Introduction To Molecular Simulation

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Computer Simulation …

- Computer experiments (simulation) become a general research tool.
- Motivation of computer …
  - Development of Nuclear Weapons
  - Code breaking

Scientific Calculation

- MANIAC, 1952
  - Metreopolis was interested in solving broad spectrum of problems on this machine.

→ Metropolis Monte-Carlo Simulation Method

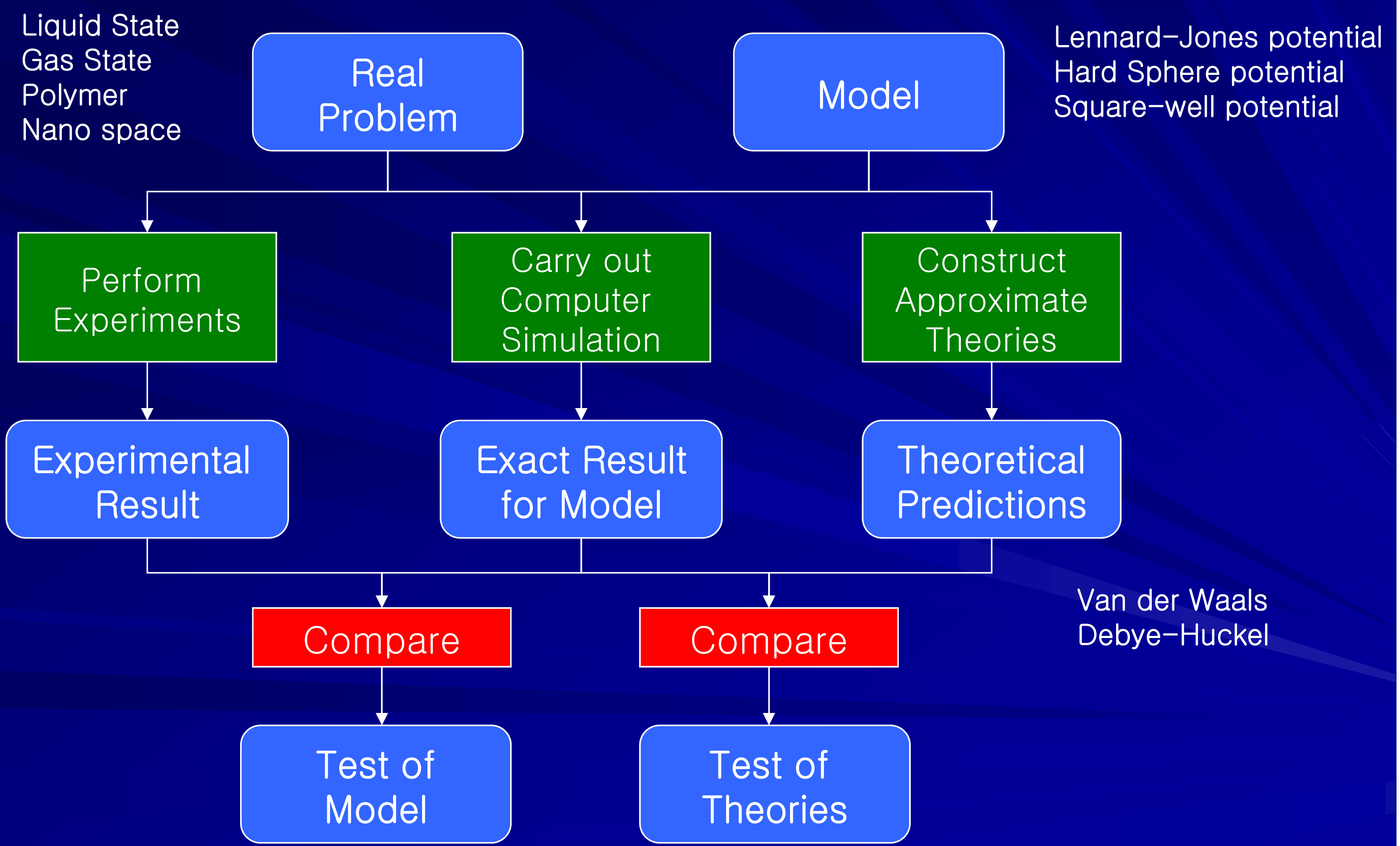
Method before computer simulation

- Approximate Theories
- Mechanical Simulation
  - Plastic foam balls
  - Metal bearings
    - Tedious, laborious
    - Quite realistic

Molecular Simulation

- A study of state of matter using computer.
  - Gas state
  - Liquid State
  - Solid State
  - Other specialized state : nano-space, structured polymers ,…
- Why computer ?
  - We cannot solve many-body problems even using simple Newtonian mechanics. (What about quantum mechanics ?)
  - There is no hope to get answer to many-body problem using pencil and paper….
- Before computer simulation …
  - Approximate theories
    - Van der Waals equation for non-polar fluids
    - Debye-Huckel for electrolytes

Use of Molecular Simulation



Use of Molecular Simulation

- Test of model
  - Test of model potential, model structure
  - Comparison with experimental data
- Test of approximate theories
  - Comparison with theoretical prediction
  - Computer-generated exact result
- Prediction of properties
  - Replacement of experimental data
  - Computer does not care about the condition….
    - Simulation at 10,000 K (?)
- Discovery of new fact
  - Alder and Wainwright (1950s) : predicted 1st order freezing transition for harsh short range repulsive molecules.

Procedure to perform molecular simulation

Model → Statistical Averaging Method → Computer Implementation → Simulation Result

Model	Statistical Averaging Method	Computer Implementation	Simulation Result
Interaction Energy model	Statistical Mechanics	Random Number Generation	Test of Model
Structural Model	Ensemble Average	Random Walk	Test of Theory
		Statistical Treatment	Property Prediction
		Method of Integration	New Discovery

Need to study molecular simulation…

- **Computer simulations (computer experiments) become general research tool.**
- **Understanding the "Black box" greatly improve the efficiency of using it.**
- **The techniques can be applied to various field of science and engineering.**
  - **Polymer science**
  - **Nano technology**
  - **Biological materials**
  - **Special structures : Zeolites, Supercritical fluid, Aerogels,….**

Recent Research Topics 2001-2003

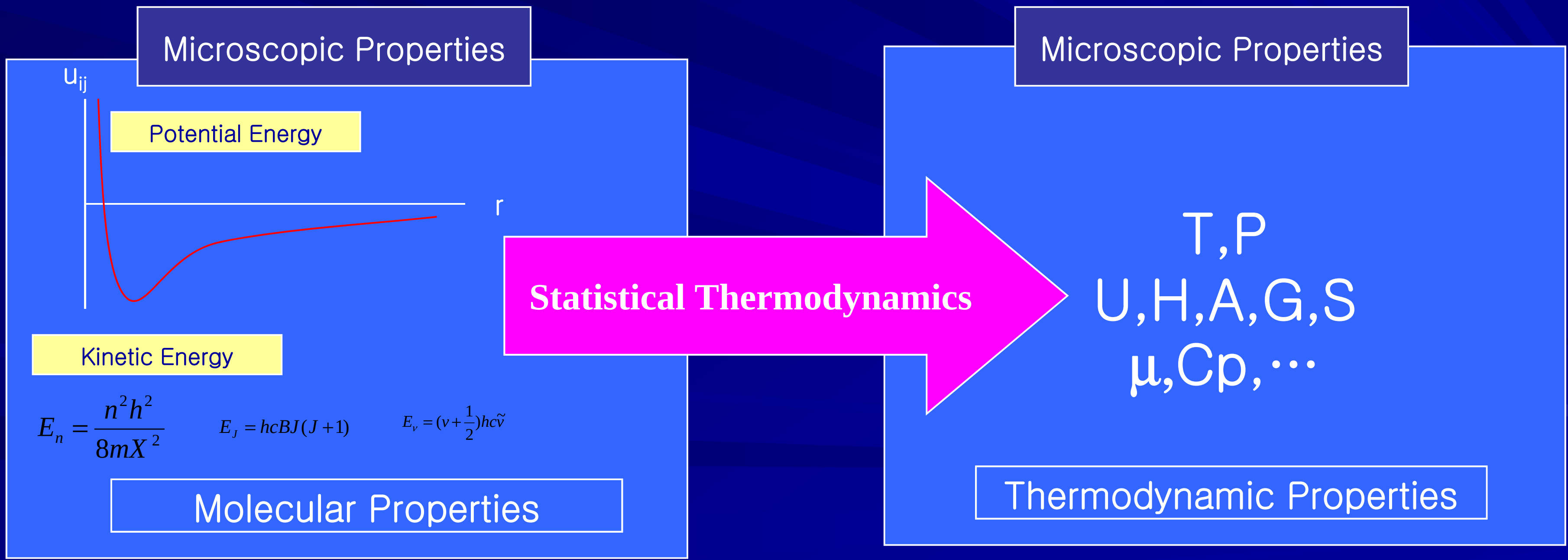
- Molecular Simulation of Diblock copolymer films
- Adsorption of materials in a single-wall carbon nano-tube
- Zeolites
- Drug delivery devices
- Viscosity in nano spacing
- Nanoscale heat transfer
- Supercritical behavior
- Aerogels

Prerequisite for the course

- **Programming skill (FORTRAN or C/C++)**
- **Statistical Mechanics**
  - **Will be covered shortly in 2 week lecture.**
- **Basic Thermodynamics**

Statistical Thermodynamics

- **Link between microscopic properties and bulk properties**



Crash course in statistical mechanics

Mechanics

- Classical Mechanics
- Quantum Mechanics

Statistical Thermodynamics

- Molecular Partition Functions
- Ensemble Averaging Method
- Phase Space Integration

$$< A > = \frac{\int A(\mathbf{r}^N)\exp(-\beta U(\mathbf{r}^N))d\mathbf{r}^N}{\int \exp(-\beta U(\mathbf{r}^N))d\mathbf{r}^N}$$

Classical Mechanics …

- **Hamiltonian : Total Energy of System**
  - **r : position vectors (N)**
  - **p: momentum vectors (N)**

$$H(\mathbf{r}^N, \mathbf{p}^N) = \text{KE(kinetic energy)} + \text{PE(potential energy)}$$

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_i \frac{\mathbf{p}_i}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

- **Using Legendre Transformation Technique,**

$$\left[\frac{\partial H}{\partial \mathbf{r}_i}\right] = -\dot{\mathbf{p}}_i$$

$$\left[\frac{\partial H}{\partial \mathbf{p}_i}\right] = \dot{\mathbf{r}}_i$$

→ Canonical Relationship →

Ex) if N= 1.E24 then

6.E24 initial values
6.E24 set of 1st order differential equations

↓

Can you solve it ?

Quantum Mechanics …

- **Failure of classic mechanics**
  - **Blackbody – radiation**
  - **The Planck distribution**
  - **Heat capacities at low T**
  - **Atomic and molecular spectra**
- **Wave-particle duality**
  - **Waves have characteristics of particles**
  - **Particles have characteristics of waves**

Conclusion of Quantum Mechanics

- **Particles can only have discrete values of energies**
- **The energy values can be calculated using Schrodinger equation**

$$-\sum_i \frac{h^2}{8\pi^2 m_i}\nabla_i^2\Psi + U\Psi = E\Psi$$

↓

Second order differential equation
Eigen value problem : series of allowed solutions

↓

Available energy values

Examples of solution to Schrodinger Equation

- **Translational motion of a free particle**

$$\psi_k(x) = C\sin kx + D\cos kx$$

$$E_k = \frac{k^2\hbar^2}{2m}, k = 0,1,2,3\ldots$$

- **Vibrational Motion (harmonic motion)**

$$E_v = (v+\frac{1}{2})\hbar\omega, \omega = \left(\frac{k}{m}\right)^{1/2}, v = 0,1,2,3\ldots$$

- **Rotational motion of a linear rotor**

$$E_r = hcBJ(J+1), J = 0,1,2,3\ldots$$