Modeling & Simulation of Glass Structure

VCG Lecture 19

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Overview …

- Historical perspective
- Simulation methodologies
  - Theoretical background
  - Monte Carlo simulation
  - Molecular dynamics simulation
  - Reverse Monte Carlo
- Force fields
- Information retrieval
  - Statistical mechanical formalisms
  - Structural analyses
  - Dynamics
- Application examples

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General References

- M. P. Allen, D. J. Tildesley (1989) Computer simulation of liquids, Oxford University Press, ISBN 0-19-855645-4
- A.R. Leach (2001), Molecular Modelling - Principles and Applications, 2nd Ed., Prentice Hall, ISBN 0-582-38210-6
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- D. C. Rapaport (1996), The Art of Molecular Dynamics Simulation, ISBN 0-521-44561-2
- Daan Frenkel, Berend Smit (2001), Understanding Molecular Simulation, Academic Press, ISBN 0-12-267351-4
- J. M. Haile (2001), Molecular Dynamics Simulation: Elementary Methods, Wiley, ISBN 0-471-18439-X
- Oren M. Becker, Alexander D. Mackerell Jr, Benoit Roux, Masakatsu Watanabe (2001), Computational Biochemistry and Biophysics, Marcel Dekker, ISBN 0-8247-0455-X
- Tamar Schlick (2002), Molecular Modeling and Simulation, Springer, ISBN 0-387-95404-X

Historical Perspective

1845	Bravais lattices
1858	concept of valence, chemical bonds in hydrocarbons A.S. Couper; F.A. Kekulé (v. Stradonitz); A.M. Butlerov
1861	J.J. Loschmidt 368 molecular structures, incl. 120 aromatic compounds (e.g. vinyl, allyl, etc.)
1865	benzene structure (Kekulé)
1890's	rotational constraints about C-C bonds J.H. van't Hoff; J.A. LeBel, C.A. Bischoff
1912	Bragg's law
1920's	Crystallographic space groups (C. Hermann, C.V. Mauguin)

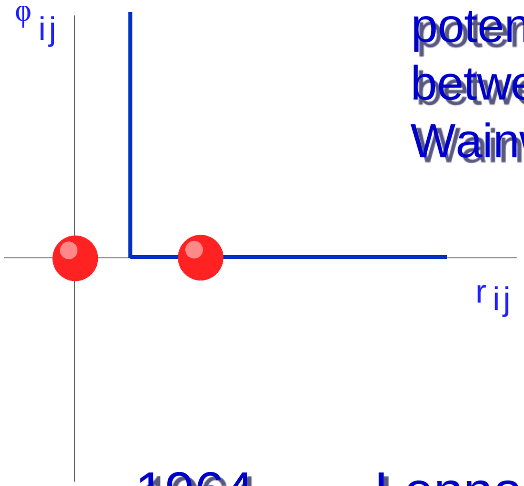
Historical Perspective

early 1900's	concept of force field in analysis of spectroscopy harmonic potential (Hooke's law)
1929	potentials named after P.M. Morse and J.E. Lennard-Jones (model vibrational excitations)
1946	molecular mechanics use Newton's equations and force fields to solve for molecular conformations (Hill, Westheimer, Mayer, etc.); eventually leads to modern drug design
1953	Monte Carlo simulations[†] during Manhattan project to compute thermodynamic properties (Metropolis, van Neuman, Teller, Fermi)

[†] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, J. Chem. Phys. **21**, p. 1087 (1953)

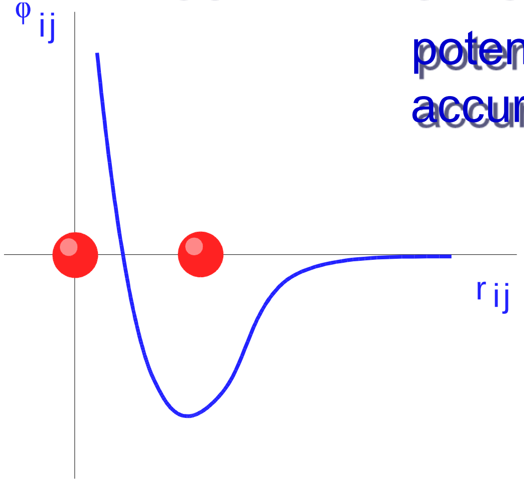
Historical Perspective

1957 hard-sphere molecular dynamics simulations*



potential non-differentiable, no force calculations, free flight between collisions, momentum balances (Alder and Wainwright)

1964 Lennard-Jones molecular dynamics†



potential differentiable, solve Newton's equation of motion, accurate trajectories (Rahman)

* B.J Alder and T.E. Wainwright, J. Chem. Phys. **27**, 1208 (1957)
†A. Rahman, Phys. Rev. **136A**, 405 (1964)

Historical Perspective

1970’s	simulation of liquids (e.g., water, molten metal, molten salts)
	Rahman, Stillinger, etc.
	simulation of ionic crystals – development of algorithms to handle long-range Coulomb interactions
	Born-Mayer-Huggins potential (BMH)
	implementation of Ewald summation method
	Singer, Catlow, etc.
1976	first simulations of silicate melts using BMH potential
	achieves tetrahedral coordination (SiO_4-units)
	Woodcock & Angell, Soules, etc.
1980	Andersen constant-pressure algorithm[§]
1980	Rahman Parrinello constant-pressure algorithm[*]

[†] L. V. Woodcock, C. A. Angell, and P. Cheeseman, J. Chem. Phys. **65**, 1565 (1976)
[§] H.C. Andersen, J. Chem. Phys. 72, 2384 (1980)
[*] A. Rahman and M. Parrinello, Phys. Rev. Letters **45**, 1196 (1980)

Historical Perspective

1985 Car-Parrinello quantum mechanical MD[†]

1990's improvement of interaction potentials

- Multi-body
- Stillinger-Weber, Vashishta, Garofalini, etc.
- Charge-transfer reactive force fields
- Goddard, Mintmire, Kieffer, etc.

… while Mohr's law keeps changing the playing field

Today massively parallel computing platforms …

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TIFF (LZW) decompressor
are needed to see this picture.

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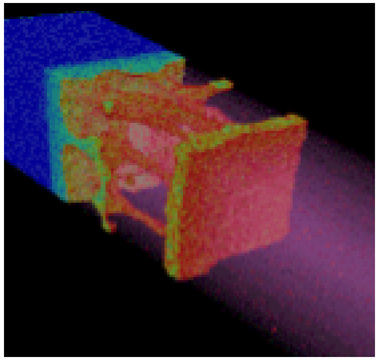

1979 (~250 atoms) 1990 (~1000 atoms) 2000 (~10^4-10^6 atoms)

[†] R. Car and M. Parrinello, Phys. Rev. Letters **55**, 2471 (1985)

Questions?

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Simulation methodologies

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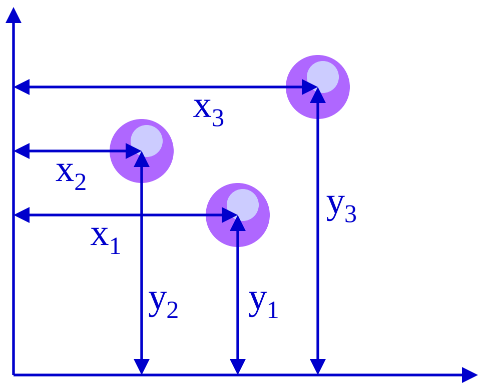
Theoretical Background

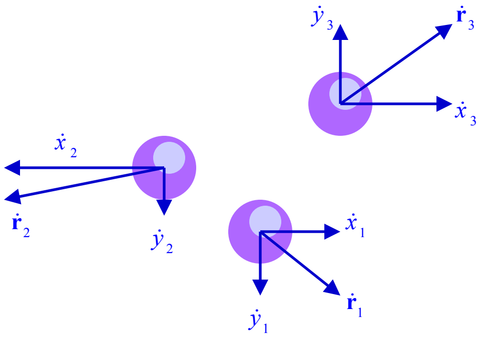
- We explore simulated systems in the framework of statistical thermodynamics
  - provides well-defined formalisms that govern the behavior of the system, e.g.,
    - Hamiltonian description of phase space
    - Lagrangian description of phase space
  - provide a multitude of formalisms to conduct statistical analyses and extract structural information and dynamic properties:
    - spatial correlations (structure)
    - ensemble averages (thermodynamic properties)
    - time correlation functions (transport and rate coefficients)

Phase space …

… is defined by the set of independent coordinates that determine the system’s thermodynamic state. For N classical particles in three dimensions, this corresponds to N coordinate vectors, $\mathbf{r}_i$, and N velocity vectors, $\dot{\mathbf{r}}_i$, i.e., 6N total coordinates.



Configuration space



Momentum space

Lagrange's formulation

Define a Lagrangian $$L = L\left(\mathbf{r}^N, \dot{\mathbf{r}}^N\right) = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i^T \dot{\mathbf{r}}_i - \sum_{i=1}^{N}\sum_{j>i}^{N} \phi\left(r_{ij}\right)$$

$$\frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\mathbf{r}}_i}\right) = \frac{\partial L}{\partial \mathbf{r}_i}$$

$$\begin{cases} \dfrac{\partial L}{\partial \dot{\mathbf{r}}_i} = m_i \dot{\mathbf{r}}_i = \mathbf{p}_i \qquad \dfrac{\partial}{\partial t}\left(\dfrac{\partial L}{\partial \dot{\mathbf{r}}_i}\right) = \dfrac{\partial \mathbf{p}_i}{\partial t} = m_i \ddot{\mathbf{r}}_i \\ \dfrac{\partial L}{\partial \mathbf{r}_i} = -\sum_{j \neq i} \dfrac{\partial \phi}{\partial r_{ij}} \dfrac{\mathbf{r}_{ij}}{\left|\mathbf{r}_{ij}\right|} = \mathbf{f}_i \end{cases}$$

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i$$

Hamilton’s formulation

Define a Hamiltonian

$$H = H\left(\mathbf{r}^N, \mathbf{p}^N\right) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i=1}^{N} \sum_{j>i}^{N} \phi\left(r_{ij}\right)$$

$$\frac{\partial H}{\partial \mathbf{p}_i} = \dot{\mathbf{r}}_i$$

$$\frac{\partial H}{\partial \mathbf{r}_i} = -\dot{\mathbf{p}}_i$$

$$\left\{ \begin{aligned} \frac{\partial H}{\partial \mathbf{r}_i} &= \sum_{j \neq i} \frac{\partial \phi}{\partial r_{ij}} \frac{\mathbf{r}_{ij}}{\left|\mathbf{r}_{ij}\right|} = -\mathbf{f}_i \\ \dot{\mathbf{p}}_i &= \frac{\partial \mathbf{p}_i}{\partial t} = m_i \ddot{\mathbf{r}}_i \end{aligned} \right.$$

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i$$

The Monte Carlo Method

- The Monte Carlo simulation method is a very popular method for studying thermodynamic and structural properties of materials.
- It is named in reference to the gambling casinos in Monte Carlo because of the use of random numbers.
- The method complements molecular dynamics (MD) and other particle-based simulation techniques and is often used in conjunction with these methods or as an alternative to these methods.
- MC may be used to simulate models of materials that are highly accurate (e.g. explicit atom models) as well as models that are more coarse-grained and use particles to represent groups of atoms.
- MC may be used with precisely the same force fields used in MD simulations.

The Monte Carlo Method

- The difference between MD and MC:
  - MD: generate successive configurations by calculating conservative forces derived from gradients in the potential energy and then solve deterministic equations of motion
  - MC: generate configurations with a probability that depends on the potential energy of a new configuration compared with the previous one; neither forces nor momenta are calculated

- Both can generate precisely the same ensemble of configurations, but in different ways.

The Monte Carlo Method

- The technique used to perform the first computer simulation of a molecular system.
- Generates configurations of a system by making *random changes* to the positions (and/or orientations and/or conformations, as appropriate) of the atoms or molecules or particles over and over again.
- In molecular simulations, “MC simulation” almost always refers to simulations performed using a technique called *importance sampling*, which generates states in a smart way that allows thermodynamic and structural properties to be computed accurately and efficiently.

The Monte Carlo Method

- In a MC simulation, the potential energy and other quantities are calculated from the positions of the atoms.

- There is *no momentum contribution* in a MC simulation, in contrast to MD (i.e. no kinetic energy).

- Thus MC samples from a 3N-dimensional space, not a 6N-dimensional space (i.e. positions only!).

So how can a MC simulation be used to calculate thermodynamic quantities, given that phase space is 6N-dimensional?

The Monte Carlo Method

The probability of finding a system in a state characterized by an energy E_i:

$$\frac{n_i}{N} = \frac{\exp\left[-E_i/k_B T\right]}{Q_{NVT}}$$

Where Q_{NVT} is the canonical partition function for the system

The Monte Carlo Method

- The canonical partition function for a system of N identical particles of mass m:

Hamiltonian = total energy

$$Q_{NVT} = \frac{1}{N!}\frac{1}{h^{3N}} \iint d\mathbf{p}^{N}\, d\mathbf{r}^{N} \exp\left[-\frac{H(\mathbf{p}^{N},\mathbf{r}^{N})}{k_{B}T}\right]$$

Indistinguishable particles

Planck’s constant

$$H(\mathbf{p}^{N},\mathbf{r}^{N}) = \sum_{i=1}^{N} \frac{\left|p_{i}^{2}\right|}{2m} + U(r^{N})$$

$$U\left(r^{N}\right) = \sum_{i=1}^{N} \sum_{j>i}^{N} \phi\left(r_{ij}\right)$$

The Monte Carlo Method

- Key point: the double integral can be separated* into two integrals, one over momenta and one over positions:

$$Q_{NVT} = \frac{1}{N!}\frac{1}{h^{3N}} \underbrace{\int d\mathbf{p}^{N} \exp\left[-\frac{|\mathbf{p}|^{2}}{2mk_{B}T}\right]}_{(2\pi m k_{B}T)^{3N/2}} \underbrace{\int d\mathbf{r}^{N} \exp\left[-\frac{U(\mathbf{r}^{N})}{k_{B}T}\right]}_{\text{Configuration integral } Z_{NVT}}$$

For ideal gas, $U(\mathbf{r}^N) = 0$, so $Z_{NVT} = V^N$.

*****if $U(\mathbf{r}^N)$ *does not depend on velocities.*

The Monte Carlo Method

- The partition function may be written as the product of an ideal gas part and a part due to deviations from ideal behavior:

$$Q_{NVT} = Q_{NVT}^{ideal} Q_{NVT}^{excess}$$

$$Q_{NVT}^{ideal} = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}$$

$$Q_{NVT}^{excess} = \frac{1}{V^N}\int d\mathbf{r}^N \exp\left[-\frac{U\left(\mathbf{r}^N\right)}{k_B T}\right]$$

- Thus thermodynamic quantities, such as the free energy $A = -k_B T \ln Q_{NVT}$, can be written as a sum.

$$A = -k_B T \ln Q_{NVT}^{ideal} Q_{NVT}^{excess} = -k_B T \ln Q_{NVT}^{ideal} - k_B T \ln Q_{NVT}^{excess} = A^{ideal} + A^{excess}$$

The Monte Carlo Method

- Upshot: all deviations from ideal gas behavior are due to interactions between the atoms or molecules or particles in the system, as calculated from the potential energy.
- The potential energy depends only on particle positions, not momenta, and thus a MC simulation can calculate the excess contributions that give rise to deviations from ideal gas behavior.
- Thus, MC simulations can explore configurational phase space and reproduce thermodynamic and structural properties and behavior.

The Monte Carlo Method

- The average potential energy can be calculated from the integral:

$$\langle U(\mathbf{r}^N)\rangle = \int d\mathbf{r}^N U(\mathbf{r}^N)\Pi(\mathbf{r}^N)$$

$$\Pi(\mathbf{r}^N) = \frac{\exp\left[-U(\mathbf{r}^N)/k_B T\right]}{Z}$$

Boltzmann factor

$$Z = \int d\mathbf{r}^N \exp\left[-U(\mathbf{r}^N)/k_B T\right]$$

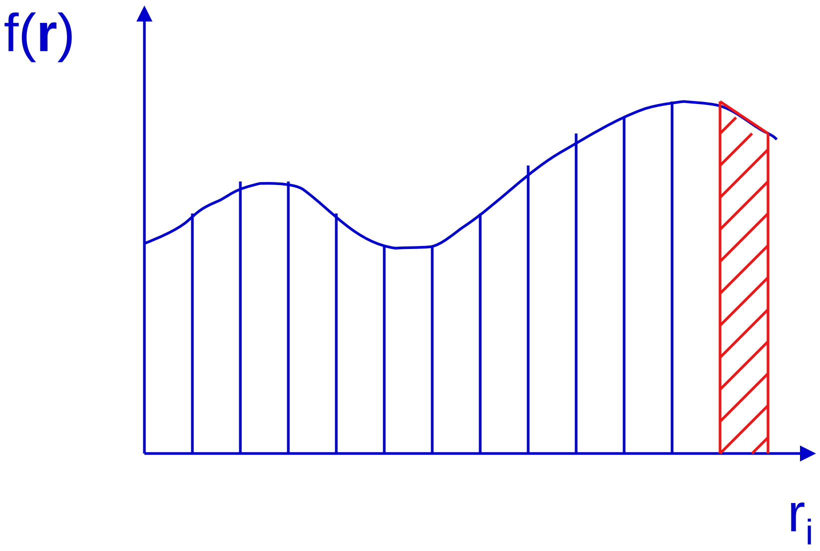
- This is a multidimensional integral over the 3N degrees of freedom of the N particles of the system, $\Pi(\mathbf{r}^N)$ is the probability of obtaining the configuration $\mathbf{r}^N$, and Z is the configurational integral defined earlier.

The Monte Carlo Method

- How to evaluate integrals in multi-dimensional space?

$$\int d\mathbf{r}^N U\left(\mathbf{r}^N\right)\Pi\left(\mathbf{r}^N\right) \text{ and } \int d\mathbf{r}^N \exp\left[-U\left(\mathbf{r}^N\right)/k_B T\right]$$

- Numerical integration:
  - First evaluate Boltzman factors, etc., for a range of values for each phase space dimension
  - Then use, e.g., trapezoid rule ....

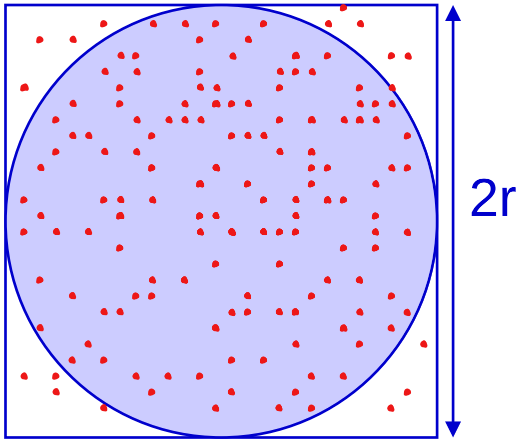


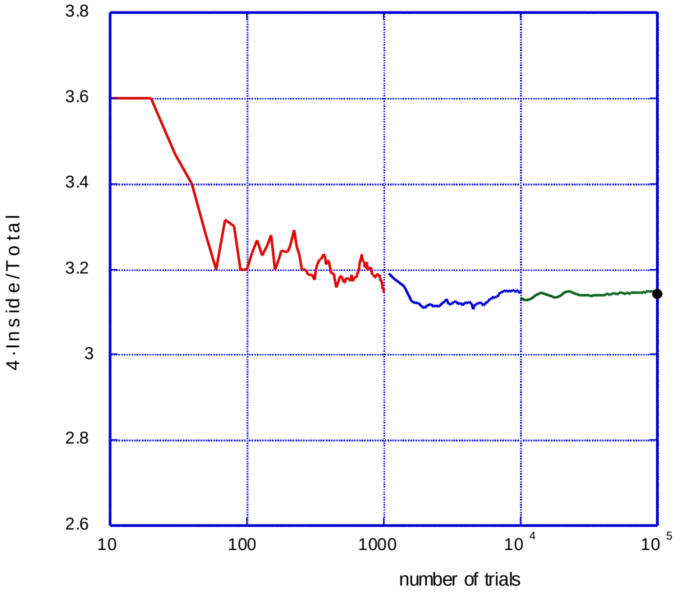
- .... too time consuming

The Monte Carlo Method

- Monte Carlo integration scheme is more efficient …
  - Shoot random darts at a surface
  - The fraction that hit is proportional to its surface
- Example: the surface of the circle relative to the encasing square is

$$\pi r^2/(2r)^2 = \pi/4$$





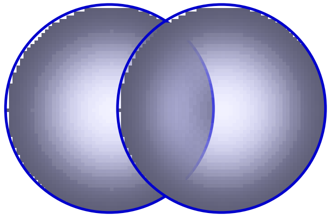
"Simple" Monte Carlo

- To calculate the average potential energy for a system of N atoms using the *"simple" MC method*:
  1. Obtain a configuration of the system by randomly generating 3N coordinates for the particles.
  2. Calculate the potential energy $U(\mathbf{r}^N)$ of the configuration.
  3. From $U(\mathbf{r}^N)$, calculate the Boltzmann factor $\exp(-U/k_B T)$.
  4. Add the BF to the accumulated sum of BFs and PExBF to its accumulated sum and return to step 1.
  5. After N_{max} iterations, calculate the average PE:

$$\left\langle U(\mathbf{r}^N)\right\rangle = \frac{\sum_{i=1}^{N_{max}} U_i(\mathbf{r}^N)\exp\left[-U_i(\mathbf{r}^N)\big/k_B T\right]}{\sum_{i=1}^{N_{max}} \exp\left[-U_i(\mathbf{r}^N)\big/k_B T\right]}$$

"Simple" Monte Carlo

- The problem: not a feasible approach.
- Why? There are a very large number of configurations that would be randomly generated that have effectively *zero Boltzmann weight* due to high-energy overlaps between the particles.



- This reflects the nature of phase space, most of which corresponds to non-physical configurations with very high energies. *Only a very small proportion of phase space corresponds to low-energy configurations with no overlapping particles and where the Boltzmann factor has an appreciable value*. These low-energy states are the physically observed states we need to sample.

“Smarter” MC: Importance Sampling

- How can we more efficiently sample (explore) phase space?
  - Generate physically observable states (those with an appreciable weight & thus contribution to the sum).
- This is the strategy adopted in *importance sampling*, and is the essence of the *Metropolis MC method* described by Metropolis, Rosenbluth, Rosenbluth, Teller and Teller in 1953.
- The Metropolis MC method is often simply called MC.
- Key feature of Metropolis MC: it *biases the generation of configurations towards those that make the most significant contribution to the integral.*
  - Simple MC generates each state with equal probability and then assigns a weight $\exp(-U(\mathbf{r}^N)/k_BT)$ to each state.
  - Metropolis MC generates states with a probability $\exp(-U(\mathbf{r}^N)/k_BT)$ and then counts each state equally.

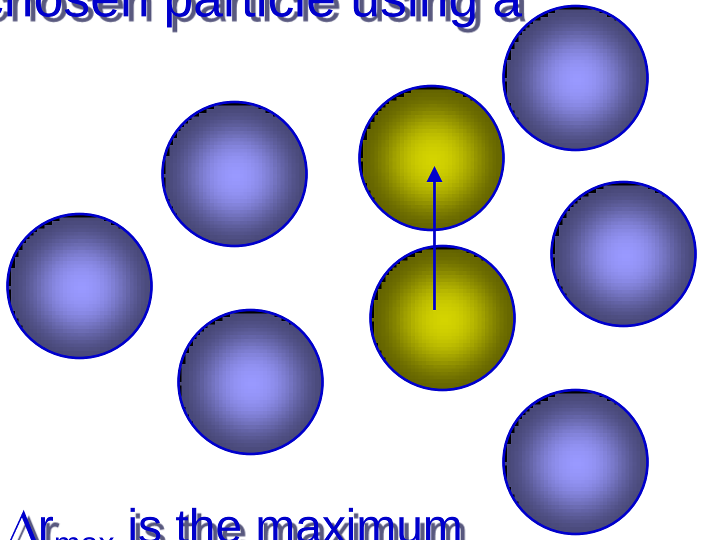
Implementing Metropolis MC

A MC simulation of a material is easy to perform.

- At each iteration of the simulation, a new configuration is generated. This is usually done by making a random change to the coordinates of a single randomly chosen particle using a random number generator (RNG).

E.g.

$$x_{new} = x_{old} + \eta_1 \delta r_{max}$$
$$y_{new} = y_{old} + \eta_2 \delta r_{max}$$
$$z_{new} = z_{old} + \eta_3 \delta r_{max}$$



Here $\eta = 2\xi - 1$ and ξ is in the range (0,1). Δr_{max} is the maximum allowed displacement in any direction.

- A unique random number is generated for each direction.

Implementing Metropolis MC

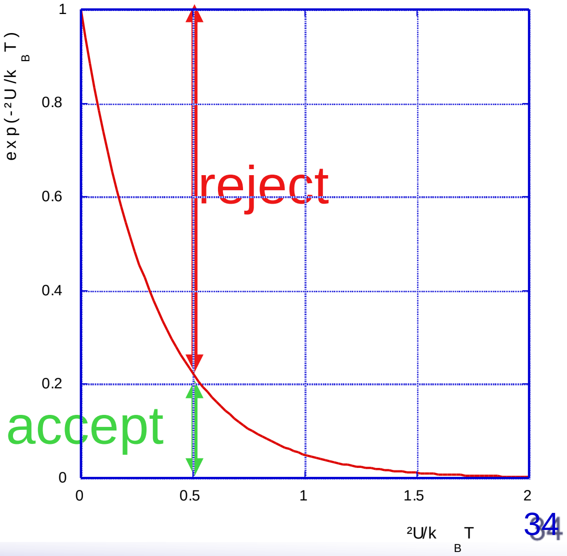
- The potential energy of the new configuration is then calculated.
  - Since the change from the previous configuration involves the motion of a single particle, only those contributions to the energy resulting from the particle's new position need to be recalculated.
  - If periodic boundaries are used, the minimum image convention must be invoked in calculating the energy (more on this later).

Implementing Metropolis MC

- If the new configuration is lower in energy than the previous configuration, then the new configuration is retained as the starting point for the next iteration.
- If not, then the Boltzmann factor $\exp(-[U_{new}-U_{old}]/k_B T)$ is calculated and compared to a random number between 0 and 1.
  - If the random number is less than or equal to the Boltzmann factor, the new configuration is accepted.
  - If the random number is greater than the Boltzmann factor, the new configuration is rejected and the previous configuration is retained for the next iteration.

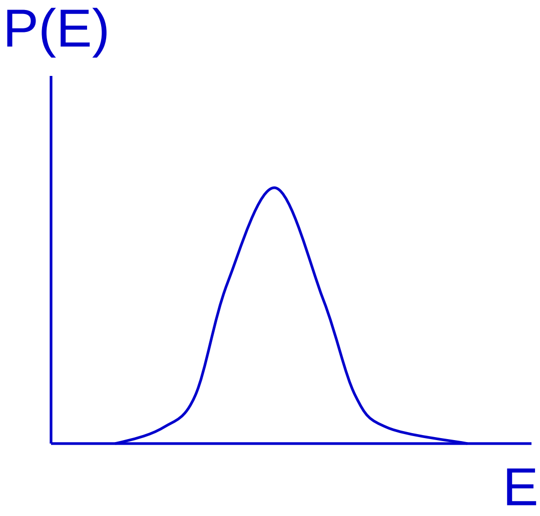
The acceptance criterion can be written as:

$$\mathrm{rand}(0,1) \leq \exp(-\Delta U(\mathbf{r}^N)/k_B T)$$



Detailed Balance

- The acceptance criterion in Metropolis Monte Carlo is derived by imposing the condition of detailed balance
- It assures unique limiting probability distribution



N possible states

Probability that state *i* is occupied:

$\rho_i = \exp[-U_i/k_B T]$

Probability distribution of states

$\rho = (\rho_1, \rho_2, \rho_3, \ldots, \rho_n, \ldots, \rho_m, \ldots, \rho_N)$

Transition matrix π:

π_{mn} = probability that system transitions from state *m* to *n*

Stochastic matrix α:

α_{mn} = probability that algorithm seeks transition from state *m* to *n*

Editor note: Lecture 19 ends here