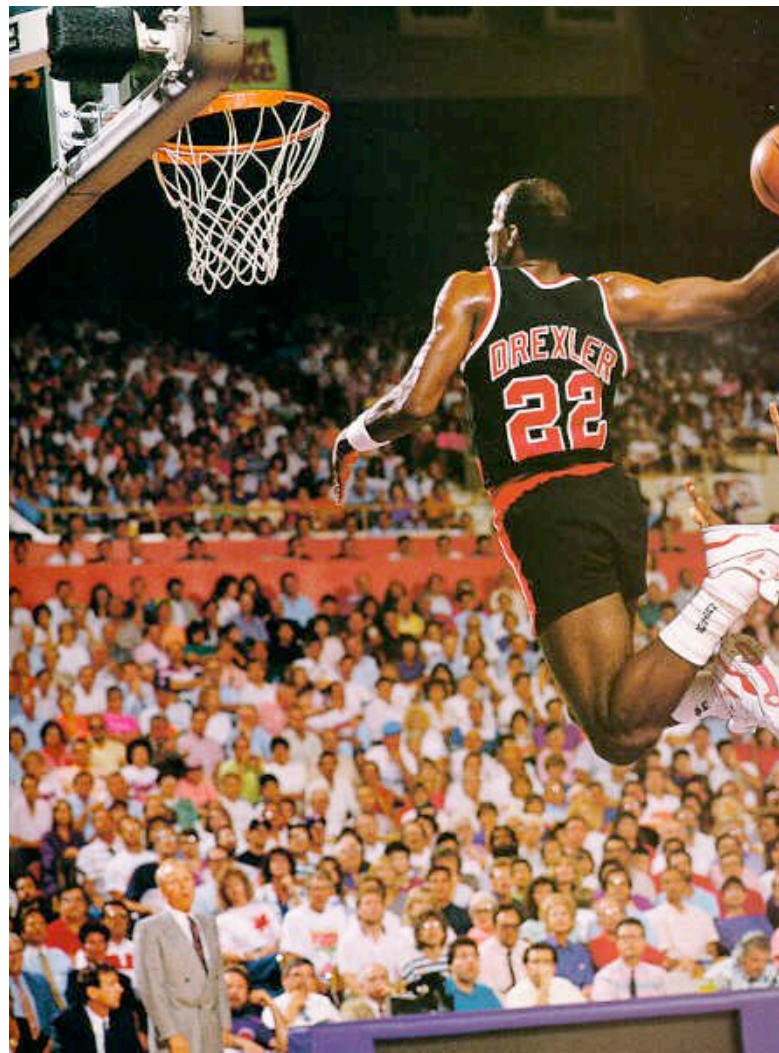
- 2nd largest Univ. System in Tx
- 35,000 students on main campus
- More Pro-Football players than any other US University!
- High Tc Superconductivity discovered.



Famous Former Students



Carl Lewis



Clyde Drexler



Brent Spiner

Infamous Former Students

Ken Lay
(PhD Economics)



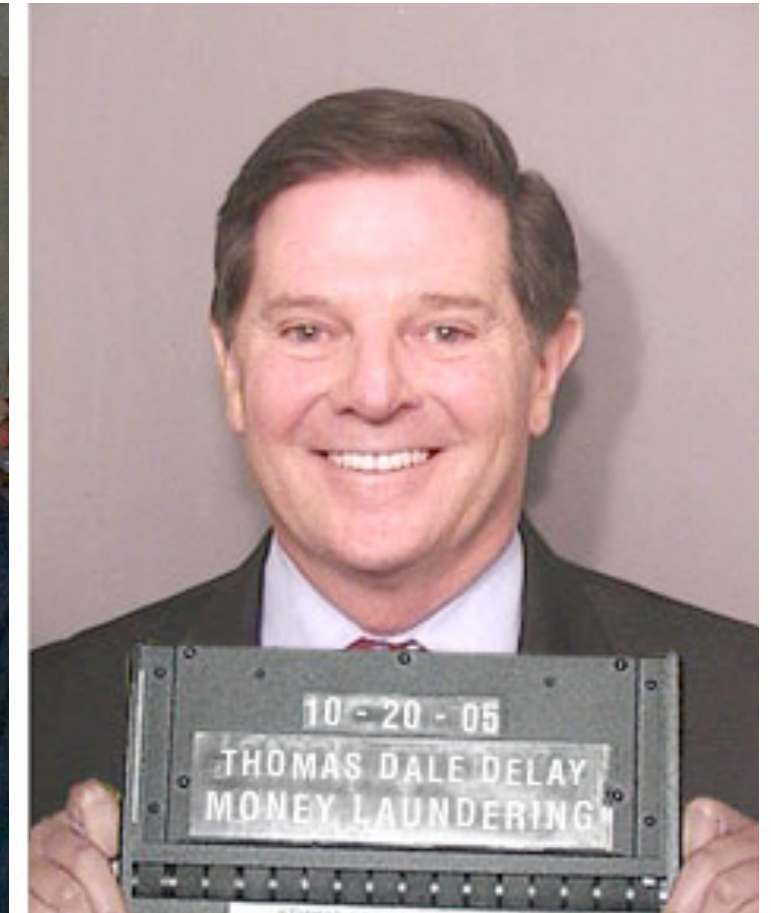
Former Enron CEO

Bridget Boisselier
(PhD, Chemistry)



Head of [Clonaid](#), the "scientific wing" of the [Raëlians](#).

Tom DeLay
(BS-Biochemistry)



Former Congressman and GOP Majority Leader