Other computational approaches

MC $(s \xrightarrow{\Delta E} s')$

at temp $T \to \{x_i\}$ ensemble. $\quad \langle x(T) \rangle = \frac{\sum x_i}{N}$

histogram technique

consider nearby temp T'.

reweight to T' ; undo original weight $e^{-\beta E_i}$

$$w_i(T') = \frac{e^{-(\beta'-\beta)E_i}}{\sum_i e^{-(\beta'-\beta)E_i}} \quad \text{— normalize}$$

$$\langle x(T') \rangle = \sum_i w_i(T') x_i$$

so within phase (have ensembles $\{x\}$ overlap) can reweight to get smooth T dep'd.

histograms w. order parameter m

$$Z = \sum_m \sum_{\substack{s_m \\ \text{states with } m}} e^{-\beta H(s_m)} = \sum_m e^{-\beta G_m}$$

$$G_m = -k_B T \ln \underbrace{\sum_{s_m} e^{-\beta H(s_m)}}_{Z_m}$$

$$p_m = \frac{e^{-\beta G_m}}{Z}$$

$$G_m = -k_B T (\ln p_m + \ln Z)$$

ie sample at $T \Rightarrow$ histogram vs $m \simeq p_m \Rightarrow G_m$.

two peaks of G_m vs $T \to T_c$: discont.
one peak vs $T \to T_c$: contin

distinguish discontinuous (latent heat, no critical point "first order")
! continuous (no latent heat, critical point "second order")

need order parameter
! sample near T_c.

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MD Molecular dynamics ($V(r) \to F \to \dot{x}, \ddot{x}$) (pot'l, force, speed, accel.)

eg pot'l from DFT or other first principles approach (eg gravity, electrostatics, etc..)

eg phenomenological Lennard-Jones "6-12" pot'l

$$\vec{F}(r_{ij}) = \frac{24\epsilon}{\sigma^2} \vec{r}_{ij} \left(2\left(\frac{\sigma}{r_{ij}}\right)^{14} - \left(\frac{\sigma}{r_{ij}}\right)^{8} \right)$$

σ = distance scale; ϵ = strength.

hard core phenomenological repulsion. / attractive Van-der-Waals (induced dipole)

NB. N^2 interactions $\Rightarrow$ computationally slow.

"long-range" (power law)

$\Rightarrow$ phenomenological cutoffs

eg hard cutoff $f = 0$ $r > 5\sigma$ local.

eg nn only $f_{ij} = 0$ unless nn.

eg polymer as beads on string.

eg. one Brillouin zone only

eg $f = 0$ $r > \frac{L}{2}$ (avoid infinite sum over periodic boundary conditions)

OR **TREE METHOD.** eg. Pfalzner/Gibbon "Many-body tree methods in physics"

- recursively group particles in boxes. (stop at scale)
- within box resolve all forces
- between boxes represent low order multipoles (eg charge, dipole, quadrupole)

pick: scale to stop at multipole, to get desired speed/accuracy

NB. easiest with $1/r^2$ gravity, electrostatics.

general rule: (ie "answer") end result should be insensitive to method knobs.

(time/accuracy is sensitive to knobs) ←

∴ pick results (what to measure) that are insensitive to knobs.

ignore results that are sensitive.

REPRODUCIBILITY SHOULDN'T REQUIRE FINE-TUNING OF NUMERICAL METHODS.

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MD+

- discretize time Δt $\Rightarrow$ discretization errors $O(\Delta t^n)$ (some exponent $n>0$)
  vanishes $\Delta t \to 0$.
  some algorithms (e.g. Verlet, leapfrog) minimize errors in E

- can add friction & noise.

Brownian Dynamics

$$\frac{d\vec{v}_i}{dt} = -\gamma \vec{v}_i + \frac{\vec{f}_i}{m} + \eta_i(t)$$

friction; noise

unbiased: $\langle \eta \rangle = 0$

$\langle \eta\eta \rangle = \frac{2\gamma k_B T}{m}\delta(t-t')$ thermal noise

★ $\eta \sim \sqrt{\Delta t}$ (like RW) if discrete Δt. ★

overdamped dynamics $\left(\frac{dv}{dt} \approx 0\right)$ $\quad \vec{v}_i = \frac{\vec{f}_i}{\gamma m}$.

NB. MD requires continuous positions $\{x\}$ & continuous time $\{t\}$.
$\Rightarrow$ realistic dynamics.

What if we have discrete states?
$\Rightarrow$ necessarily stochastic? (i.e. large changes in coordinates)

or track probabilities of discrete states

"Master eq'n" $\frac{\partial P(q,t)}{\partial t} = \sum_{q'} \left[W(q,q')P(q',t) - W(q'/q)P(q,t) \right]$

(q: state; W: transition rate.)

various approximations if not just a few states.

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simulate discrete transitions **SSA** stochastic simulation algorithm.

observation: radioactive decay occurs as constant rate process for each nucleus.

$$\dot{N} = -\frac{N}{\tau} \rightarrow N(t) = N_0 e^{-t/\tau}$$

$$\dot{N} = -\frac{N_0}{\tau} e^{-t/\tau}$$

$$\frac{\dot{N}}{N_0} = -\frac{e^{-t/\tau}}{\tau}$$ per particle distn of decay times exponential.

$$\int_0^\infty \frac{e^{-t/\tau}}{\tau} dt = 1$$ decay sometime $0 \to \infty$.

$$x = \int_0^t \frac{e^{-t'/\tau}}{\tau} dt'$$ cum. distn $x \in [0,1]$.

$$= 1 - e^{-t/\tau}.$$

Gillespie algorithm
J Phys Chem 1977
Ann Rev Phys Chem 2007.

$$t = -\tau \ln(1-x)$$ uniform random # $[0,1]$

$$\boxed{t_{event} = -\tau \ln \text{RAND1}}$$

Kinetic Monte Carlo
Gibson & Bruck
J Phys Chem A 2000

$$\Gamma_{TOT} = \sum \Gamma_i$$ independent rates

$$\boxed{t_{next} = -\frac{1}{\Gamma_{TOT}} \ln \text{RAND1}} \qquad \tau = \frac{1}{\Gamma}$$

$$\boxed{p_i = \frac{\Gamma_i}{\Gamma_{TOT}}}$$ prob. of ith rate being next is p_i

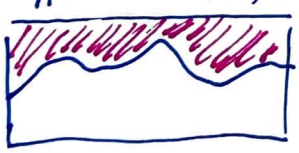
NB. SOME TRICKS TO PICK i^{th} event efficiently.

algorithm: determine $\{\Gamma_i\} \to \Gamma_{TOT} \to t_{next}$; $t \mathrel{+}= t_{next}$; do i

iterate

✓ exactly sample the event times

Q: what happens if $\Gamma_i(t)$ time-dependent rates?



eg Holubec, Marcus EPL 2011 etc...

A. if $\Gamma_{TOT}(t) \le \Gamma_{MAX}$ ie if it is bounded.

add $\Gamma_{blank}(t) = \Gamma_{MAX} - \Gamma_{TOT}(t)$
nothing ! if selected do nothing.

only need $\Gamma_{MAX} = \text{const}$.