CE 530 Molecular Simulation

Lecture 17
Beyond Atoms: Simulating Molecules

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Review

○ Fundamentals

- *units, properties, statistical mechanics*

○ Monte Carlo and molecular dynamics as applied to atomic systems

- *simulating in various ensembles*
- *biasing methods for MC*

○ Molecular models for realistic (multiatomic) systems

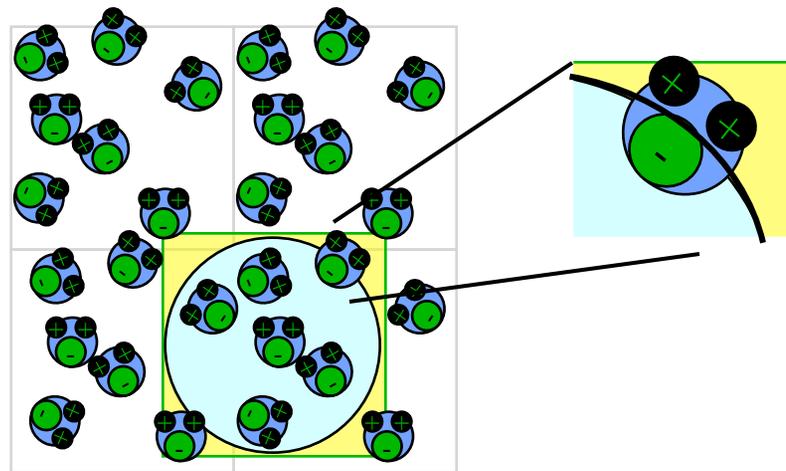- *inter- and intra- atomic potentials*
- *electrostatics*

○ Now examine differences between simulations of monatomic and multiatomic molecules

Truncating the Potential

○ Many molecular models employ point charges for electrostatic interactions

○ Potential-truncation schemes must be careful not to split the charges

○ For a 9Å truncation distance, using water-like charges, the interaction energy for a molecule with bare charge is (huge)

○ Always use cutoff based on molecule separation, not atom

• *for large molecules, OK to split molecule but do not split subgroups*

Volume-Scaling Moves

○ Scaling atom displacements leads to large strain on intramolecular bonds

○ Instead perform volume scaling moves using molecule centers-of-mass (or something similar)

- *Let $\mathbf{R}_i$ be COM of molecule i*

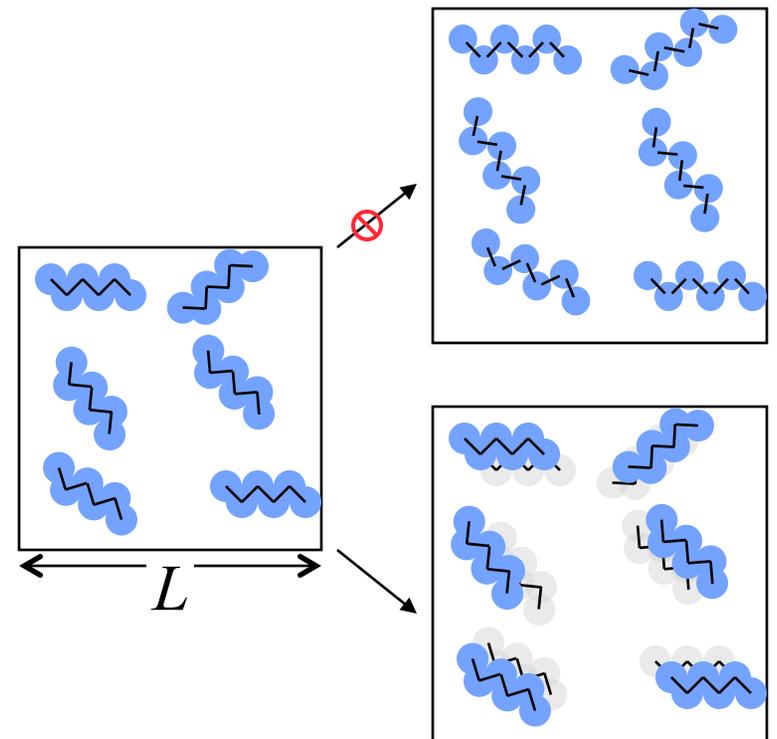$$\mathbf{R}_i = \sum_{\text{atoms on i}} m_i \mathbf{r}_j^{(i)}$$

- $\mathbf{q}_j^{(i)}$ *be position of atom j w.r.t.* $\mathbf{R}_i$

$$\mathbf{q}_j^{(i)} = \mathbf{r}_j^{(i)} - \mathbf{R}_i$$

- *For size scaling* s, $L^{new} = sL^{old}$

$$\mathbf{r}_j^{(i)}(\text{new}) = s\mathbf{R}_i + \mathbf{q}_j^{(i)}$$

- *Acceptance based on change in* $-\beta(U + PV) + N_m \ln V$ *(not atoms)*

Number of molecules

L

Rigid vs. Nonrigid Molecules

○ MC and MD can be performed on molecules as already described

- *MD moves advance atom positions based on current forces*
- *MC moves translate atoms and accepts based on energy change*
- *both are done considering inter- and intra-molecular forces*
- *limiting distribution has same form*

$$\pi = \frac{1}{h^{3N}} dp^N dr^N e^{-\beta \sum p_i^2 / 2m_i} e^{-\beta U(r^N)} \qquad N = Number\ of\ atoms$$

- *if this is all that is done, there is nothing more to say*

○ Often it is much more efficient to use a rigid-bond model

- *MD integration then doesn't have to deal with fast intramolecular dynamics, so a larger time step can be used*
- *MC can sample configurations more efficiently using rigid-body moves (even if model does not have rigid bonds)*
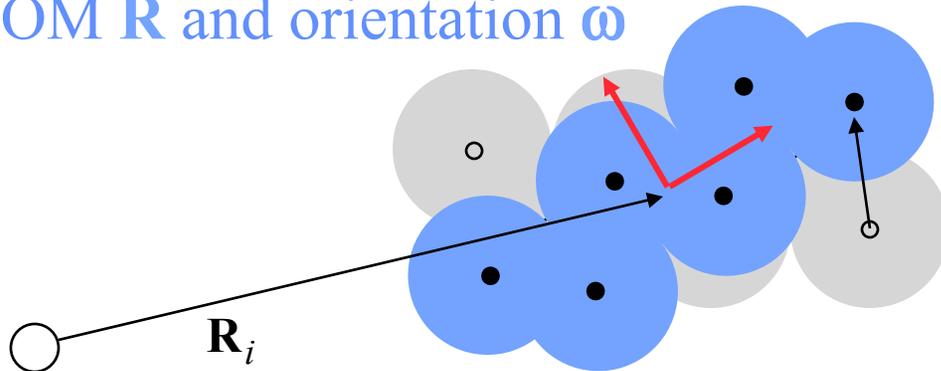   but much care is needed to do this properly

Molecule Coordinate Frame

○ Molecule-frame coordinates are defined w.r.t. molecule COM with molecule in a reference orientation

q_j
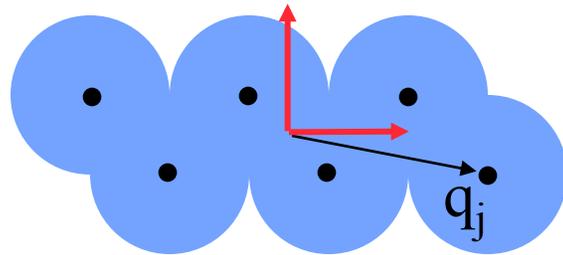
○ Simulation-frame coordinate is determined by molecule COM **R** and orientation ω
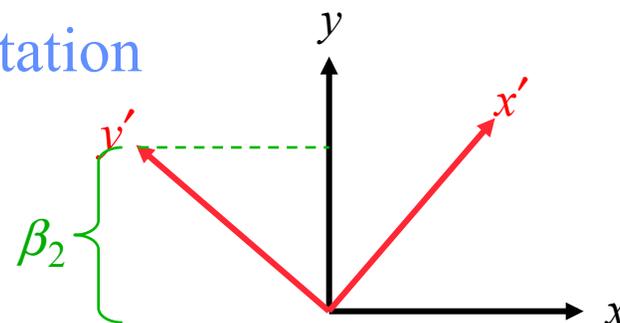

$\mathbf{R}_i$

○ For rigid molecules, the molecule-frame coordinates never change

Orientation 1.

○ Orientation described in terms of rotation of molecule frame

○ Direction cosines can be used to describe rotation

$$\alpha_1 = \mathbf{e}'_x \cdot \mathbf{e}_x \quad \alpha_2 = \mathbf{e}'_x \cdot \mathbf{e}_y$$
$$\beta_1 = \mathbf{e}'_y \cdot \mathbf{e}_x \quad \beta_2 = \mathbf{e}'_y \cdot \mathbf{e}_y$$
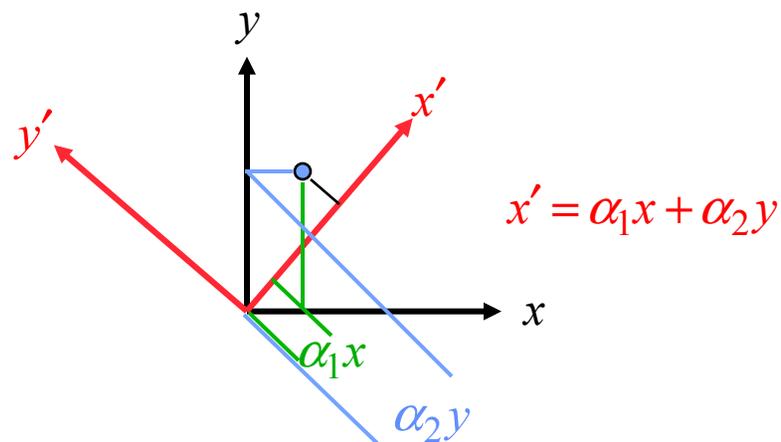
○ Relation between same point in two frames

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \alpha_1 & \alpha_2 \\ \beta_1 & \beta_2 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

○ Rotation matrix

$$A = \begin{pmatrix} \alpha_1 & \alpha_2 \\ \beta_1 & \beta_2 \end{pmatrix} \qquad \boxed{\mathbf{r}' = A\mathbf{r}}$$

$$x' = \alpha_1 x + \alpha_2 y$$

○ Kinematics of rigid-molecule rotation described in terms of rotation of the molecule coordinate frame (*i.e.* the direction cosines)

• *r' never changes in a rigid molecule*

Orientation 2.

○ We also need to invert the relation

- *get the simulation-frame coordinate from the molecule frame value*

  $$\mathbf{r} = A^{-1}\mathbf{r}' = A^T\mathbf{r}'$$

○ Direction cosines are not independent

- *in 2D, all can be described by just one parameter*
- *use rotation angle θ*

$$A = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \qquad A^{-1} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}$$
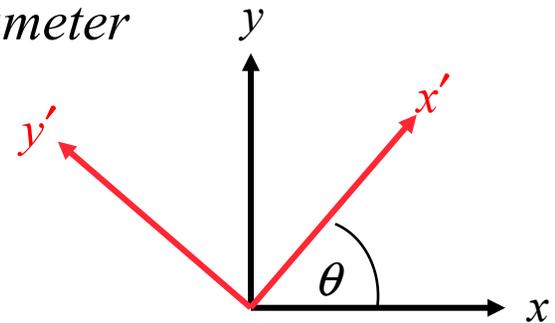
- *inverse can be viewed as replacing θ with -θ*

Euler Angles

○ The picture in 3D is similar: (x, y, z) → (x', y', z')

○ Nine direction cosines

○ Three independent coordinates specify orientation

○ Euler angles are the conventional choice $\boldsymbol{\omega} = \phi\theta\psi$

  • *three rotations give the simulation-frame orientation*
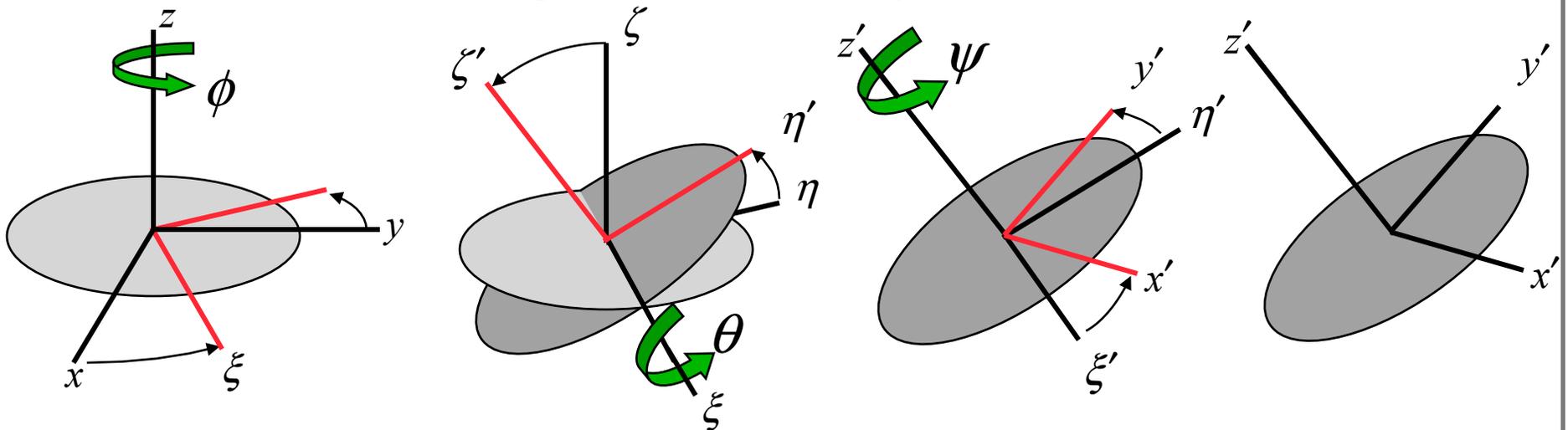
3D Rotation Matrix

○ Rotation matrix expressed in terms of Euler angles $\quad \mathbf{r}' = A\mathbf{r}$

$$A = \begin{pmatrix} \cos\psi\cos\phi - \cos\theta\sin\phi\sin\psi & \cos\psi\sin\phi + \cos\theta\cos\phi\sin\psi & \sin\psi\sin\theta \\ -\sin\psi\cos\phi - \cos\theta\sin\phi\cos\psi & -\sin\psi\sin\phi + \cos\theta\cos\phi\cos\psi & \cos\psi\sin\theta \\ \sin\theta\sin\phi & -\sin\theta\cos\phi & \cos\theta \end{pmatrix}$$

○ To get space-fixed coordinate, multiply molecule-fixed vector by A^{-1}

- *again, $A^{-1} = A^T$* $\qquad \mathbf{r} = A^T\mathbf{r}'$

Transforming Coordinates 1.

○ Consider a simple diatomic

- *positions of two atoms described by*
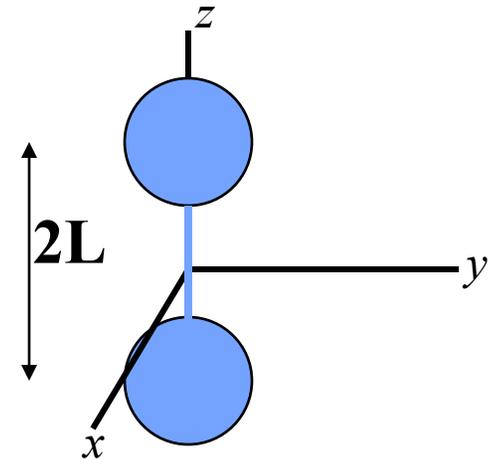
    $x_1, y_1, z_1, x_2, y_2, z_2$

- *can instead describe by molecule COM and stretch/orientation coordinates*

    X, Y, Z, L, θ, ϕ

- *in molecule frame, each atom position is given by*

    $\mathbf{r}_1' = L\mathbf{e}_z$

    $\mathbf{r}_2' = -L\mathbf{e}_z$

Transforming Coordinates 2.

○ To get space-fixed coordinates, use rotation matrix

$$\mathbf{r}_1 = \mathbf{R} + A^T \mathbf{r}_1'$$

$$\mathbf{r}_2 = \mathbf{R} + A^T \mathbf{r}_2'$$

$$\mathbf{R} \equiv (X, Y, Z)$$

$$\mathbf{r}_1' = L\mathbf{e}_z$$

$$\mathbf{r}_2' = -L\mathbf{e}_z$$
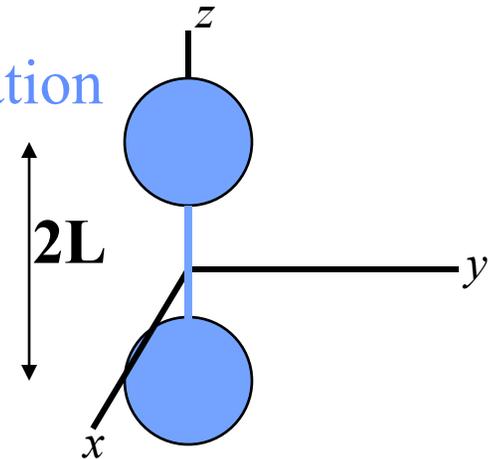
- *matrix*

$$A^T = \begin{pmatrix} \cos\phi & \sin\phi & \sin\theta\sin\phi \\ -\cos\theta\sin\phi & \cos\theta\cos\phi & -\sin\theta\cos\phi \\ 0 & \sin\theta & \cos\theta \end{pmatrix}$$

- *the result is*

$$x_1 = X + L\sin\theta\sin\phi \qquad x_2 = X - L\sin\theta\sin\phi$$

$$y_1 = Y - L\sin\theta\cos\phi \qquad y_2 = Y + L\sin\theta\cos\phi$$

$$z_1 = Z + L\cos\theta \qquad z_2 = Z - L\cos\theta$$

Transforming Coordinates 3.

○ The ensemble distribution for the transformed coordinates is obtained via the Jacobian

$$\pi = \frac{1}{Qh^{3N}} dp^N dr^N e^{-\beta \sum p_i^2/2m_i} e^{-\beta U(r^N)}$$

$$= \frac{1}{Qh^{3N}} dp^N dq^N |\mathbf{J}| e^{-\beta \sum p_i^2/2m_i} e^{-\beta U(q^N)}$$

- *the elements of J are the derivatives* $\quad J_{\alpha\beta} = \dfrac{\partial r_\alpha}{\partial q_\beta}$

$$
\begin{array}{c}
 \\
\mathbf{x_1} \\
\mathbf{y_1} \\
\mathbf{z_1} \\
\mathbf{x_2} \\
\mathbf{y_2} \\
\mathbf{z_2}
\end{array}
\begin{array}{ccc}
\mathbf{X}\ \mathbf{Y}\ \mathbf{Z} & \mathbf{L} & \boldsymbol{\phi} & \boldsymbol{\theta}
\end{array}
$$

	X	**Y**	**Z**	**L**	**ϕ**	**θ**
x₁	1	0	0	$\sin\theta\sin\phi$	$L\sin\theta\cos\phi$	$L\cos\theta\sin\phi$
y₁	0	1	0	$-\sin\theta\cos\phi$	$L\sin\theta\sin\phi$	$-L\cos\theta\cos\phi$
z₁	0	0	1	$\cos\theta$	0	$-L\sin\theta$
x₂	1	0	0	$-\sin\theta\sin\phi$	$-L\sin\theta\cos\phi$	$-L\cos\theta\sin\phi$
y₂	0	1	0	$\sin\theta\cos\phi$	$-L\sin\theta\sin\phi$	$L\cos\theta\sin\phi$
z₂	0	0	1	$-\cos\theta$	0	$L\sin\theta$

$$x_1 = X + L\sin\theta\sin\phi$$
$$y_1 = Y - L\sin\theta\cos\phi$$
$$z_1 = Z + L\cos\theta$$
$$x_2 = X - L\sin\theta\sin\phi$$
$$y_2 = Y + L\sin\theta\cos\phi$$
$$z_2 = Z - L\cos\theta$$

- *For this transformation* $\quad |\mathbf{J}| = 8L^2\sin\theta$

○ But we also need to transform the momenta

Transforming Coordinates 4.

○ Begin with the Lagrangian

- *in the original coordinate system*

$$L = K - U$$

$$= \tfrac{1}{2}(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2 + \dot{x}_2^2 + \dot{y}_2^2 + \dot{z}_2^2) + U(x_1, y_1, z_1, x_2, y_2, z_2)$$

assume m=1

$$= \tfrac{1}{2}\sum_i \dot{r}_i^2 + U(\mathbf{r})$$

- *transform to new coordinates*

$$\dot{x}_1 = \frac{\partial x_1}{\partial X}\dot{X} + \frac{\partial x_1}{\partial Y}\dot{Y} + \frac{\partial x_1}{\partial Z}\dot{Z} + \frac{\partial x_1}{\partial L}\dot{L} + \frac{\partial x_1}{\partial \theta}\dot{\theta} + \frac{\partial x_1}{\partial \phi}\dot{\phi}$$

$$\dot{y}_1 = etc.$$

- *in general*

$$\dot{r}_i = \sum_\alpha \frac{\partial r_i}{\partial q_\alpha}\dot{q}_\alpha$$

$$\dot{r}_i^2 = \sum_\beta \sum_\alpha \frac{\partial r_i}{\partial q_\alpha}\frac{\partial r_i}{\partial q_\beta}\dot{q}_\alpha \dot{q}_\beta$$

$$= \dot{\mathbf{q}} \cdot \mathbf{g}_i \cdot \dot{\mathbf{q}}$$

$$\sum_i \dot{r}_i^2 = \dot{\mathbf{q}} \cdot G \cdot \dot{\mathbf{q}}$$

$$\mathbf{r} = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \end{pmatrix} \qquad \mathbf{r}' = q = \begin{pmatrix} X \\ Y \\ Z \\ L \\ \theta \\ \phi \end{pmatrix}$$

Transforming Coordinates 5.

○ Derive momenta

$$L = \tfrac{1}{2}\dot{\mathbf{q}} \cdot G \cdot \dot{\mathbf{q}} - U(\mathbf{q})$$

$$\mathbf{p} = G\dot{\mathbf{q}}$$

Uses G and thus G^{-1} are symmetric

$$\dot{\mathbf{q}} = G^{-1}\mathbf{p}$$

$$p_\alpha \equiv \frac{\partial L}{\partial \dot{q}_\alpha} = \sum_\beta G_{\alpha\beta}\dot{q}_\beta$$

$$\dot{\mathbf{q}} \cdot G \cdot \dot{\mathbf{q}} = \mathbf{p} \cdot G^{-1} \cdot \mathbf{p}$$

○ The Hamiltonian is

$$H = K(\mathbf{p},\mathbf{q}) + U(\mathbf{q})$$
$$= \tfrac{1}{2}\mathbf{p} \cdot G^{-1} \cdot \mathbf{p} + U(\mathbf{q})$$

○ The Jacobian for the momentum transformation is the reciprocal of the Jacobian for the coordinate transformation

$$\pi = \frac{1}{Qh^{3N}} dp_q{}^N dq^N \left| J \right| \left| J \right|^{-1} e^{-\beta\frac{1}{2}\mathbf{p}_q \cdot G^{-1} \cdot \mathbf{p}_q} e^{-\beta U(q^N)}$$

• *we don't have to worry about the Jacobian with the full transform*

Integrating Over Momenta

○ If we integrate out the momentum coordinates, the Jacobian again arises

$$\pi(\mathbf{p},\mathbf{q}) = \frac{1}{Qh^{3N}} dp^N dq^N e^{-\beta\frac{1}{2}\mathbf{p}\cdot G^{-1}\cdot\mathbf{p}} e^{-\beta U(q^N)}$$

$$\pi(\mathbf{q}) = \frac{1}{Qh^{3N}} dq^N e^{-\beta U(q^N)} \int dp^N e^{-\beta\frac{1}{2}\mathbf{p}\cdot G^{-1}\cdot\mathbf{p}}$$

$$= \frac{1}{Qh^{3N}} dq^N e^{-\beta U(q^N)} |\mathbf{G}|^{1/2}$$

○ For the diatomic, this term is

$$|\mathbf{G}|^{1/2} = |\mathbf{J}| = cL^2 \sin\theta \qquad c = \text{constant}$$

○ In MC simulation, the terms must be included in the construction of the transition-probability matrix

Averages with Constraints 1.

○ Very stiff coordinates are sometimes treated as rigidly constrained

  - *e.g., the bond length L in the diatomic may be held at a constant value*

○ MC and MD have different ways to enforce this constraint

○ Regardless of simulation technique, the constrained-system ensemble average may differ from the unconstrained value

  - *even when compared to the limit of an infinitely stiff bond!*

○ Why the difference?

  - *A rigid constraint implies no kinetic energy in vibration*

  - *Examine the Lagrangian*

$$L = \frac{1}{2} \sum_{\beta \neq L} \sum_{\alpha \neq L} \frac{\partial r_i}{\partial q_\alpha} \frac{\partial r_i}{\partial q_\beta} q_\alpha q_\beta - U(\mathbf{q}^S; L)$$

s = "soft" coordinate

$$= \frac{1}{2} \dot{\mathbf{q}}^S \cdot G^S \cdot \dot{\mathbf{q}}^S - U(\mathbf{q}^S; L)$$

Averages with Constraints 2.

○ The Jacobian for the coordinate transform is the same as for the unconstrained average

○ But the momentum Jacobian no longer has the term for the constrained coordinate

○ Thus, in general, the distribution of unconstrained coordinates differs

$$\pi(\mathbf{p}_s, \mathbf{q}_s; L) = \frac{1}{Qh^{3N-l}} dp_s^{N-l} dq_s^{N-l} e^{-\beta \frac{1}{2} \mathbf{p}_s \cdot G_s^{-1} \cdot \mathbf{p}_s} e^{-\beta U(q_s^N)}$$

$$\pi(\mathbf{q}_s; L) = \frac{1}{Qh^{3N-l}} dq_s^{N-l} e^{-\beta U(q_s^N)} \int dp_s^{N-l} e^{-\beta \frac{1}{2} \mathbf{p} \cdot G^{-1} \cdot \mathbf{p}}$$

$$= \frac{1}{Qh^{3N-l}} dq_s^{N-l} e^{-\beta U(q_s^N)} |\mathbf{G}_s|^{1/2}$$

○ The difference is

$$\frac{\pi(q_s)}{\pi(q_s; L)} = \sqrt{\frac{|G_s|}{|G|}}$$

Averages with Constraints 3.

○ To get correct (unconstrained-system) averages from a simulation using constraints, averages should be multiplied by this factor

$$\left\langle M \right\rangle_{unconstained} = \left\langle M \sqrt{|G_s|/|G|} \right\rangle_{constrained}$$

○ Evaluating this quantity could be tedious

- *but there is a simplification*
- *the ratio of determinants (of N-by-N and (N-l)-by-(N-l) matrices) can be given in terms of the determinant of an l-by-l matrix*

$$\frac{|G_s|}{|G|} = |H| \qquad H_{\alpha\beta} = \sum_i \frac{\partial\sigma_a}{\partial r_i} \frac{\partial\sigma_\beta}{\partial r_i}$$

- *for the diatomic with L constrained, H = 1*

Rotational Dynamics

○ For completely rigid molecules, only translation and rotation are performed

○ Translational dynamics uses methods described previously, but now applied to the COM

○ Rotational dynamics must consider angular velocities and accelerations

○ Can treat via rotation of the molecule-frame coordinates in the spaced-fixed frame

$$\dot{\mathbf{e}}^s = \dot{\omega} \times \mathbf{e}^s$$

Angular velocity

- *changes in angular velocity are given via torque on molecule*

Quaternions

○ Rate of change of the Euler angles looks like this

$$\dot{\phi} = -\omega_x^s \frac{\sin\phi\cos\theta}{\sin\theta} + \omega_y^s \frac{\cos\phi\cos\theta}{\sin\theta} + \omega_z^s$$

○ A problem arises when θ is near 0

- *no physical significance, but very inconvenient to integration of equations of motion*

○ Quaternions can be used to circumvent the problem

- *describe orientation with 4 (non-independent) variables*
- *rotation matrix, equations of motion simply expressed in terms of these quantities*
- *note:* $q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1$

$$q_0 = \cos\frac{\theta}{2}\cos\frac{\phi+\psi}{2}$$

$$q_1 = \sin\frac{\theta}{2}\cos\frac{\phi-\psi}{2}$$

$$q_3 = \sin\frac{\theta}{2}\sin\frac{\phi-\psi}{2}$$

$$q_4 = \cos\frac{\theta}{2}\sin\frac{\phi+\psi}{2}$$

Monte Carlo Rotations

○ MC simulations of molecules include rotation moves

- *must do this to sample orientations of rigid molecules*
- *not strictly necessary for non-rigid molecules, but very helpful*
- *very easy to do this incorrectly*

○ Trial rotation of a linear molecule

- *Let present orientation be given by vector* **u**
- *Generate a unit vector* **v** *with random orientation*
- *Let new trial orientation be given by*

$$\mathbf{u}^{new} = \mathbf{u}^{old} + \gamma \mathbf{v}$$

  where γ is a fixed scale factor that sets the size of the perturbation

○ Nonlinear molecule

- *same procedure, but do perturbation on the 4-dimensional vector of quaternions*

Random Vector on a Sphere

○ Acceptance-rejection method of von Neumann

○ Iterate

(a) Generate 3 uniform random variates, r_1, r_2, r_3 on (0,1)

*(b) Calculate $z_i = 1-2r_i$, i=1,3, so that the vector **z** is distributed uniformly in a cube of side 2, centered on the origin*

(c) Form the sum $z^2 = z_1^2 + z_2^2 + z_3^2$

(d) If $z^2 < 1$, take the random vector as $(z_1/z, z_2/z, z_3/z)$ and quit

(e) Otherwise, reject the vector and return to (a)

○ Alternative algorithms are possible