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MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO) 17 May 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-119**
Jerry Boatz (PRSP), "Design of New Materials Using CCM – Materials by Design CHSSI Portfolio" (Viewgraphs)

DoD Users Group Conference **(Statement A)**
(Austin, TX, 10-14 June 2002) **(Deadline: 07 June 2002)**

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
Comments:_____

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Comments:_____

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Comments:_____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division

Design of New Materials Using CCM

Materials by Design CHSSI Portfolio - 01

DoD UGC, 10-14 Jun 02

Austin, TX

Jerry Boatz

Senior Research Chemist

Propulsion Directorate

Air Force Research Laboratory

(cc) 02-118

Materials by Design - 01

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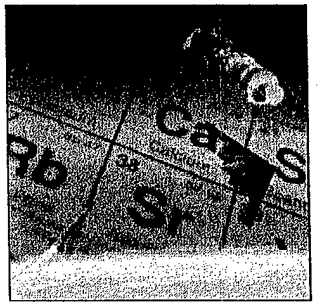
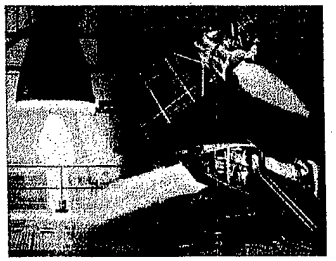


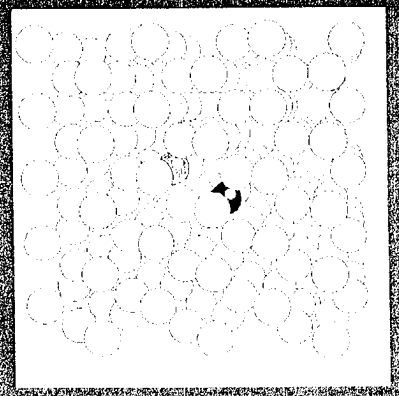
Dr. Jerry Boatz, AFRL/PRSP

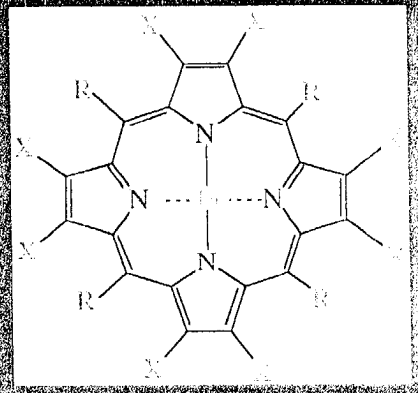


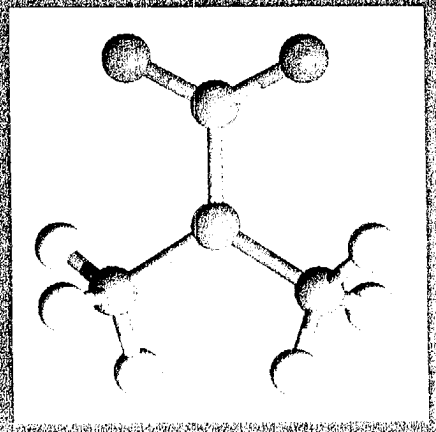
MBD-01: Goal

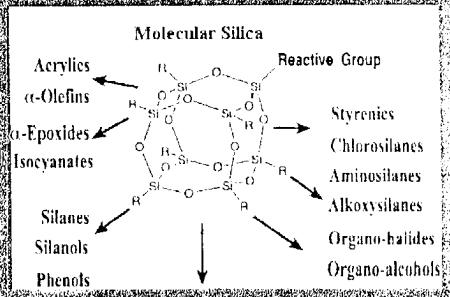
Enable use of state-of-the-art methods in computational chemistry and materials science (CCM) to design new materials with specific properties, such as:

1. High energy density materials for rocket propulsion
2. New non-linear optical (NLO) absorbing materials for protection of sensors from laser weapons.
3. POSS for high-temp coatings, ablatives, lubricants, etc.
4. Environmentally benign solvents for extraction processes (e.g., enviromental cleanup).









CHSSI MBD-01: Concept

Most novel materials require quantum chemical methods for reliable characterization

=> Development of scalable algorithms for high-level quantum-chemical methods

Complex materials exhibit dynamics on multiple time/length scales

=> Development of scalable algorithms for coupling of microscopic (Ångstroms/nanoseconds) and mesoscale/macroscopic (mm/seconds) time/length regimes

CHSSI MBD-01: Concept

Example of a "multiple-domain" material: Cryogenic HEDM (e.g. metal atoms embedded in solid hydrogen)

- **Microscopic regime:**
  - Is a metal atom stable in sH2?
  - What is the potential energy surface for a metal atom interacting with one or more H2 molecules?
- **Micro/meso regimes:**
  - What are the concentration limits and lifetimes?
  - What are the diffusion and recombination rates of M atoms in sH2?
- **Meso/macro regimes:**
  - What are the combustion characteristics of M/sH2? ("Will it burn faster than it melts?")
  - What are the transport properties (e.g., thermal conductivity) of M/sH2?

MBD-01: Software Development Plan

Development of three codes

- GAMESS quantum chemistry code
  - multiconfigurational molecular wavefunctions
  - solvation models
  - linear scaling algorithms
- Symmetry-Adapted Perturbation Theory (SAPT)
  - intermolecular interaction potentials
- TANTALUS code
  - interface between NEMD/DPD/MPM

GAMESS

General Atomic and Molecular Electronic Structure System

(FMI, visit http://www.msg.ameslab.gov)

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}\right]\Psi_{el} = E_{el}\Psi_{el}$$

Categories of approximate solutions:

a) "Self-consistent field" (SCF): reasonably good geometries

b) "Electron correlation": post-SCF correction, required for reliable energetics (e.g., barriers).

GAMESS

Program Capabilities

- RHF, UHF, ROHF, GVB, MCSCF self-consistent field wavefunctions.
- CI or MP2 energy corrections to all SCF wavefunctions.
- Semiempirical MNDO, AM1, or PM3 wavefunctions (RHF, UHF, or ROHF).
- Analytic energy gradients for all SCF wavefunctions, plus closed shell MP2 or CI.
- Optimizes molecular geometries using Cartesian or internal coordinates.
- Searches for potential energy surface saddle points, traces gradient extremal curves.
- Computes the energy hessian, normal modes, vibrational frequencies, IR and Raman intensities.
- Obtains anharmonic vibrational frequencies and intensities (fundamentals or overtones).
- Traces the intrinsic reaction coordinate (IRC) from a saddle point to reactants and products.
- Traces gradient extremal curves.

GAMESS

Program Capabilities (continued)

- Follows the dynamic reaction coordinate, a classical mechanics trajectory on the potential energy surface.

- Computes radiative transition probabilities.

- Evaluates spin-orbit coupled wavefunctions.

- Applies finite electric fields, extracting linear polarizability and 1st and 2nd order hyperpolarizabilities.

- Evaluates analytic frequency dependent NLO polarizability properties for RHF wavefunctions.

- Obtains localized orbitals by the Foster-Boys, Edmiston-Ruedenberg, or Pipek-Mezey methods, with optional SCF or MP2 energy analyis of the LMOs.

GAMESS

Program Capabilities (continued)

•Calculates the following molecular properties:

a. dipole, quadrupole, and octupole moments
b. electrostatic potential
c. electric field and electric field gradient
d. electron density and spin density
e. Mulliken and Löwdin population analysis
f. virial theorem and energy components
g. Stone's distributed multipole analysis

•Models solvent effect by

a. effective fragment potentials (EFP)
b. polarizable continuum model (PCM)
c. conductor-like screening model (COSMO)
d. self-consistent reaction field (SCRF)

•When combined with the add-on TINKER molecular mechanics program, performs Surface IMOMM or IMOMM QM/MM type simulations.

GAMESS

Current status of parallel GAMESS

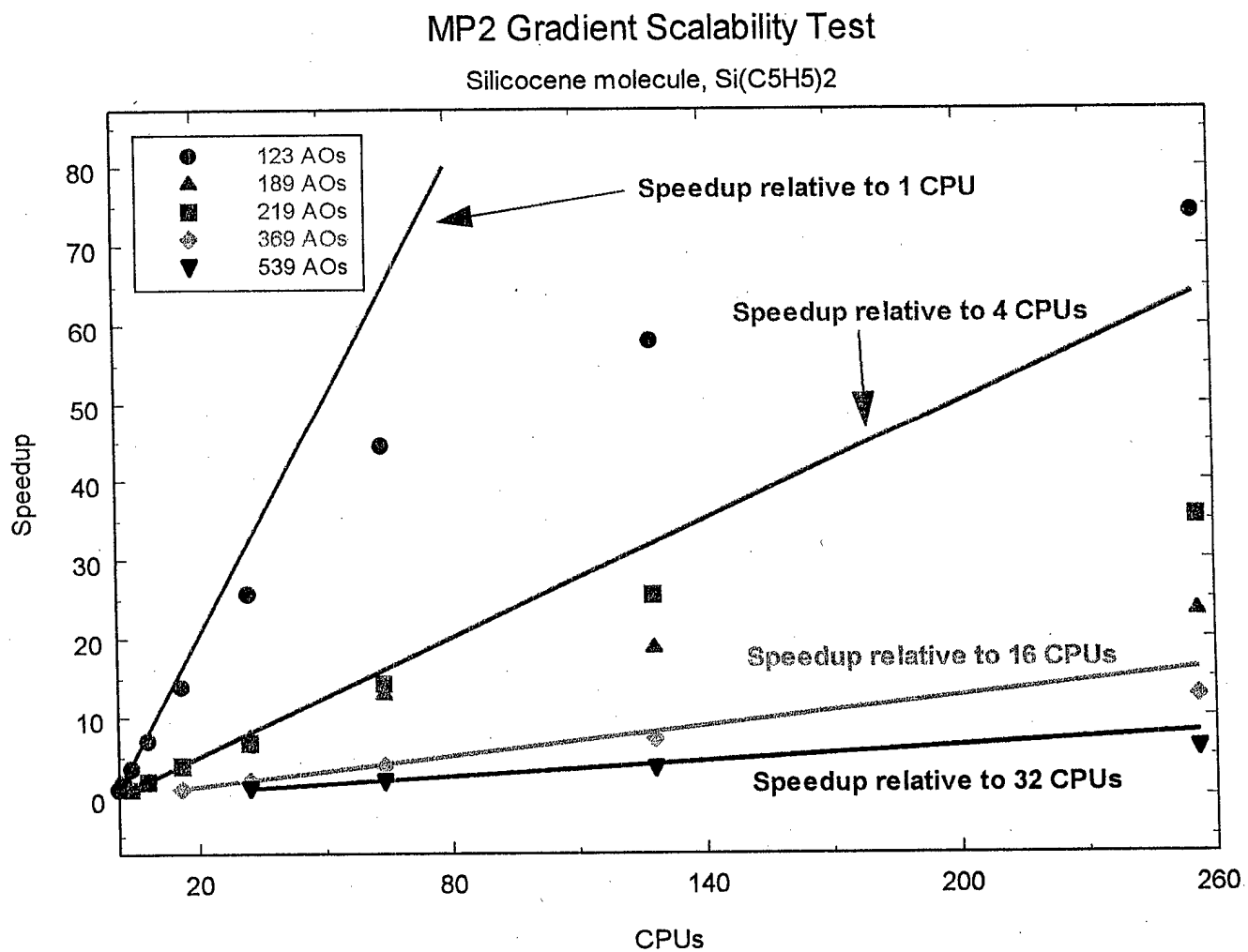
	RHF	ROHF	UHF	GVB	MCSCF
Energy	cdp	cdp	cdp	cdp	cdp
Analytic Gradient	cdp	cdp	cdp	cdp	cdp
Numeric Hessian	cdp	cdp	cdp	cdp	cdp
Analytic Hessian	cdp	cdp	-	cdp	-
MP2 energy	cdp	cdp	cdp	-	c p
MP2 gradient	cdp	-	cd	-	-
CI energy	cdp	cdp	-	cdp	cdp
CI gradient	cd	-	-	-	-
DFT energy	cdp	cdp	cdp	-	-
DFT gradient	cdp	cdp	cdp	-	-

c = conventional disk storage of AO integrals

d = direct evaluation of AO integrals

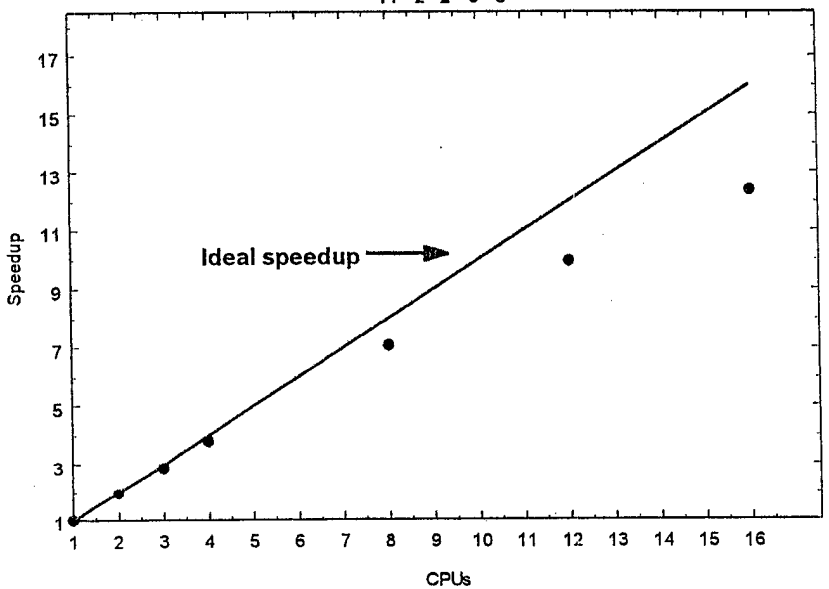
p = runs in parallel

GAMESS

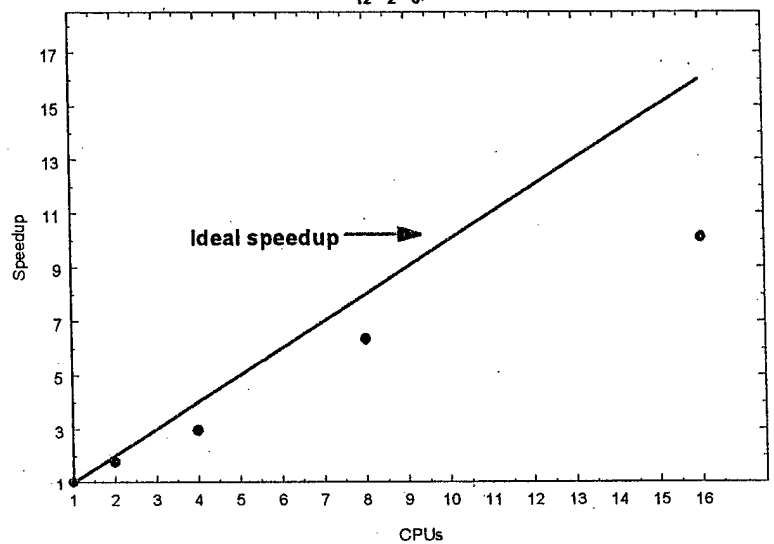

MP2 Gradient Scalability Test
Silicocene molecule, Si(C5H5)2
123 AOs
189 AOs
219 AOs
369 AOs
539 AOs
Speedup relative to 1 CPU
Speedup relative to 4 CPUs
Speedup relative to 16 CPUs
Speedup relative to 32 CPUs
Speedup
0
10
20
30
40
50
60
70
80
20
80
140
200
260
CPUs

GAMESS

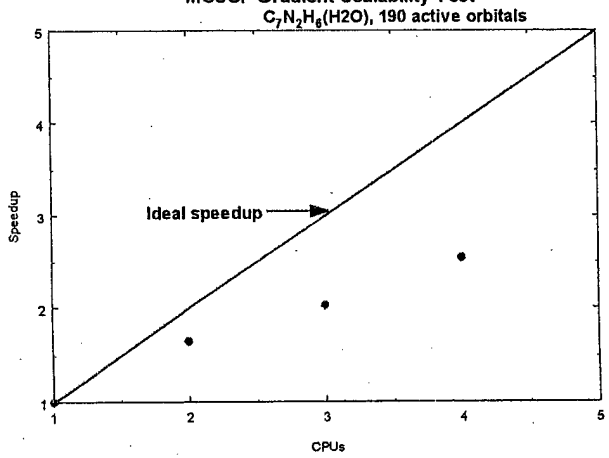
Direct SCF Gradient Scalability Test
$C_{11}N_2S_2O_3H_8$, 294 AOs



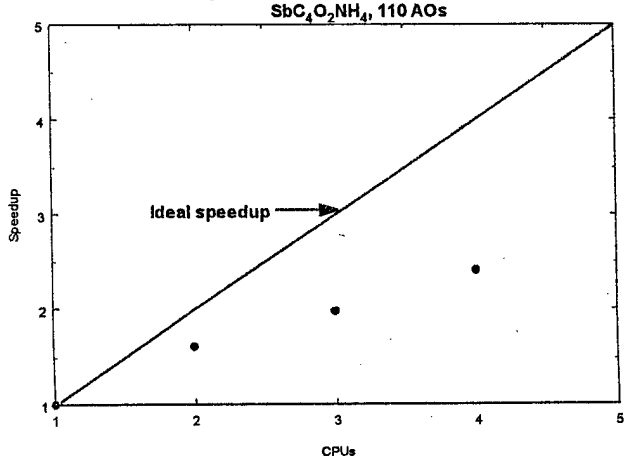
MCQDPT(2) Energy Scalability Test
$C_{12}N_2H_6$, 219 AOs



MCSCF Gradient Scalability Test
$C_7N_2H_6(H2O)$, 190 active orbitals



Analytic RHF hessian Scalability Test
$SbC_4O_2NH_4$, 110 AOs



GAMESS

Supported Hardware

- UNIX computers

"Supported"	"Acquainted"
Compaq AXP	Cray T3E, SV1, PVP
HP 9000	SGI Origin
IBM RS/6000	ConvexSPP
IBM SP	Fujitsu AP and VPP
Intel Pentium under RedHat Linux	Hitachsi SR
Sun ultraSPARC.	NEC SX

- IBM computers running MVS or VM.

- Compaq AXP or VAX computers running VMS.

SAPT

Symmetry-Adapted Perturbation Theory

A Scalable *Ab Initio* Electronic Structure Program for Calculation of Intermolecular Interactions

FMI, visit

http://www.physics.udel.edu/wwwusers/mas/group.htm

What is SAPT?

- SAPT = many-body perturbation theory ⟶ like MBPT(=MP)/CC
- SAPT calculates interaction energy E_{int} of closed-shell molecules directly, starting from the Hartree-Fock description of isolated monomers
- In contrast, regular (supermolecular) MBPT/CC uses subtraction to get E_{int}
- The Hamiltonian is split as: $H = F + V + W$

  F - sum of Fock operators

  V - interaction potential (all Coulomb interactions between A and B)

  W - intramonomer correlation potential (sum of Moller -Plesset potentials for A and B)
- The interaction energy is represented by a sum of double perturbation corrections

$$E_{\text{int}} = \sum_{v=1,w=0} E^{(v,w)}$$

What is SAPT?

- Symmetry adaptation = wave function corrections are fully antisymmetrized before evaluating interaction energy = exchange of electrons between A and B
- Corrections are naturally split into physical components:
  - electrostatic
  - induction
  - dispersion
  - exchange
- E_{int} - sum of components with clear physical interpretation
- For large intermolecular separations R SAPT becomes an asymptotic expansion in inverse powers of R (relation to monomer properties such as multipole moments and polarizabilities)
- Modeling of the interaction potential surface transparent due to known radial/angular behavior of components
- No basis-set superposition error (a problem in supermolecular approach)
- Faster execution times than equivalent MBPTn in the same orbital basis set (factor of about 3 at MBPT4 level with about 100 orbitals)
- Pair interactions and 3-body nonadditivity
- Programs available at: http://www.physics.udel.edu/wwwusers/mas/group.htm

SAPT Theory Levels

LEVEL 1:

Interaction energy at the SCF + dispersion level represented in terms of fast-to-compute low-order SAPT corrections. Suitable for larger systems in small-to-medium basis sets. Examples: DMNA-CO_2, DMNA-CH_3CN, DMNA-DMNA.

LEVEL 2:

Approximately equivalent to MBPT2 (MP2) level. Includes intramonomer correlation corrections to electrostatics, exchange, and induction, and the lowest-order dispersion term. Suitable for small and medium systems in medium and large basis stes. Examples: CH_3CN-CH_3CN, CH_3OH-CH_3OH, CO_2-CO_2, CO_2-CH_3OH, CO_2-CH_3CN.

LEVEL 3:

Approximately equivalent to MBPT4 (MP4) level. Includes all terms from LEVEL 2 plus intramonomer correlation corrections to dispersion and higher--order corrections to electrostatic and exchange energies. Recommended for generating very accurate (spectroscopic quality) potentials. In practice, suitable for small-to-medium systems in large basis sets. Examples: He-He, H_2O-H_2O, CO_2-CO_2, Ar-HF, Ar-H_2O, Ar-CO_2, Ne-HCN.

SAPT Theory Levels

- LEVEL 1:

  Interaction energy at the SCF+dispersion level represented in terms of fast-to-compute low-order SAPT corrections. Suitable for larger systems in small-to-medium basis sets. Examples: DMNA-CO_2, DMNA-CH_3CN, DMNA-DMNA

- LEVEL 2:

  Approximately equivalent to MBPT2 (MP2) level. Includes intramonomer correlation corrections to electrostatics, exchange, and induction, and the lowest-order dispersion term. Suitable for small and medium systems in medium and large basis sets. Examples: CH_3CN-CH_3CN, CH_3OH-CH_3OH, CO_2-CO_2, CO_2-CH_3OH, CO_2-CH_3CN.

- LEVEL 3:

  Approximately equivalent to MBPT4 (MP4) level. Includes all terms from LEVEL 2 plus intramonomer correlation corrections to dispersion and h igher-order corrections to electrostatic and exchange energies. Recommended for generating very accurate (spectroscopic quality) potentials. In practice, suitable for small-to-medium systems in large basis sets. Examples: He-He, H_2O-H_2O, CO_2-CO_2, Ar-HF, Ar-H_2O, Ar-CO_2, Ne-HCN.

SAPT Scalability

Level 3 calculation for the CO_2 dimer in 149-term MCBS basis set.
Entries in the Table are in the form **CPU time (in minutes) /**

Number of processors

Program	1	8	16	32
gamess	135	175 / 77%	200 / 68%	293 / 46%
ptran	325	516 / 63%	638 / 51%	718 / 45%
pcc	36	102 / 35%	189 / 19%	472 / 8%
psapt	611	762 / 80%	837 / 73%	1173 / 52%
Total	1107	1555 / 71%	1864 / 59%	2656 / 42%

SAPT Availability

SGI Origin2000	(parallel version tested at ARL)
IBM SP2	(parallel version tested at ERDC)
IBM RS6000	(sequential version available)
LINUX	(sequential version available)

Documentation:

SAPT theory manual

SAPT I/O manual

Asymptotics manual for SAPT users

Representative publications about the SAPT methodology

B. Jeziorski, R. Moszynski, and K. Szalewicz, Chem. Rev. **94**, 1887 (1994).

K. Szalewicz and B. Jeziorski, in *Molecular Interactions - From van der Waals to Strongly Bound Complexes*, edited by S. Scheiner (Wiley, New York, 1997), p. 3.

B. Jeziorski and K. Szalewicz, *Intermolecular Interactions by Perturbation Theory* in *Encyclopedia of Computational Chemistry*, edited by P. von Raguè Schleyer *et al.*, Wiley, New York, 1998.

Further information soon available at

http://www.udel.edu/wwusers/mas/group.html

TANTALUS

A Dissipative Particle Dynamics (DPD) code for bridging multiple time, length (micro/meso/macro) domains

FMI, contact Prof. Gregory Voth, University of Utah

voth@chemistry.utah.edu

Dissipative Particle Dynamics

Atomistic

$$\dot{\mathbf{r}}_i = \mathbf{p}_i / m + \mathbf{u}(\mathbf{r}_i, t)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i$$

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} U(\mathbf{r})$$

$$\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N\}$$

$$\left\langle \sum_{i=1}^{N} \frac{1}{m} p_i^2 \right\rangle = \frac{3dk_b T}{2}$$

DPD

$$\mathbf{F}_i = \sum_{j \neq i, r_{ij} < r_{cut}}^{N} \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R$$

$$\mathbf{F}_{ij}^C = -\nabla_{\mathbf{r}_{ij}} U(\mathbf{r}_{ij})$$

$$\mathbf{F}_{ij}^D = -\gamma w^D(r_{ij})(\mathbf{r}_{ij} \bullet \mathbf{v}_{ij}) \frac{\mathbf{r}_{ij}}{r_{ij}^2}$$

$$\mathbf{F}_{ij}^R = \sigma w^R(r_{ij}) \theta_{ij} \frac{\mathbf{r}_{ij}}{r_{ij}}$$

Continuum

$$\nabla \bullet \sigma + n\mathbf{F}_e = \rho \mathbf{a}$$

$$\dot{\sigma} = \underline{\mathbf{T}} : \dot{\varepsilon}$$

$$\sigma = \underline{\mathbf{N}} : \dot{\varepsilon}$$

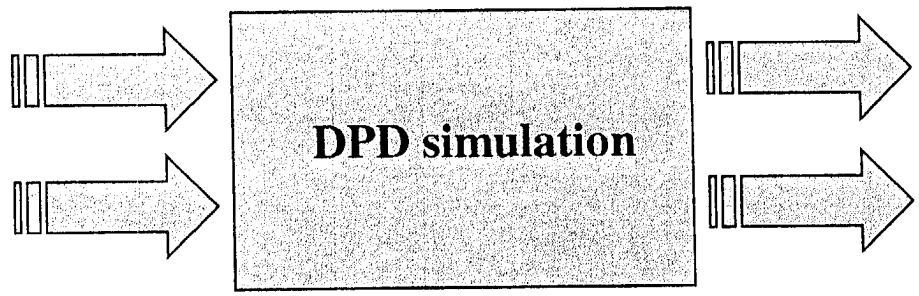
$$\dot{\varepsilon} = \frac{1}{2}\left[\nabla \mathbf{u} + (\nabla \mathbf{u})^T\right]$$

DPD contains aspects of atomistic and continuum dynamics, and is similar to a pair-wise additive Brownian dynamics model

DPD: The big picture

DPD is a spatial/temporal *interface* bridge. It can take information from microscopic scales, and then operate in time and length-scales beyond the micro-scale.

Averaged microscopic quantities, e.g., P, dP/dV,η(T,P)



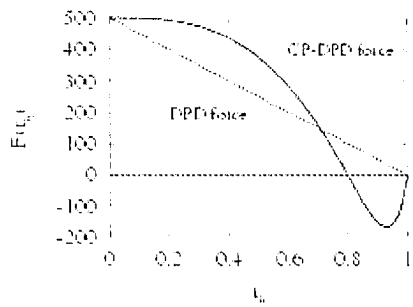
Spatial and thermal fluctuations in e.g., ρ,T,P to act as new state parameters for new micro-scale simulation

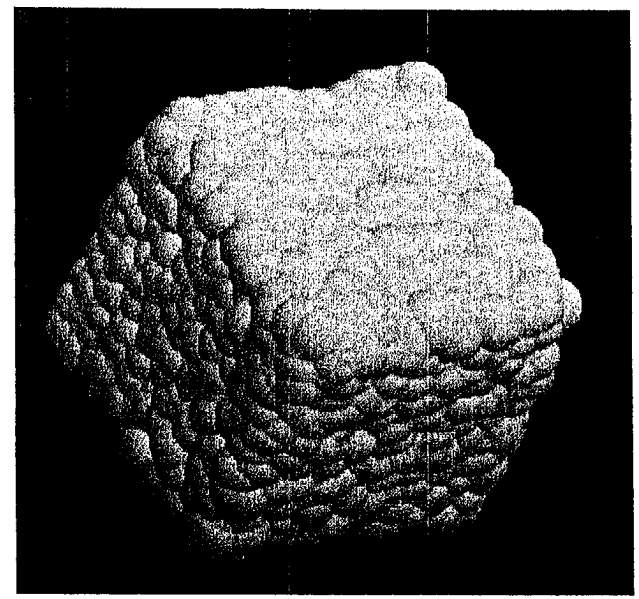
The *key* is that information must be integrated and averaged at smaller scales.

DPD operates in the low frequency peculiar velocity modes, thus it can model long-wavelength thermal fluctuations that are too slow for MD.

Test: DPD fluid

Tunable parameters
Density is resolution
Note the timestep!





Groot and Warren's system
N=4000
Density =3 DPD particles/unit volume
T* = 1
a=25, σ=3,δt=0.04 (cf. 0.0025)

Note that the DPD particles overlap: they are hydrodynamic volumes, not molecules

Parameter	TANTALUS	Groot and Warren
<T>	1.002+/- 0.005	1.0 +/-0.01
<P>	23.67+/-0.05	23.6+/-0.5

Example: DPD water

Use the condensed phase DPD model CP-DPD to generate a model fluid at the meso-scale that possesses certain key properties of water. In this case, we chose two parameters: isothermal compressibility, and the Diffusion coefficient.

Water at 298 K, 1 atm:

$$K_T^{-1} = \rho \partial P / \partial \rho = 1.2 \times 10^3 \, \text{amu/nmps}^2$$

$$D = 2.4 \times 10^{-3} \, \text{nm}^2/\text{ps}$$

$$\mathbb{F}_{ij}^{CP-DPD} = \left\{ \frac{a_{ij}}{\sigma_{DPD}} \left(1 - \frac{2r_{ij}^{\,n}}{\sigma_{DPD}} + \frac{r_{ij}^{\,m}}{\sigma_{DPD}}\right) \frac{\mathbf{r}_{ij}}{r_{ij}}, r_{ij} < r_{cut}, r_{cut} = \sigma_{DPD} \right.$$

$$a_{ij} = 750\text{amu}(\text{nm/ps})^2, \sigma_{DPD} = 1.0\text{nm}, n = 2, m = 6$$

$$N_{H_2O}/N_{DPD} \approx 10; D_{DPD} \frac{N_{H_2O}}{N_{DPD}} = D_{H_2O}$$

CP-DPD simulation results

$$K_T^{-1} = 330\text{amu/nmps}^2$$

$$K_{T\ \text{idealgas}}^{-1} = 0.06\text{amu/nmps}^2$$

$$D_{DPD} = 3.3 \pm 1 \times 10^{-4} \, \text{nm}^2/\text{ps}$$

there is about 10 water molecules per DPD particle, and the timestep is 20 times that of MD...

Some Questions:

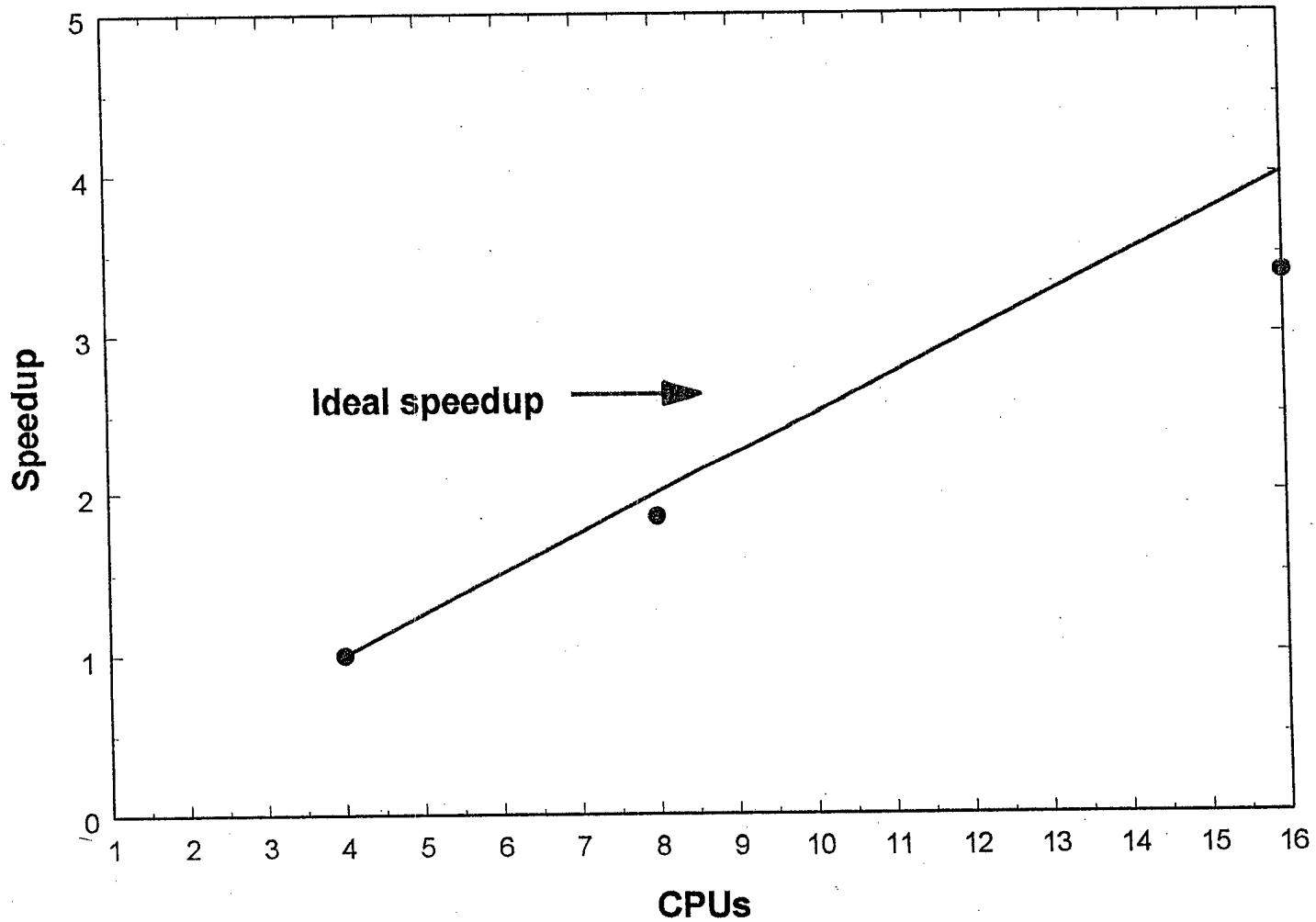
1) Is this water? No. It is a model whose material properties in a certain region are similar to water. Much like a finite-element simulation of water, where only the shear viscosity is specified

2) Where are the electrostatics? The *effect* of electrostatics are collapsed into the material properties, for example the isothermal compressibility and shear viscosity. Again, much like is done with continuum level simulation

3) Why use DPD? 1) forces are gradients of pair potentials, rather than related to strain-rates. 2) operates at time and length-scales an order of magnitude or two above MD. 3) Still retains "thermal" effects, in contrast to continuum level simulation.

4) What can we do with it? Imagine a "tagged" DPD particle. By tagged, it could represent an ion, or large molecule. It's diffusion has been "tuned" correctly. Now imagine it finally contacts another "tagged" particle… perhaps a reactive site...

TANTALUS Scalability



DPD Summary

1) DPD is a mesoscale simulation method designed to operate in the regime where thermal perturbations still exist, but just below the "flow" regime.

2) It can be shown that the equations of motion of DPD generate the canonical ensemble by virtue of dissipative and thermal forces

3) DPD employs *soft* conservative potentials, that is DPD "particles" can "pass" through each other. This is a consequence of the fact that DPD particles represent small clusters of molecules.

4) With condensed phase extensions (CP-DPD), a variety of systems can be modeled.

5) When coupled with microscopically obtained parameterizations, DPD can represent complex systems.