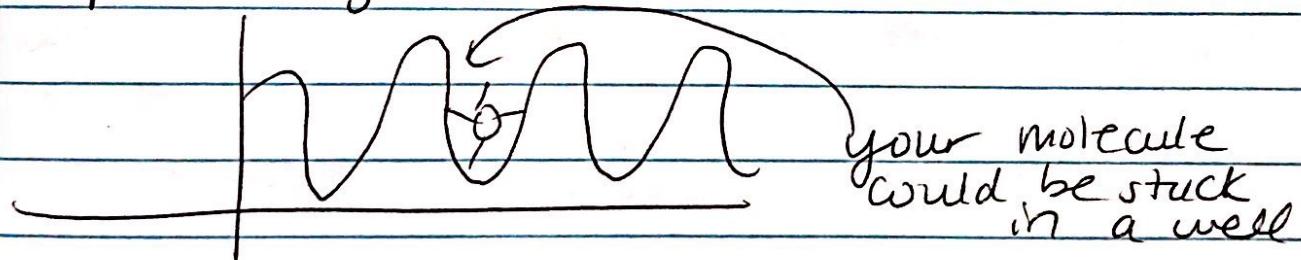


### 3. Simulations of Molecular Ensembles

#### 3.1 Relationship Between MM optima and Real Systems

→ When comparing theory to experiment, it is found that a minimum-energy structure (local min. on PES) is not very important  
↓ ↗ photo-electron spectroscopy  
even at 0K, the molecule probably has a range of diff. structures  
only accurate for small/stiff molecules

large molecules w/ 'loose' molecular coordinates + 'soft' torsional nodes will have a delocalized probability distribution.



\* Just as zero point vibration introduces probabilistic weightings to single-molecules, so too thermodynamics dictates that, given a large collection of molecules, probabilistic distribution of structures will be found about different local minima on the PES at non-zero absolute temperatures

\* We seek computational techniques capable of accurately reproducing experimental aspects of molecular behavior

## 3.2. Phase Space and Trajectories

- The state of a classical system can be completely described by specifying the positions and momenta of all particles.

Space = three dimensions  
each particle has 6 coordinates  
6N space = phase space

N particles →  
6N coordinates

$$\chi' = (x_1, y_1, z_1, p_{x,1}, p_{y,1}, p_{z,1}, x_2, y_2, z_2, p_{x,2}, \dots)$$

Used for  
ease of  
notation

$$q = (x_1, y_1, z_1, x_2, y_2, z_2, \dots)$$

position coordinates

$$p = (p_{x,1}, p_{y,1}, p_{z,1}, p_{x,2}, p_{y,2}, \dots)$$

Reordered phase space point:

$$\chi = (q, p)$$

Over time, a dynamical system maps out a 'trajectory' in a phase space. The trajectory is the curve formed by the phase points the system passes through

### 3.2.1 Properties as Ensemble Averages

$$\langle A \rangle = \iint A(q, p) P(q, p) dq dp$$

$\langle A \rangle$  = average value of a property  $A$  at equilibrium (i.e. its expectation value) for a system having a constant temperature, volume, and number of particles

$P$  = probability of being at a particular phase point

$$P(q, p) = Q^{-1} e^{-E(q, p)/k_B T} \rightarrow \text{temp.}$$

$Q =$  system partition function       $k_B =$  Boltzmann's constant       $E =$  total energy (sum of kinet + potential)

$$Q = \iint e^{-E(q, p)/k_B T} dq dp$$

↓ normalization constant for  $P$

\* One can't practically evaluate  $\langle A \rangle$  or  $E$  in a phase space numerically because you would have to solve an integral for ~~600 points~~  $2^{6N}$  such points for each coordinate

So instead, we should pick a few ~~6~~ important (i.e. high probability) points

### 3.2.2. Properties as Time Averages of Trajectories

$$\langle A \rangle = \frac{1}{M} \sum_i^M A(t_i)$$

how to compute a property average ~~sample~~:  
 compute the value of the property periodically  
 at times  $t_i$

$M = \#$  of times the property is sampled

If we limit the sample continuously and follow  
 the trajectory indefinitely, the equation becomes:

$$\rightarrow \star \quad \langle A \rangle = \lim_{t \rightarrow \infty} \frac{1}{T} \int_{t_0}^{t_0+T} A(\tau) d\tau$$

'ergodic hypothesis' → this equation is valid  
 + independent of  $t_0$

estimation of how a real system behaves

Conclusion → we have not yet provided a  
 description of how to "follow" a  
 phase-space trajectory.

If we start a system at some 'reasonable' (ie,  
 low-energy) phase point, its energy-conserving  
 evolution over time seems likely to sample  
 relevant regions of phase space

### 3.3 Molecular Dynamics

- One interesting property of a phase point that has not yet been emphasized is that, since it is defined by the positions and momenta of all particles, it determines the location of the next phase point in the absence of outside forces acting upon the system.

• Moreover, since time-independent Hamiltonians are necessarily invariant to time reversal, a single phase point completely determines a full trajectory



As a result, phase space trajectories cannot cross themselves (since there would then be two different points leading away (in both time directions) from a single point of intersection).

### 3.3.1 Harmonic Oscillator Trajectories

→ Phase space in a one-dimensional classical harmonic oscillator has only two dimensions, position and momentum.

You can define the origin of this phase space to correspond to the ball of mass  $m$  being at rest (i.e. zero momentum) w/ the spring at its equilibrium length

Relationship b/w two positions:  $q(t_2) = q(t_1) + \int_{t_1}^{t_2} \frac{p(t)}{m} dt$

Relationship b/w velocity + momentum:  $v = \frac{p}{m}$

Relationship b/w two momentum vectors:  $p(t_2) = p(t_1) + m \int_{t_1}^{t_2} a(t) dt$

Newton's Second Law

$$a = \frac{F}{m} \rightarrow \text{Force}$$

Leads To:

$$q(t) = b \cos\left(\sqrt{\frac{k}{m}} t\right)$$

$$p(t) = -b \sqrt{mk} \sin\left(\sqrt{\frac{k}{m}} t\right)$$

These equations map out the oval phase space trajectory of a harmonic oscillator. The cos and sin functions show how the harmonic oscillator is periodic

### 3.3.2 Non-analytical systems

For non-harmonic systems, it is almost never possible to write down analytical expressions for the position and momentum components of the phase space trajectory as a function of time.

But they can be approximated! (Euler)

$$q(t + \Delta t) = q(t) + \frac{p(t)}{m} \Delta t$$

$$p(t + \Delta t) = p(t) + m a(t) \Delta t$$

set of initial positions and momenta

→ a means for computing the forces acting on each particle at any instant

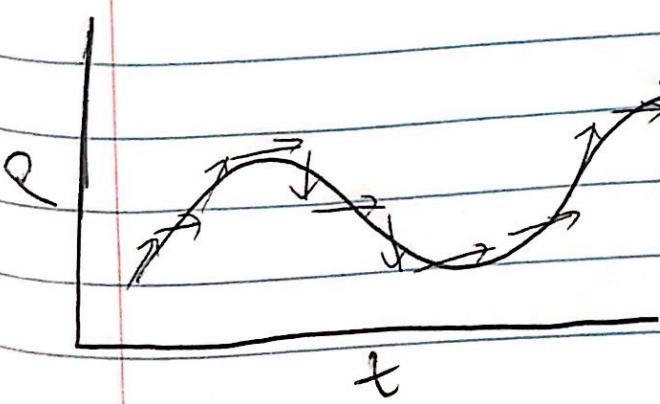
→ now we have a formalism for "simulating" the true phase-space trajectory

$$T(t) = \frac{1}{(3N-n)k_B} \sum_{i=1}^N \frac{|p_i(t)|^2}{m_i}$$

↓  
relationship between temperature and momentum

→ N = total # of atoms

n = # of constrained degrees of freedom



phase-space trajectory vs.  
approximate trajectory

### 3.3.3 Practical Issues in Propagation

→ Euler's approximation is not very stable. More sophisticated integration schemes have been developed for propagating trajectories.

They derive from Taylor expansions:

$$q(t + \Delta t) = q(t) + v(t)\Delta t + \frac{1}{2!} a(t)(\Delta t)^2 + \frac{1}{3!} \frac{d^3 q(t)}{dt^3} \Big|_{t=t} (\Delta t)^3$$

↓                      ↓                      ↓  
 position vector      velocity      acceleration  
 (1<sup>st</sup> derivative)    (2<sup>nd</sup> derivative)    (3<sup>rd</sup> derivative)

Verlet → considers sum of Taylor expansions corresponding to forward and reverse time steps  $\Delta t$

Verlet (original)

$$q(t + \Delta t) = 2q(t) - q(t - \Delta t) + a(t)(\Delta t)^2$$

for any particle, each subsequent position is determined by the current position, the previous position, and the particle's acceleration

↓  
with velocities.

$$q(t + \Delta t) = q(t) + v(t + \frac{1}{2}\Delta t)\Delta t$$

$$v(t + \frac{1}{2}\Delta t) = v(t - \frac{1}{2}\Delta t) + a(t)\Delta t$$

Scaling of the velocities can be accomplished to control temperature

leaping method

position depends on velocities as computed one-half time step out of phase

### 3.3.4 Stochastic Dynamics

If we just want to watch a particular system evolve dynamically in a larger system, computational savings can be made by modelling the larger system stochastically

$$\ddot{\mathbf{r}}(t) = -\frac{1}{m} \mathbf{p}(t) + \frac{1}{m} [\mathbf{F}_{\text{intra}}(t) + \mathbf{F}_{\text{continuum}}(t)]$$

Langevin dynamics

the equation of motion for each particle

force

continuum characterized by  
microscopic friction coefficient

we can approximate  
this to be  $\propto$

Now: set l.h.s of the equation to 0 and integrate

$$\mathbf{r}(t) = \mathbf{r}(t_0) + \frac{1}{\zeta} \int_{t_0}^t [\mathbf{F}_{\text{intra}}(\tau) + \mathbf{F}_{\text{continuum}}(\tau)] d\tau$$

Brownian dynamics

momentum degrees

of freedom are removed

Now we only propagate the position vector

Langevin + Brownian dynamics are very efficient because a potentially very large surrounding medium is represented by a simple continuum