Towards models with a complete description of long range forces

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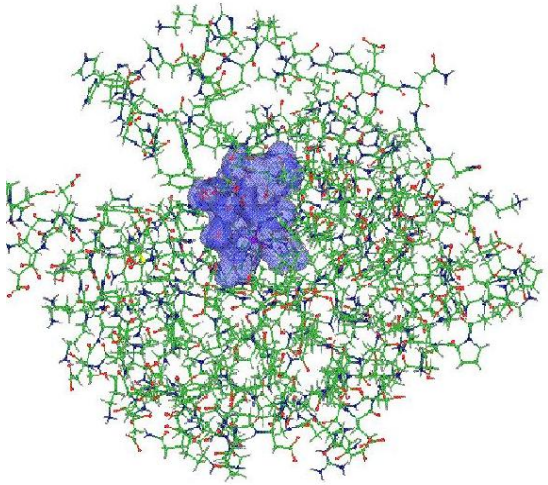
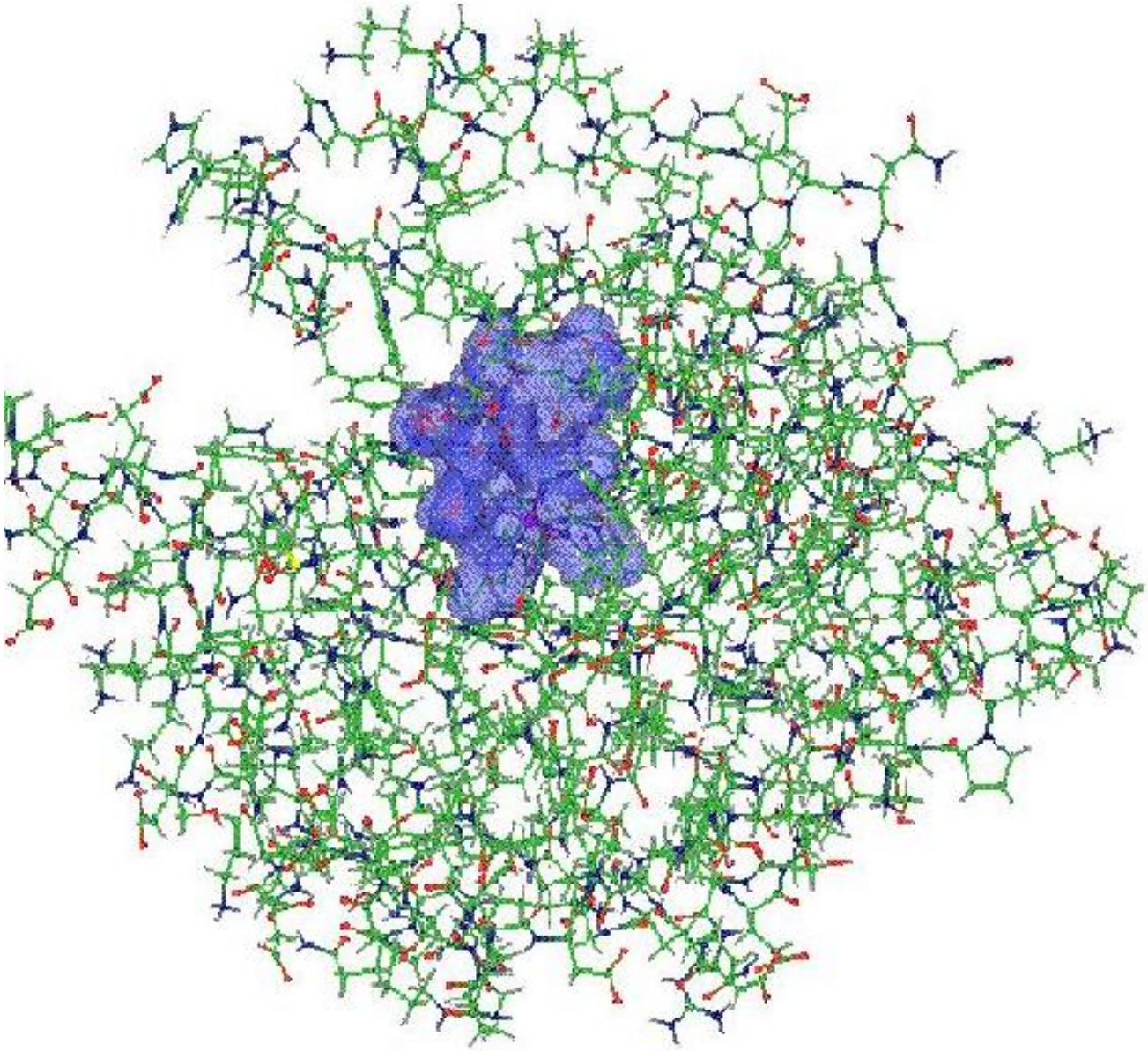


Chem Phys. Lett. (2006)
J. Chem. Phys. (2007)
Phys. Rev. B (2009)
Phys. Rev. Lett. (2009) submitted

Goal : Study complex heterogeneous interfaces



Characteristics of current models

Empirical Models: Fixed charge,
non-polarizable,
pair dispersion.

Ab Initio Models: GGA-DFT,
Self interaction present,
Dispersion absent.

Problems with current models

Dipole Polarizability : Including dipole polarizability changes solvation shells of ions and drives them to the surface.

Higher Polarizabilities: Quadrupolar and octapolar polarizabilities are NOT SMALL.

All Manybody Dispersion terms: Surface tensions and bulk properties determined using accurate pair potentials are incorrect. Surface tensions and bulk properties are both recovered using manybody dispersion and an accurate pair potential. An effective pair potential destroys surface properties but reproduces the bulk.

Force fields cannot treat chemical reactions:

Future Models

- All Polarizablities
- Many Body Dispersion
- Charge Transfer*

*New independent work by Mueser group and Martinez group.

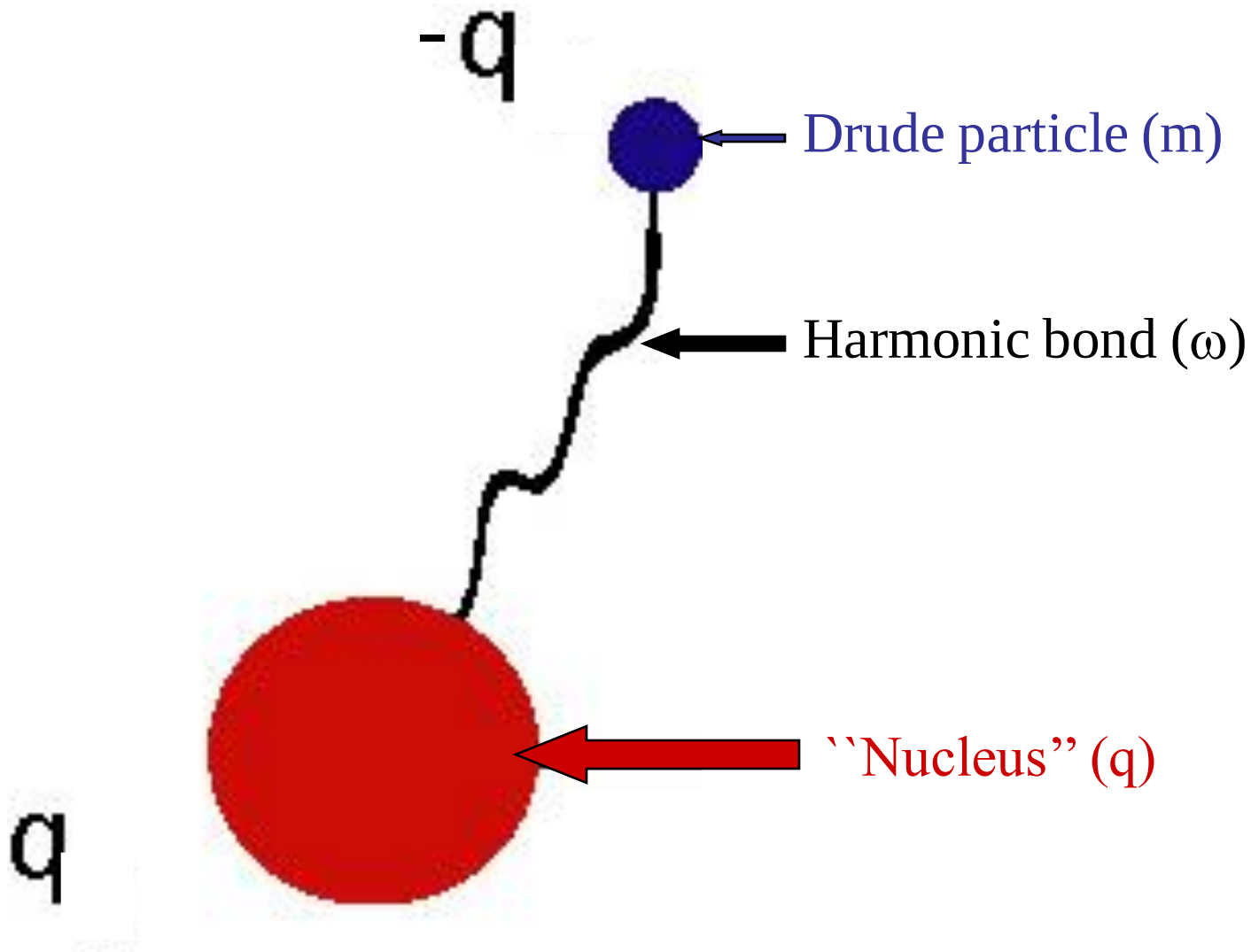
Future Solutions

Requirements : Simple in Concept and Application*

- Easy to Implement : Particle based approaches.
- Low Cost : Easy on the doo-dads.
- Efficient Solvers : Auxiliary Eqs. satisfied quickly.
- Sample Phase Space : Allow new techniques to be used.

**Restrict the discussion to insulators with no low lying albeit spatially localized electronic excited states.*

The Drude Oscillator Model



Model true response by a *harmonic* atom : Free parameters {m,q,ω}

Future Solution : The Drude model

One Solution : Back to the future!!

Drude model treated quantum mechanically.

Harmonic ``one-electron'' atoms. No Fermi statistics/sign problem!

Drude models are OLD:

Hirschfelder, Curtis and Bird : Quantum and classical theory.

Dick and Overhauser (1958); Cochran (1959) shell model.

Sangster and Dixon *Adv. Phys.* **25,** 247 (1976) : Review simulation.

Drude models are NEW/CURRENT/``IN''

P. Madden : Molten Salts (classical).

B. Roux : Biological systems (classical).

J. Cao and B.J. Berne : Lennard Jones (quantum dipole limit).

The work presented here (full quantum model).

Future Solutions : The Drude model

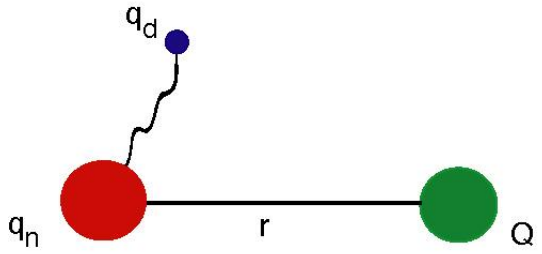
Types of Drude Models:

- Classical limit : Dipole Polarization only!
- Dipole limit quantum model : Dipole polarization, many body dipole dispersion.
- Full quantum model : All polarizabilities, all dispersion terms

Future Solutions: The Drude model

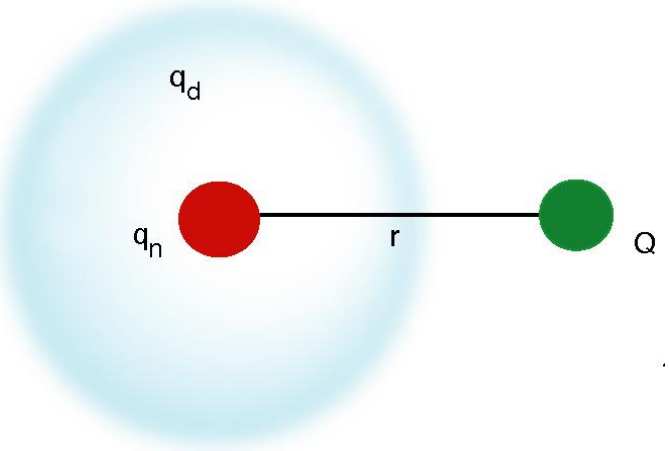
Classical Treatment: Charge-Polarizable Center

$$E_0(r) = -\frac{eQ\alpha_{\mathrm{dip}}}{2r^4} = -\frac{eQ\alpha_0}{2r^4}$$



Full Quantum Treatment: Charge-Polarizable Center

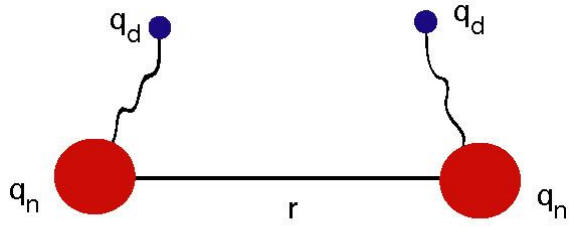
$$E_0(r) = -\sum_{k=0}^{\infty} \frac{eQ\alpha_k}{2r^{2k+4}}$$



Future Solutions: The Drude model

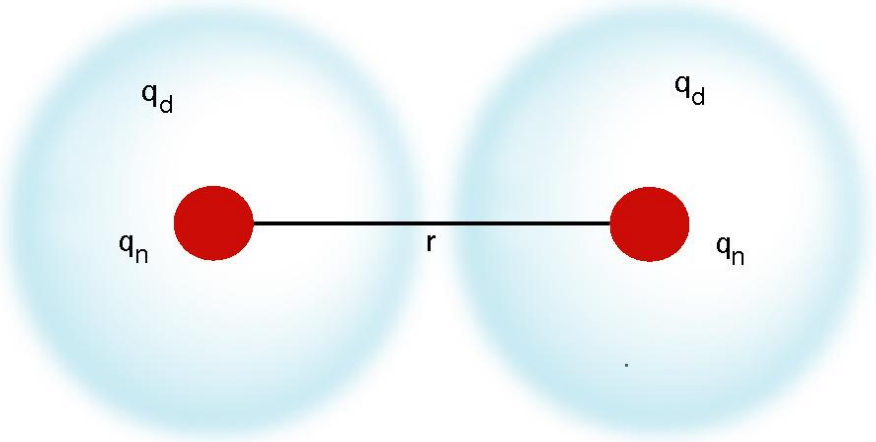
Classical Treatment: Polarizable Center-Polarizable Center

$$E_0(r) = 0$$



Full Quantum Treatment: Polarizable Center-Polarizable Center

$$E_0(r) = -\sum_{k=0}^{\infty} \frac{C_{2k+6}}{r^{2k+6}}$$



Future Solutions: The Quantum Drude model

Solving the Drude Model :

Our approach : Path Integral Molecular Dynamics (PIMD)

Computational Cost /Efficiency :

- “P” extra cites.
- Sampling phase space tricky.
- Dynamics?
- Calculating energy and pressure tricky.

Path Integral Form of the Quantum Drude Model

Discrete Path Integral Form :

$$\begin{aligned} Q(NVT) &= \mathrm{Tr}\ \exp(-\beta\hat{H}) = \mathrm{Tr}\ \hat{\rho}(\beta) \\ &= \int d\mathbf{r}_1 \ldots d\mathbf{r}_P\ \rho(\mathbf{r}_1, \mathbf{r}_2; \epsilon) \ldots \rho(\mathbf{r}_P, \mathbf{r}_1; \epsilon) \end{aligned}$$

where $\epsilon = \beta/P$.

In order to keep P small, a good approx. to $\rho(\mathbf{r}, \mathbf{r}'; \epsilon)$ is required:*

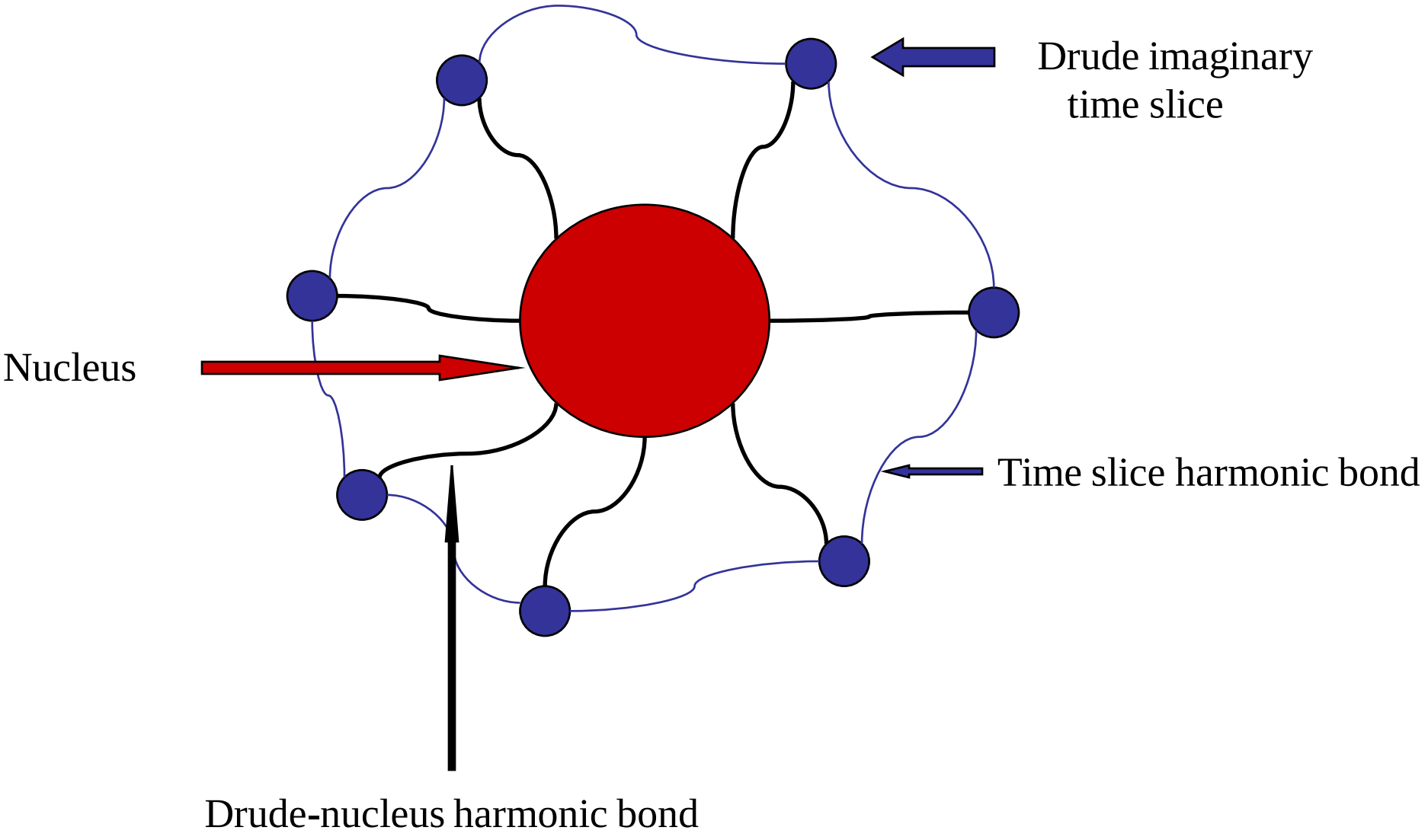
$$\rho(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon) = \rho^{(2nd)}(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon) + \mathcal{O}(\epsilon^3)$$

$$\begin{aligned} \rho^{(2nd)}(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon) &= \left\langle \mathbf{r}_i \left| e^{-\epsilon\phi^{(ext)}/2} e^{-\epsilon H_{HO}} e^{-\epsilon\phi^{(ext)}/2} \right| \mathbf{r}_{i+1} \right\rangle \\ &= \rho^{(HO)}(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon) \exp(-\epsilon[\phi^{(ext)}(\mathbf{r}_i) + \phi^{(ext)}(\mathbf{r}_{i+1})]/2) \end{aligned}$$

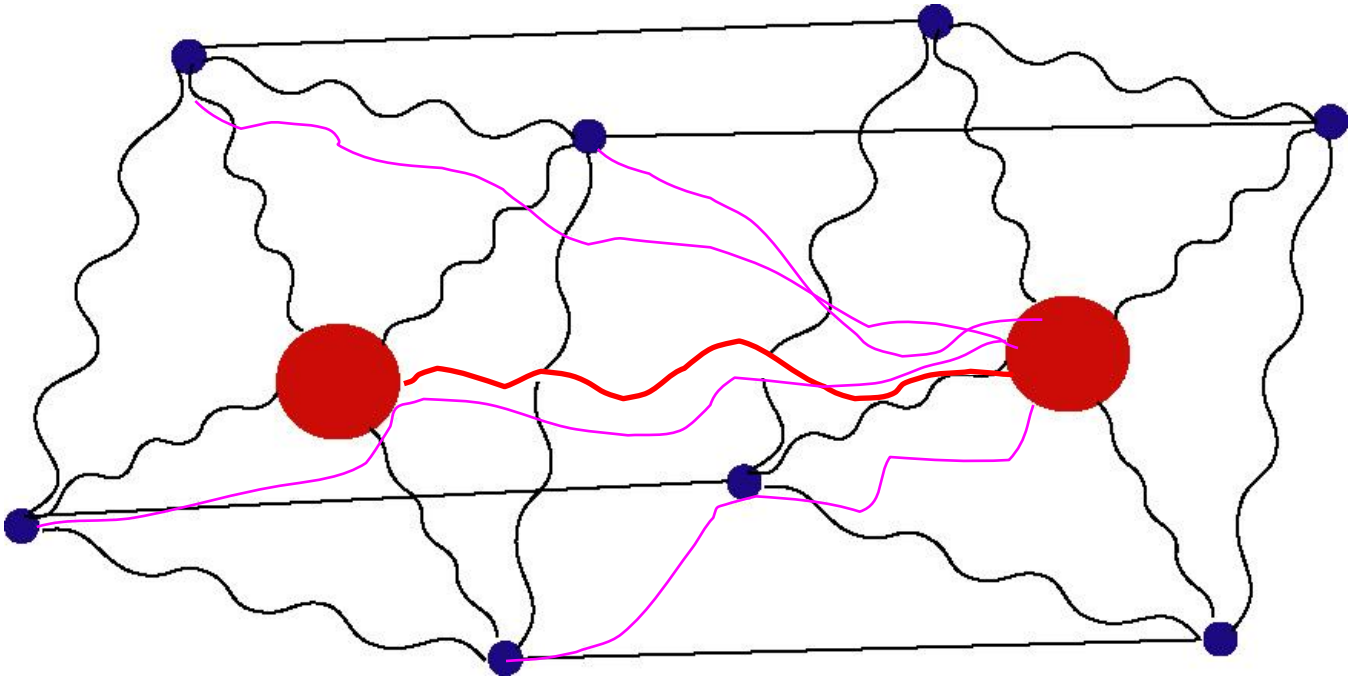
$$\begin{aligned} \rho^{(HO)}(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon) &= \left[\frac{m\omega}{2\pi\hbar \sinh(\epsilon\hbar\omega)}\right]^{3/2} \\ &\times \exp\left(-\left[\frac{m\omega}{2\hbar \sinh(\epsilon\hbar\omega)}\right]\left[\cosh(\epsilon\hbar\omega)(\mathbf{r}_i^2 + \mathbf{r}_{i+1}^2) - 2\mathbf{r}_i\mathbf{r}_{i+1}\right]\right) \end{aligned}$$

*Improved propagators needed!

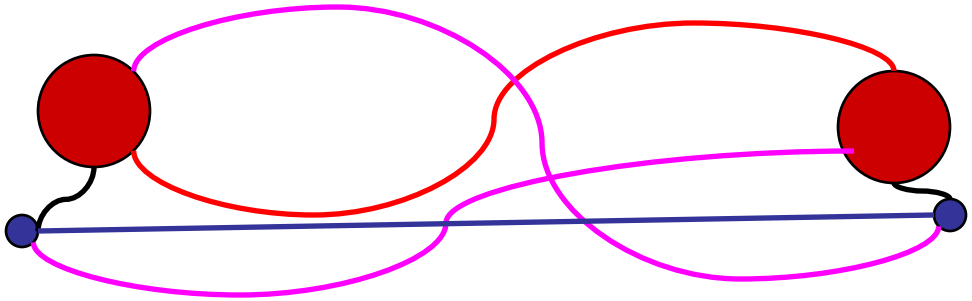
Drude Model as a Path Integral : P=6



Two Interacting Drude Oscillators : P=4



Classical Limit :



Due to time slice to time slice intermolecular interactions the computational cost only increases by factor of P.

Coupling the Drude Model to the Nuclear Motion

Dynamics :

•Drude Oscillators are fast and remain in the ground state. Work in the B.O. approximation.

• The dynamics is just nuclear motion on the ground state energy surface provided by the Drude Oscillators.

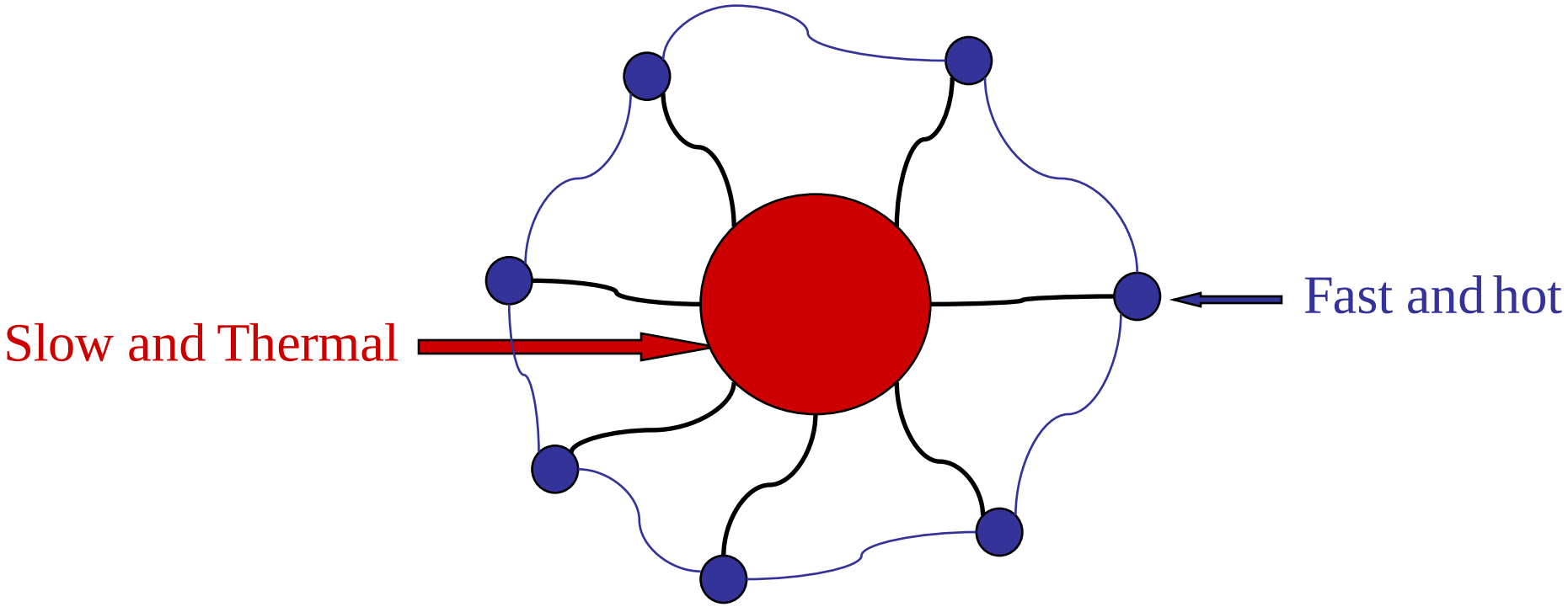
• In the B.O. approximation, the temperature of the Drude particles is artificial. Choose it such that $\hbar\omega / kT_{Drude}$ >> 1

•Move the Drude degrees of freedom rapidly at $T_{Drude.}$ Use an adiabatic principle to generate the results.

The Model

Summary:

- ``P'' realizations/beads of blue Drude particles are introduced.
- The blue beads are moving fast compared to red nuclei.
- The blue beads are at an elevated temperature.



Assessment of the Quantum Drude model

Computational Cost :

- "P" more force evaluations easily parallelized.
- An adiabatic separations if required. Use multiple time step (MTS) methods.
- Two temperatures are required. Use NVT-MD methods.

Modern Simulation Techniques can handle the model **PROVIDED …**

Assessment of the Quantum Drude model

- The extra degrees of freddom can be sampled efficiently.
- Good estimators for the energy can be derived.

Assessment of the Quantum Drude model

Energy estimators:

- Energy of the oscillators is HUGE (electronic scale).
- The energy of interest ($E_{tot} - E_{vac}$) is small compared to E_{vac}.
- Standard energy estimators will have HUGE variance.

Low variance estimators for the Quantum Drude model

The approximate partion function is

$$Q_P(NVT) = \int d\mathbf{r}_1 \ldots d\mathbf{r}_P \exp[-\epsilon \sum_k \phi^{(ext)}(\mathbf{r}_k)] \times \prod_{i=1}^{P} \rho^{(HO)}(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon)$$

$$\rho^{(HO)}(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon) = \left\langle \mathbf{r}_i \left| e^{-H_{HO}} \right| \mathbf{r}_{i+1} \right\rangle$$

where $\mathbf{r}_{P+1} = \mathbf{r}_1$.

Introducing the identity

$$\prod_{i=1}^{P} \rho^{(HO)}(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon) = \rho^{(HO)}(\mathbf{r}_1, \mathbf{r}_1; \beta) \times \prod_{k=2}^{P} \left[\frac{\rho^{(HO)}(\mathbf{r}_1, \mathbf{r}_k; (k-1)\epsilon) \rho^{(HO)}(\mathbf{r}_k, \mathbf{r}_{k+1}; \epsilon)}{\rho^{(HO)}(\mathbf{r}_1, \mathbf{r}_{k+1}; k\epsilon)} \right]$$

Low variance estimators for the Quantum Drude model

For Quadratic Propagators

$$\prod_{k=2}^{P} \frac{\rho^{(HO)}(\mathbf{r}_1, \mathbf{r}_k; (k-1)\epsilon)\rho^{(HO)}(\mathbf{r}_k, \mathbf{r}_{k+1}; \epsilon)}{\rho^{(HO)}(\mathbf{r}_1, \mathbf{r}_{k+1}; k\epsilon)} = \prod_{k=2}^{P} \left[\frac{1}{2\pi\sigma_k^2}\right]^{3/2} e^{-(\mathbf{r}_k - \mathbf{r}_k^*)^2/(2\sigma_k^2)}$$

This defines a natural linear coordinate transformation

$$\begin{aligned} \mathbf{u}_1 &= \mathbf{r}_1 \\ \mathbf{u}_k &= \mathbf{r}_k - \mathbf{r}_k^* \end{aligned}$$

with unit Jacobean.

In the new variables, it can be shown that

$$\begin{aligned} \left\langle \frac{m\omega^2 \mathbf{r}_1^2}{2} \right\rangle &= \left\langle \frac{m\omega^2 \mathbf{u}_1^2}{2} \right\rangle \\ &= \frac{3\hbar\omega}{4\tanh(\beta\hbar\omega/2)} - \frac{m\omega^2}{2} \left\langle \phi^{(corr)} \right\rangle \end{aligned}$$

where

$$\phi^{(corr)} = \frac{1}{P} \sum_k c_k \mathbf{r}_1 \cdot \nabla \phi^{(ext)}(\mathbf{r}_k)$$

Low variance energy estimator

Internal energy for liquid xenon at 210K.

Property	Virial estimator	Transformed virial estimator
E_{tot}/k (Kelvin)	-1100 ± 400	-1300 ± 8

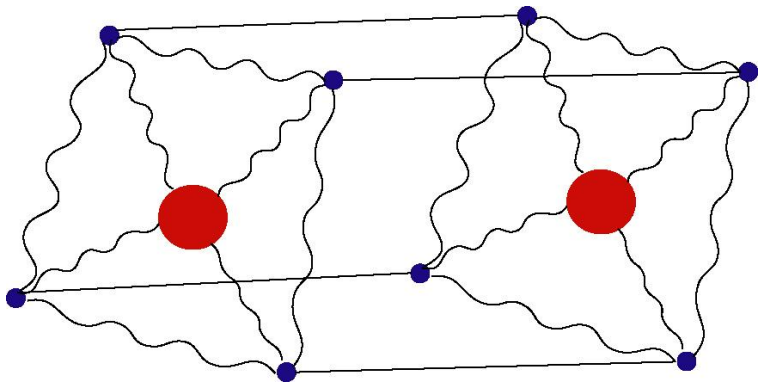
New energy estimator saves three orders of magnitude in CPU time.

The Quantum Drude model : Sampling

- Only the canonical ensemble is meaningful: Use ``massive NHC method or more modern NVT-MD methods.

- High frequency of oscillators : Use MTS integrators.

- Broad frequency spectrum : Introduce momentum conjugate to staging variables (u) and choose masses to equalize frequencies.



The Quantum Drude model : Sampling

Use the staging transformation to diagonalize the harmonic part and introduce ``P'' Gaussian degrees of freedom.

$$
\begin{aligned}
Q_P(NVT) &= \int d\mathbf{r}_1 \ldots d\mathbf{r}_P \exp[-\epsilon \sum_k \phi^{(ext)}(\mathbf{r}_k)] \\
&\quad \times \prod_{i=1}^{P} \rho^{(HO)}(\mathbf{r}_i, \mathbf{r}_{i+1}; \epsilon) \\
&= \int d\mathbf{u}_1 \ldots d\mathbf{u}_P \exp[-\epsilon \sum_k \phi^{(ext)}(\mathbf{r}_k(\mathbf{U}))] \\
&\quad \times \rho^{(HO)}(\mathbf{u}_1, \mathbf{u}_1; \beta) \prod_{k=2}^{P} \left[\frac{1}{2\pi\sigma_k^2}\right]^{3/2} e^{-(\mathbf{u}_k)^2/(2\sigma_k^2)} \\
&= C(\bar{m}) \int d\bar{\mathbf{p}}_1 \ldots d\bar{\mathbf{p}}_P \int d\mathbf{u}_1 \ldots d\mathbf{u}_P \exp[-\beta H_{eff}(\mathbf{U}, \bar{\mathbf{P}})]
\end{aligned}
$$

where an effective classical Hamiltonian is, now, defined

$$
\begin{aligned}
H_{eff}(\mathbf{U}, \bar{\mathbf{P}}) &= \sum_{k=1}^{P} \frac{\bar{\mathbf{p}}_k^2}{2\bar{m}_k} + \frac{1}{P} \sum_{k=1}^{P} \phi^{(ext)}(\mathbf{r}_k(\mathbf{U})) \\
&\quad + \sum_{k=2}^{P} \frac{\mathbf{u}_k^2}{2\beta\sigma_k^2} + \frac{m\omega \tanh(\beta\hbar\omega/2)\mathbf{u}_1^2}{\hbar\beta}
\end{aligned}
$$

The Quantum Drude model : Sampling

Use the free parameters to equalize the frequencies:

The fictitious masses are free parameters that can be chosen to narrow the frequency spectrum

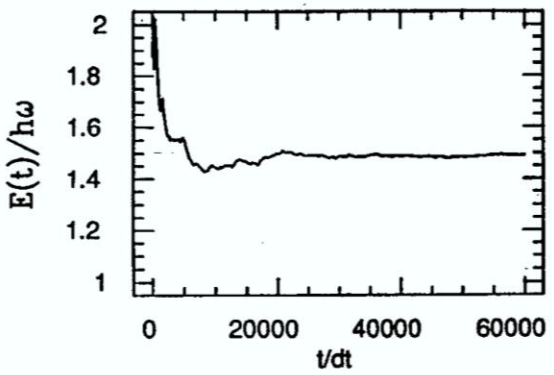
$$\bar{m}_1 = \frac{2m\omega \tanh(\beta\hbar\omega/2)}{\beta\hbar\omega_0^2}$$

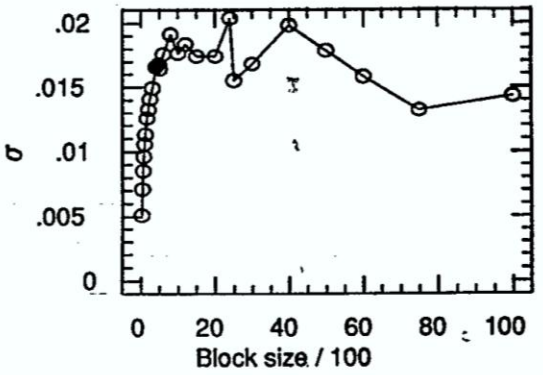
$$\bar{m}_k = \frac{1}{\beta\sigma_k^2\omega_0^2} \qquad k = 2...P$$

where ζ_0 is the single frequency present in the pseudo-dynamics if the external potential is zero/off.

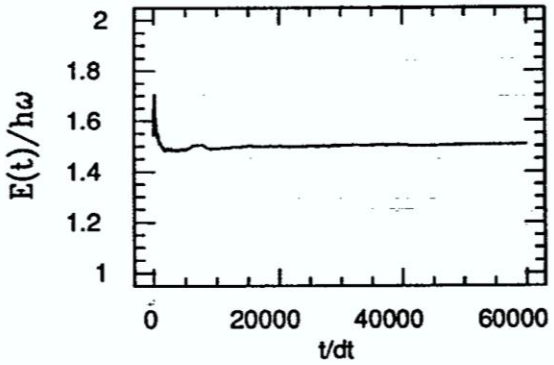
Efficient sampling of harmonic oscillator

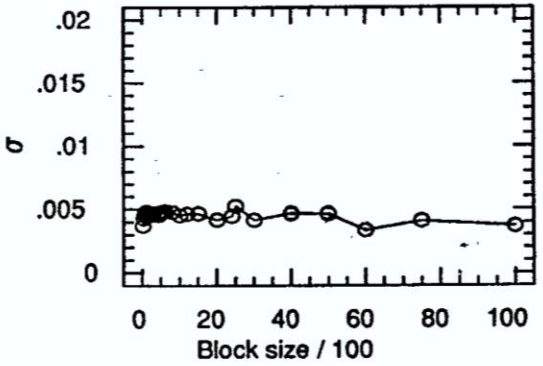
MTS-NHC-MD-NO_STAGING



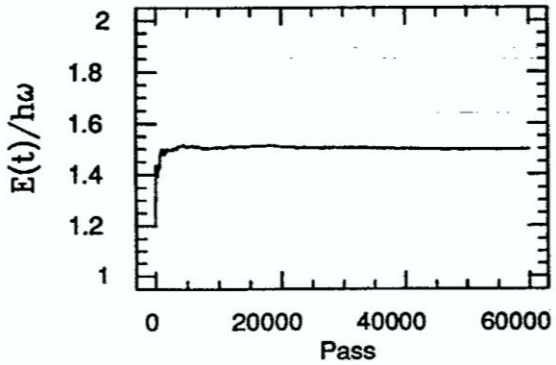


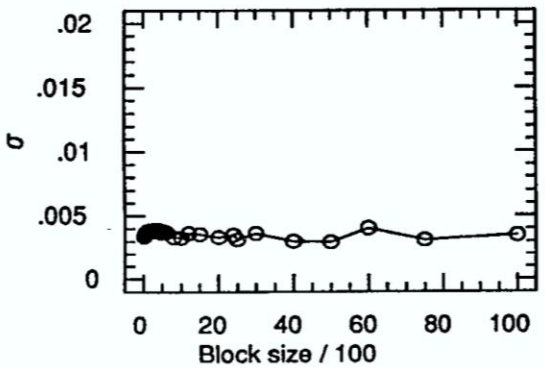
MTS-NHC-MD-STAGING





MC-STAGING





Efficiency gain : **5x** from MTS : **20x** from Staging → **100x**

Without "Massive" NHC no convergence!

The Quantum Drude model : Predictions

Dispersion Coefs : Gaussian Statistics

$$C_6^{(A-A)} = \frac{3\hbar\omega_A}{4}[\alpha_{dip}^{(A)}]^2$$

$$C_8^{(A-A)} = [5C_6^{(A-A)}]\left[\frac{\hbar}{m\omega_A}\right]$$

$$C_{10}^{(A-A)} = \left[\frac{245C_6^{(A-A)}}{8}\right]\left[\frac{\hbar}{m\omega_A}\right]^2$$

$$C_9^{(A-A-A)} = \left[\frac{C_6^{(A-A)}}{4}\right]\alpha_{dip}^{(A)}$$

$$C_6^{(A-B)} = \left[\frac{3\hbar\omega_A\omega_B}{2(\omega_A+\omega_B)}\right]\left[\alpha_{dip}^{(A)}\alpha_{dip}^{(B)}\right]$$

The Quantum Drude model : Predictions

Polarizabilities : Gaussian Statistics

$$\alpha_{dip} = \frac{\delta_q^2}{m\omega^2}$$

$$\alpha_{quad} = \left[\frac{3\alpha_{dip}}{4}\right]\left[\frac{\hbar}{m\omega}\right]$$

$$\alpha_{oct} = \left[\frac{5\alpha_{dip}}{4}\right]\left[\frac{\hbar}{m\omega}\right]^2$$

The Quantum Drude model : Predictions

Generalized combining rule:

$$R = \frac{7C_8}{2\sqrt{5C_6C_{10}}} = 1$$

Atom	R	Percent Error
He	0.98	2
Ne	0.97	3
Ar	0.98	2
Kr	1.02	2
Xe	1.03	3

Tang, Norbeck, Certain, J. Chem. Phys. (1976)

The Quantum Drude model : Predictions

Generalized mixed combining rule:

$$R = \left[\frac{1}{C_6^{(A-B)}}\right]\left[\frac{2C_6^{(A-A)}C_6^{(B-B)}\alpha_{dip}^{(A)}\alpha_{dip}^{(B)}}{C_6^{(A-A)}(\alpha_{dip}^{(B)})^2 + C_6^{(B-B)}(\alpha_{dip}^{(A)})^2}\right] = 1$$

A	B	R	Percent Error
He	Ne	1.02	2
He	Ar	1.01	1
He	Kr	1.03	3
He	Xe	1.04	4
Ne	Ar	0.99	1
Ne	Kr	0.98	2
Ne	Xe	1.06	6
Ar	Kr	1.00	0
Ar	Xe	1.03	3
Kr	Xe	1.01	1

Tang, Norbeck, Certain, J. Chem. Phys. (1976)

The Quantum Drude model : Predictions

Generalized 3-body combining rule:

$$R = \frac{C_6^{(A-A)} \alpha_{dip}^{(A-A)}}{4 C_9^{(A-A-A)}} = 1$$

Atom	R	Percent Error
He	1.02	2
Ne	1.07	7
Ar	1.06	6
Kr	1.06	6
Xe	1.05	5

Tang, Norbeck, Certain, J. Chem. Phys. (1976)

The Quantum Drude model : Predictions

Generalized polarizability combining rule:

$$R = \frac{2\sqrt{5}\alpha_{quad}}{3\left[\alpha_{dip}\alpha_{oct}\right]^{1/2}} = 1$$

Atom	R	Percent Error
He	0.98	2
Ne	1.06	6
Ar	1.02	2
Kr	1.10	10
Xe	1.10	10

Tang, Norbeck, Certain, J. Chem. Phys. (1976)

Fitting parameters from experimental polarizabilities and dispersion coefficients

$q = 1.357$
$m = 0.2541$
$\omega = 0.5152$

Quantity	Value	Target	Bounds	Percent Deviation
α_{dip}	27.30	27.3		0.0
α_{quad}	156.41	212.6		26.0
α_{oct}	1991.30	3602.0		44.7
C_6	288.00	288.0	(272-325)	0.0
C_8	11000.00	11000.0	(8900-13900)	0.0
C_{10}	514670.13	660000.0	(428000-675000)	22.0

$q = 1.2086$
$m = 0.2456$
$\omega = 0.4583$

Quantity	Value	Target	Bounds	Percent Deviation
α_{dip}	28.31	27.3		3.7
α_{quad}	188.60	212.6		11.2
α_{oct}	2792.19	3602.0		22.5
C_6	275.47	288.0	(272-325)	4.4
C_8	12234.81	11000.0	(8900-13900)	11.2
C_{10}	665669.44	660000.0	(428000-675000)	0.9

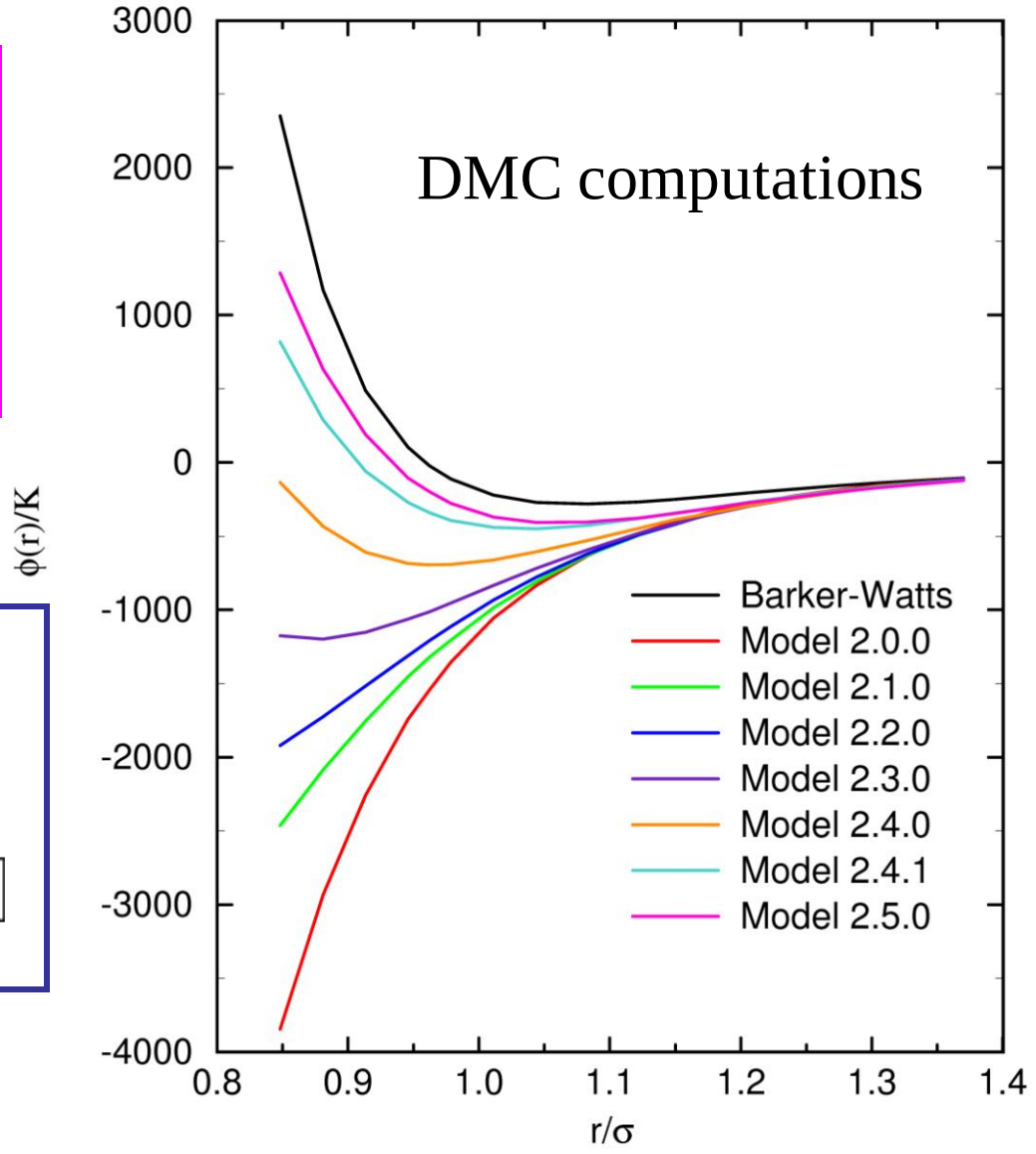
Choosing a damping for the Coulomb interaction

Particles interact with a **damped** Coulombic form:

$$\phi_{\eta\nu}(r_{ij}) = q_i q_j f_{\eta\nu}(r_{ij})/r_{ij}$$

The damping should approach unity/zero for big/small arguments:

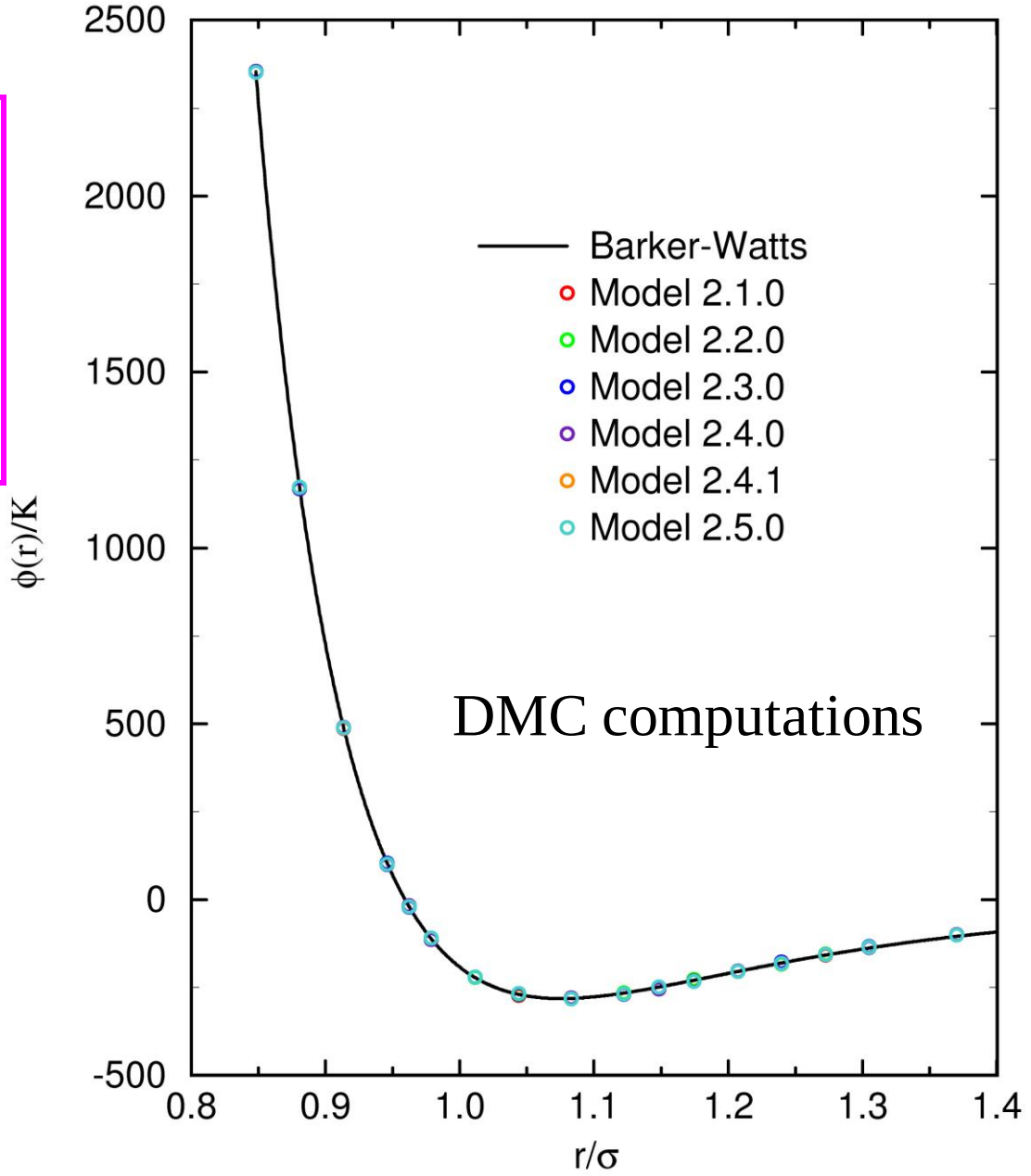
$$f_{\eta\nu}(r_{ij}) = 1 - \exp[-(r_{ij}/\gamma_{\eta\nu})^4]$$



Fitting repulsion to a pair potentials

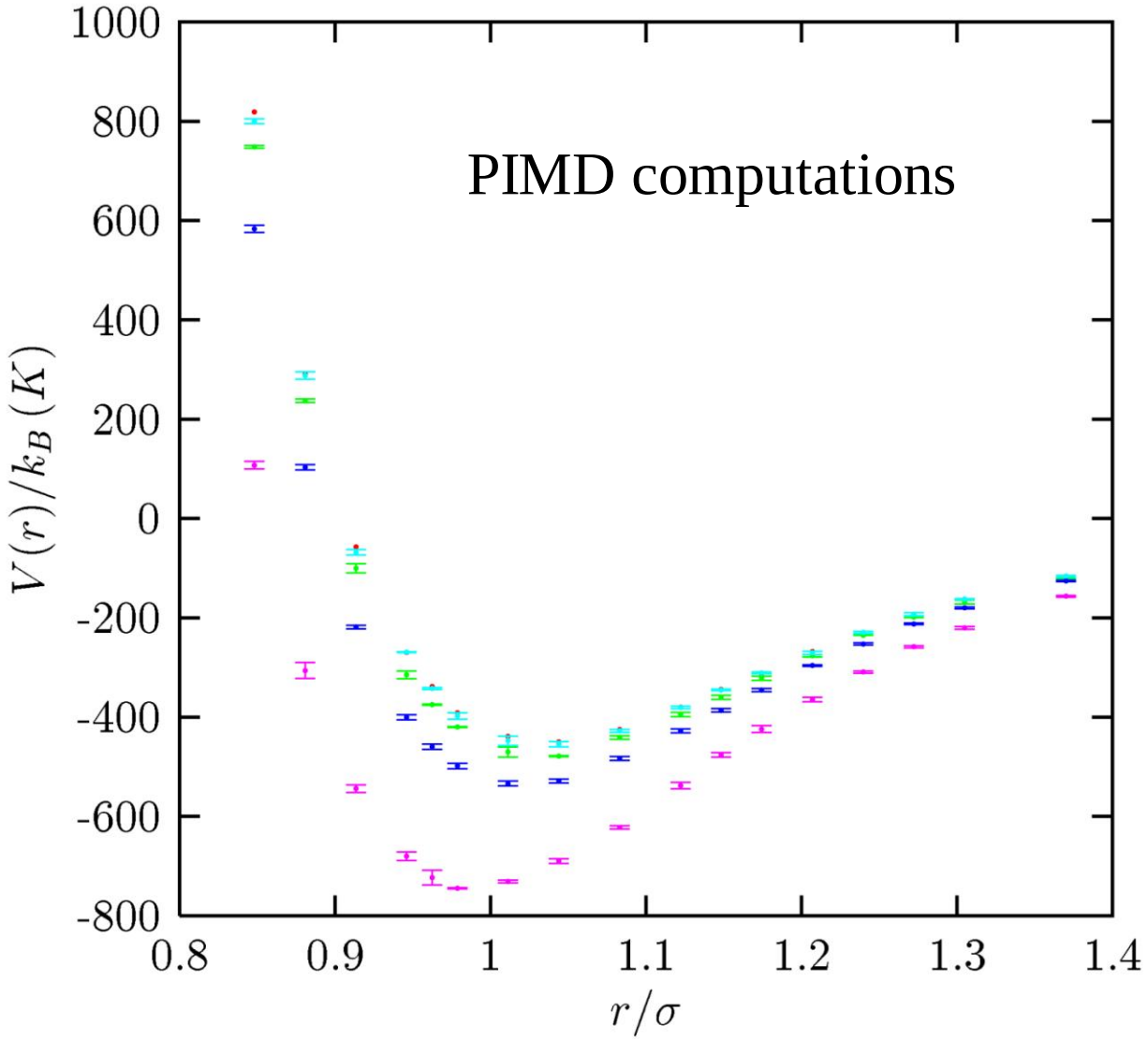
An accurate pair potential* used to fit repulsive wall:

$$v_{\mathrm{rep}}(r) = \sum_{k=1}^{3} A_k \exp[-\alpha_k r]$$



*JA Barker et al JCP **61**, 3081 (1974).

Convergence for xenon dimer surface with P

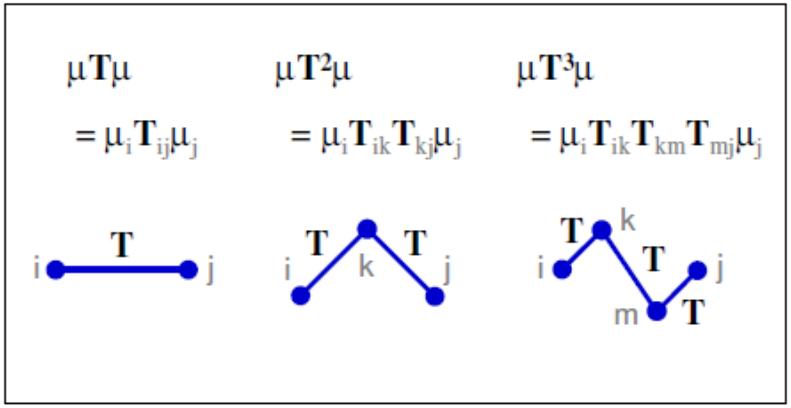


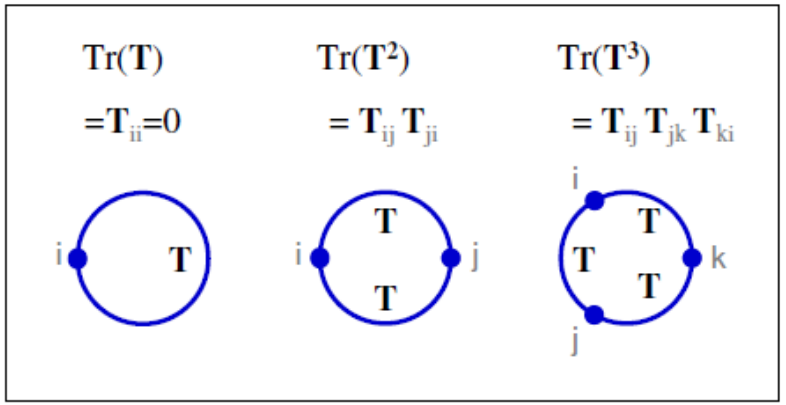
Drude model xenon dimer energies from Diffusion Monte Carlo (red) and PIMD with P=20 (magenta), P=40 (blue), P=80 (green) and P=160 (cyan).

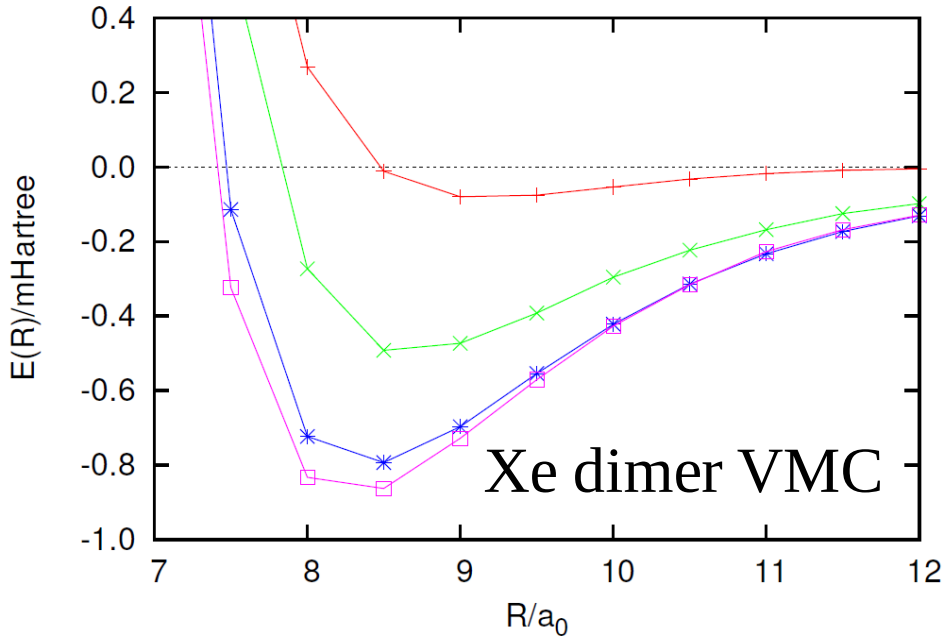
Improving Performance with P

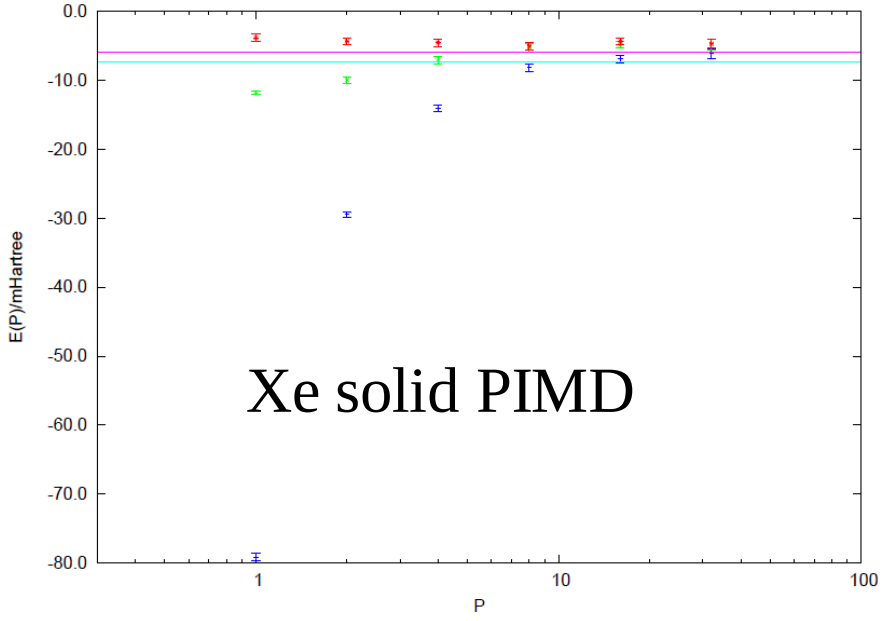
- Use the dipole limit as a reference system about which to build new high temperature approximations.
- Develop a simple diagramatic expansion to avoid diagonalization of large matrices.
- Develop pair density matrices for harmonic oscialltors interacting with coulomb scatterers.
- New results suggest P=20 is possible.

Improved trial functions for DMC and propagators for PIMD

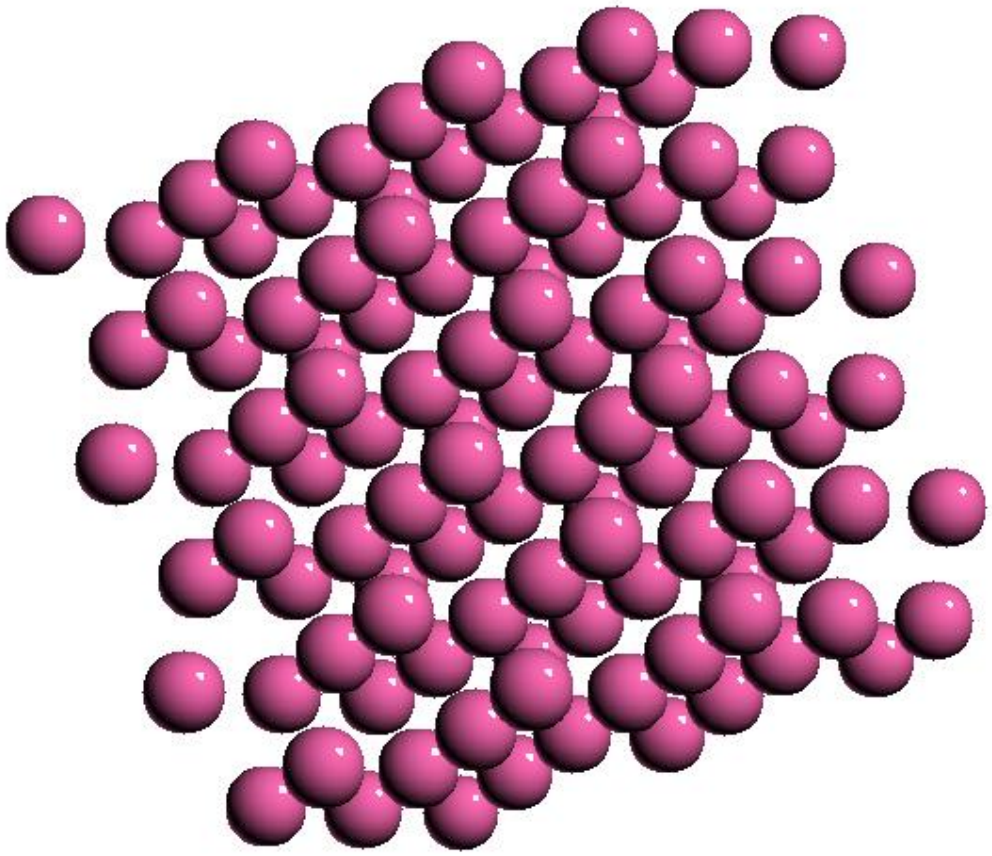






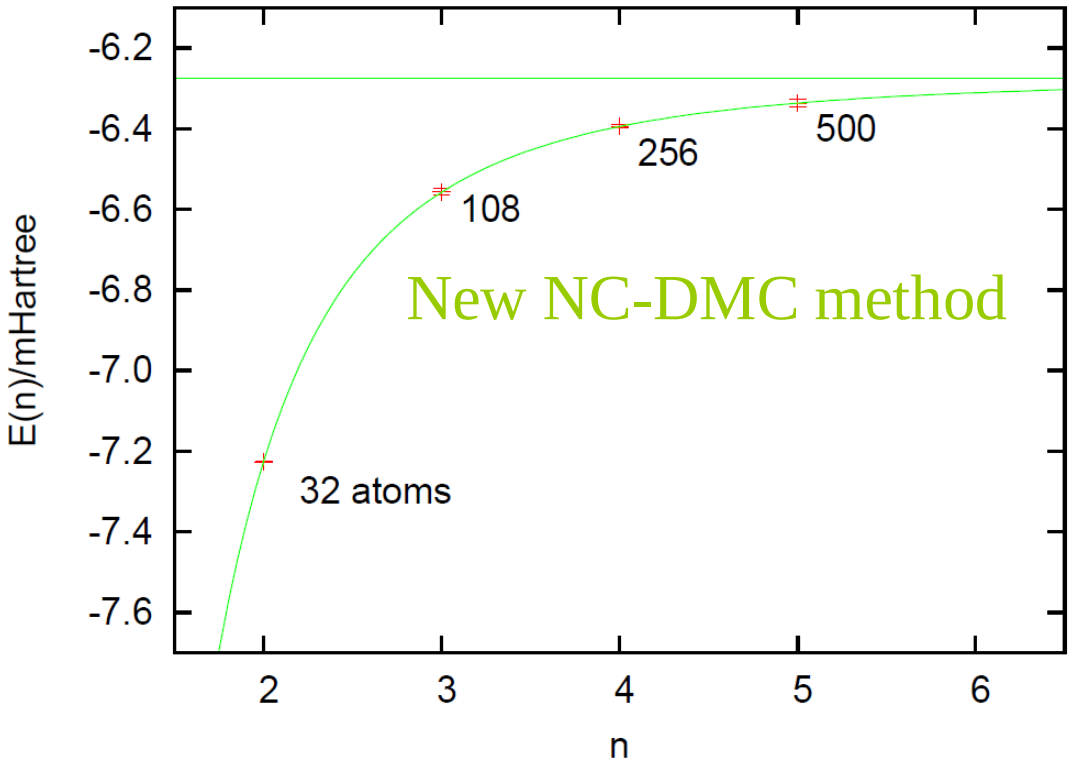


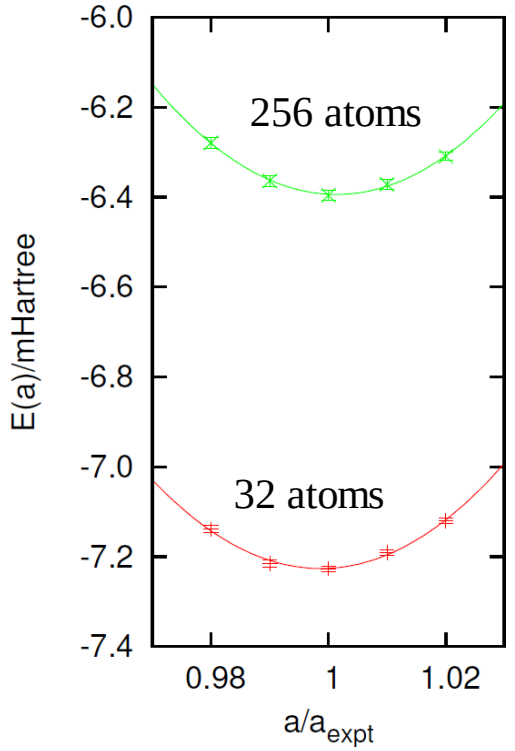
Application to solid xenon



Finite size effects

Quantum Drude model converges to experimental cohesive energy - after accounting for finite size effects - for N > 500 atoms.





E = -6.27mH/atm + 0.2mH/atm = -6.07mH/atm : exp. -6.05mH/atm

φ = 4.0GPa – 0.3GPa = 3.7GPa : exp. 3.64GPa

Comparison with classical pair models:

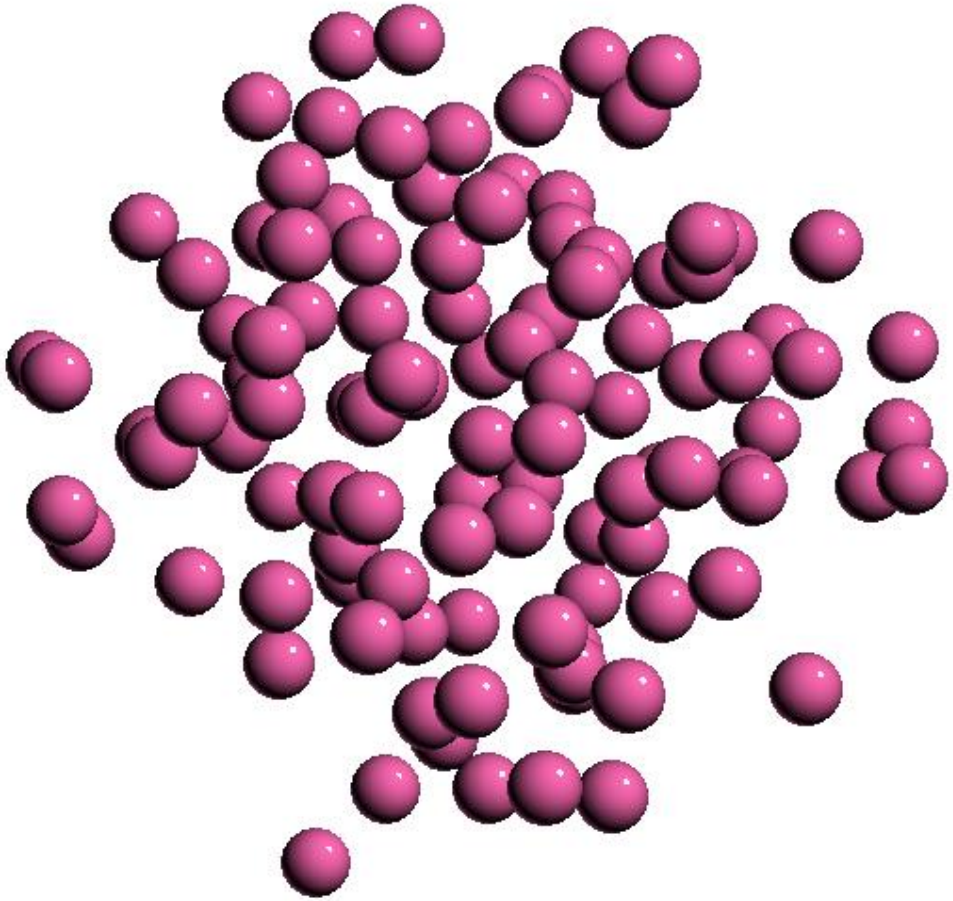
I.) Cohesive energy at the experimental lattice constant:

Property	Experiment	BW
Nearest-neighbour distance ($\AA$)	4.3357	
Cohesive energy (cal/mole)	-3910 $\pm$ 20	-4288
Pressure (bar)		-1546
Property	($\sigma = 4.055\AA$)	LJ
Nearest-neighbour distance ($\AA$)	4.3357	
Cohesive energy (cal/mole)	-3910 $\pm$ 20	-3857
Pressure (bar)		2624

II.) Cohesive energy at the zero pressure lattice constant:

Property	($\sigma = 4.055\AA$)	LJ
Nearest-neighbour distance ($\AA$)	4.3357	4.4208
Cohesive energy (cal/mole)	-3910$\pm$20	–3917
Pressure (bar)		0

Application to fluid xenon



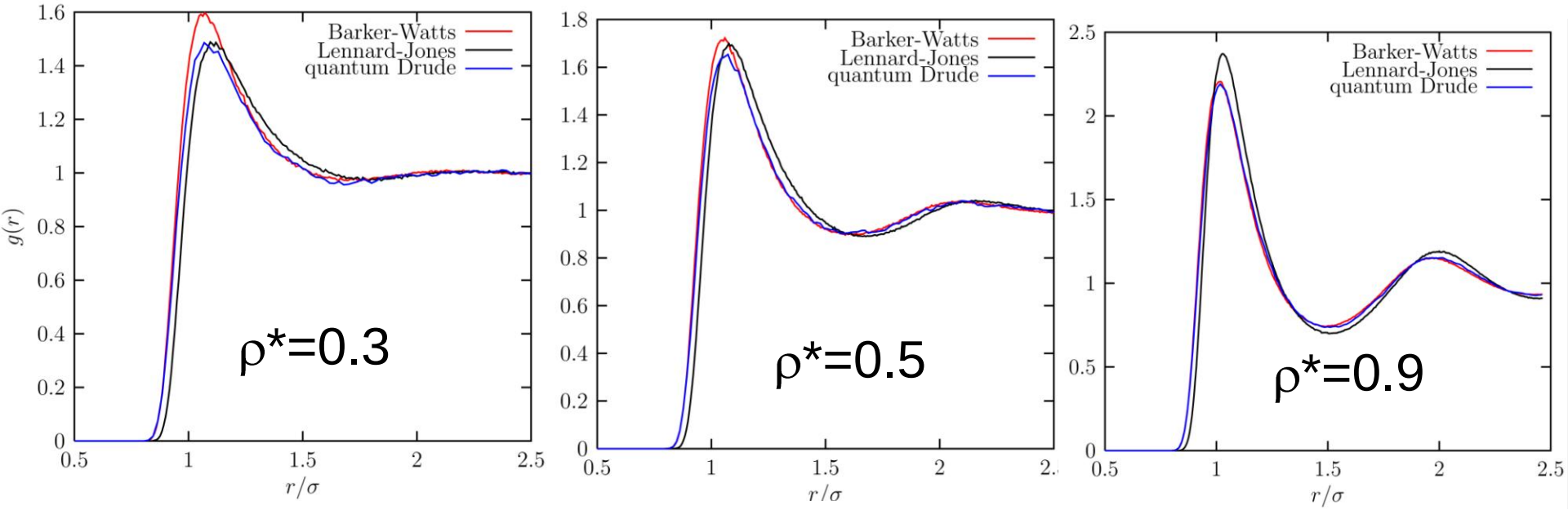
Adiabaticity study of the quantum Drude model: Fluid xenon

Property	Experiment	$m_n = 100$	$m_n = 200$	$m_n = 400$
Pressure (bar)		-90 ± 80	-30 ± 50	-100 ± 90
Potential Energy/k_B (K)		-1490 ± 30	-1510 ± 30	-1490 ± 30
T_n	210	210 ± 2	210 ± 2	208 ± 2
T_D	16,268	$16,263 \pm 4$	$16,266 \pm 4$	$16,266 \pm 4$

Fluid xenon at 210K using P=80* pseudoparticles: The parameter ``m_n'' is ratio of nuclear particle mass to the Drude particle mass.

*New propagators : P=20.

Many-body effects on the structure of fluid xenon at T=610K

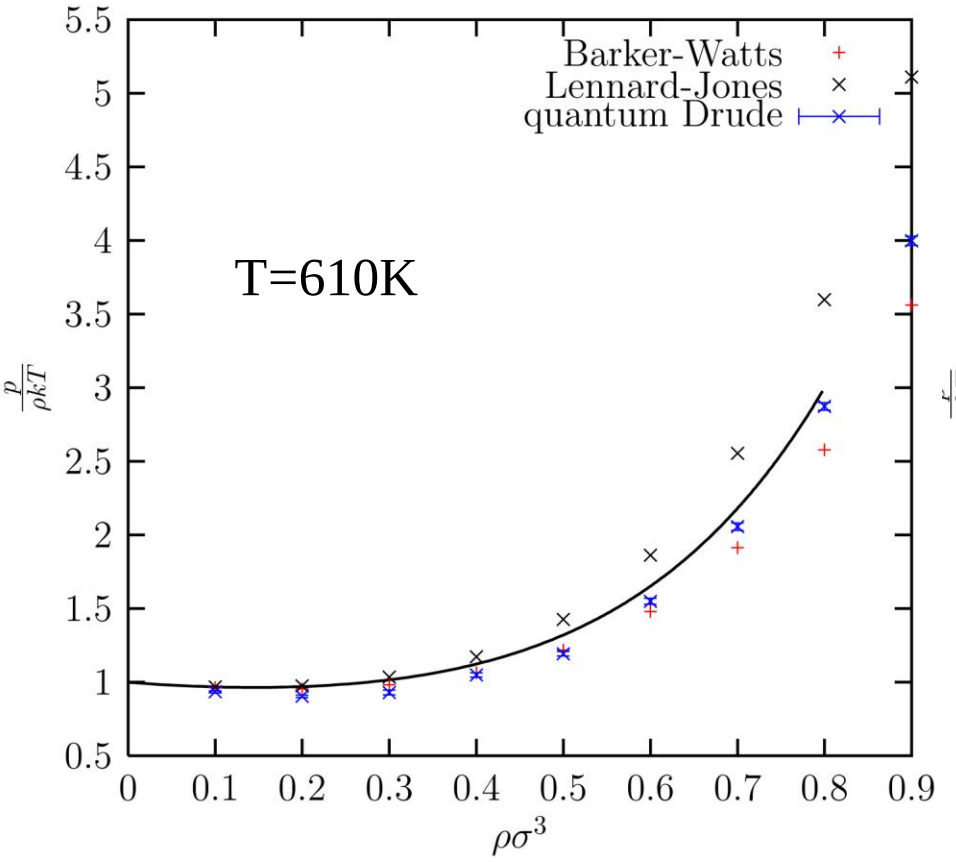


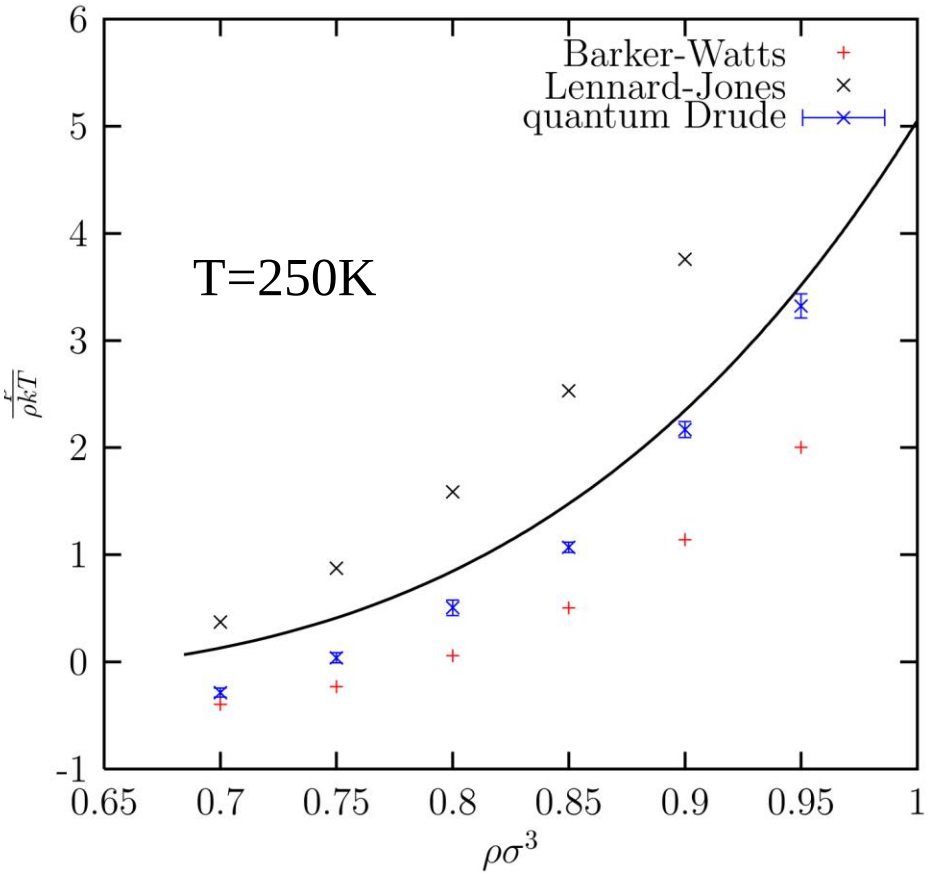
Gas phase pair potential over-structures the fluid at low density

Effective pair potential over-structures the fluid at high density!

Quantum drude model is just right!

Isotherms of fluid xenon



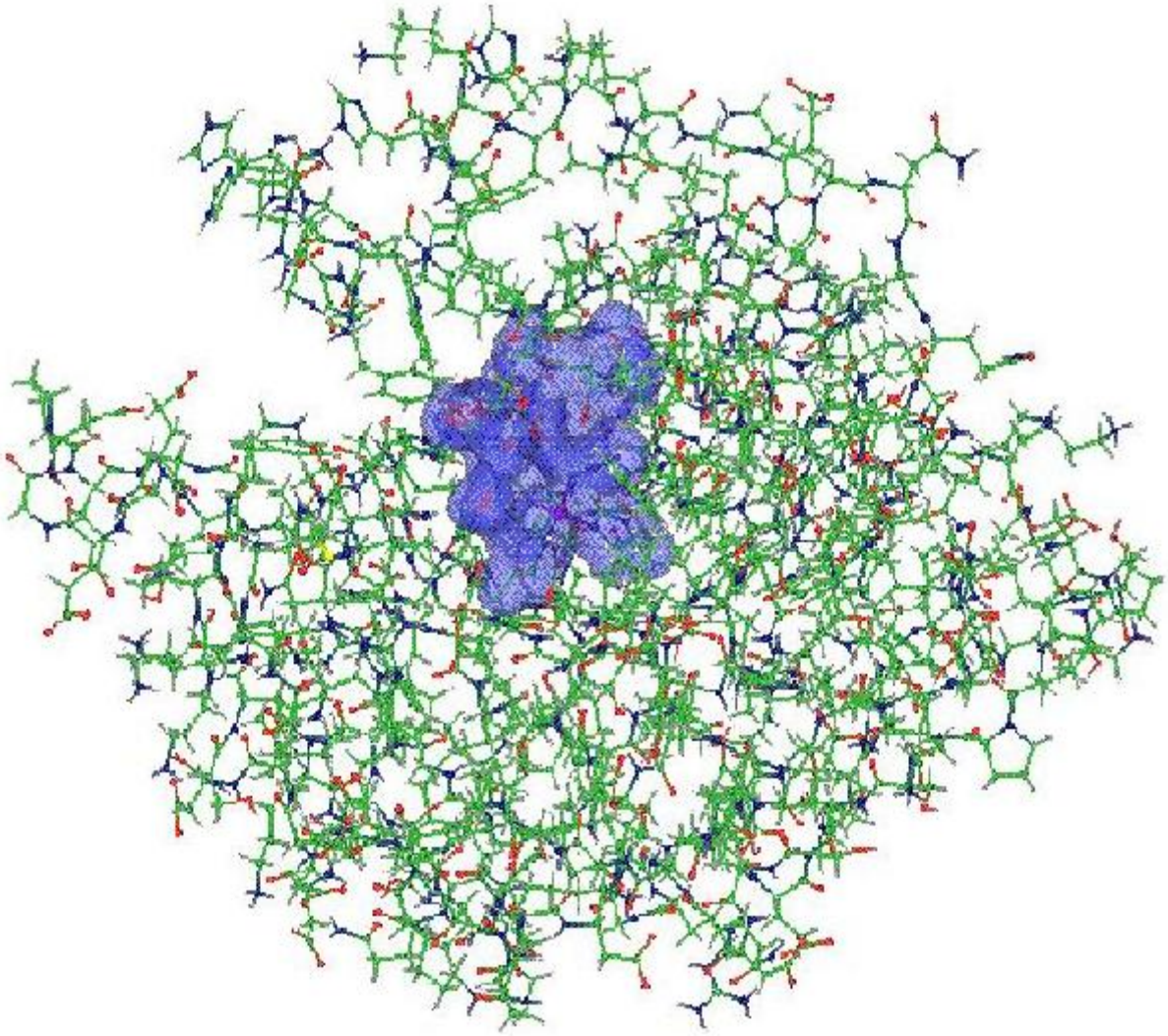


Gas phase pair potential over-bound at high density!

Effective potential under-bound at high density!

Quantum drude oscillator just right!

Progress Towards Modeling Complex Interfaces



Summary and Conclusion

- Quantum Drude Model provides a complete description of many body long range forces.

- Quantum Drude Model can be simulation using PIMD techniques with high efficiency.

- Using the Quantum Drude Model, force field designers can fit intermediate and short range forces while maintaining many body long range forces by construction.

- We are currently porting our high T approxs. and trial wavefunctions to water, finally.