

Physics 750: Lecture 12

Thursday, October 5, 2017

Choice of time step

The motion of a particle is hardest to resolve when it is subject to large and sudden acceleration. Since $\mathbf{a} = \mathbf{F}/m = -\nabla U/m$, the worst numerical problems coincide with large potential gradients and small masses (relative to other particles in the system).

For example, the Lennard-Jones pair potential has a repulsive inner part that is nearly hard core on a length scale $\sim \sigma$. The potential rises dramatically over small distances and thus generates extremely large forces. For two colliding particles that are unbound (or only weakly bound), the pair potential at the classical turning point r_{cl} is extremely steep, and it becomes difficult to ensure that there is no penetration into the energetically forbidden region. Managing the numerical discrepancies in energy $\Delta E \sim U'(r)\Delta l$ is a matter of controlling the spatial resolution Δl of the simulation. The estimate of what length scale is sufficiently small, $\Delta l \ll |\Delta E/U'(r_{cl})|$, is dominated by the large forces felt at r_{cl} .

Thus, to handle the nearly hard core repulsion correctly, the time step must be chosen small enough to satisfy $\Delta t \ll \Delta l/v$, where v is the typical velocity of an incident particle. On the other hand, the total computational work over a fixed time window is proportional to $1/\Delta t$, so we want to use the biggest time step we can get away with. One option is to adjust the time step on the fly—using, say, a Δt that tracks the smallest interparticle separation. This works quite well for few-body problems in which close approaches are rare. But it doesn't offer much in the way of savings for a dense gas.

Distribution of masses

For a system of particles in thermal equilibrium with a broad distribution of masses, the lightest particles—the ones travelling fastest—control the time step bound. This is a straightforward consequence of the equipartition theorem.

Consider a two-species gas with particles of mass m and $M \gg m$. We expect the time-averaged velocities to satisfy

$$\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}M\langle V^2 \rangle = \frac{3}{2}kT.$$

Hence, we need both

$$\Delta t \ll \Delta l \sqrt{\frac{m}{3kT}} \quad \text{and} \quad \Delta t \ll \Delta l \sqrt{\frac{M}{3kT}}$$

to hold. The first condition, however, dominates completely.

If m/M is sufficiently small, it may be better to analytically integrate out the fast modes and attempt to simulate a model of the mass- M particles moving in an effective medium. In the simplest case, this leads to Langevin dynamics: the mass- m particles act as a viscous soup that introduces drag and brownian motion terms. The modified equations of motion read

$$\begin{aligned} \mathbf{V}_i &= \dot{\mathbf{R}}_i, \\ M\dot{\mathbf{V}}_i &= - \sum_{j \neq i} U'(R_{i,j}) \hat{\mathbf{R}}_{i,j} - \gamma \mathbf{V}_i + f_i(t), \end{aligned}$$

and constitute a set of *stochastic* differential equations. Here, γ is a damping coefficient and the force $f_i(t)$ is a source of thermal, Gaussian noise. We can assume that $\langle f_i(t)f_j(t') \rangle \sim k_B T \delta_{i,j} \delta(t-t')$, which is to say that $f_i(t)$ for each particle is correlated on a time scale much shorter than the Δt step appropriate for the slow masses M .

Particle assemblies

Clusters of point particles that are held together by mutual forces generate internal times scales of their own. For example, atoms bound stiffly into molecules move relative to one another much faster than their molecular centres of mass.

A bound pair of atoms approximated by a classical spring is described by

$$\frac{1}{2}\mu v^2 + \frac{1}{2}k(r-d)^2,$$

where μ is the effective mass of the pair, k is the spring constant, and d is the equilibrium length of the bond. The spring has a natural frequency $\Omega = \sqrt{k/\mu}$ which must be resolved numerically on a time scale $\Delta t \ll \sqrt{\mu/k}$. Clearly, simulations get expensive when k gets large. (Again, smaller Δt implies more times steps over a fixed time interval.)

Molecular assemblies involving more than two atoms will also have degrees of freedom associated with the angular displacements of the bonds.

Internal coordinates

Consider a diatomic gas in which the molecular pairs are described by parameters $m_i, \mathbf{r}_i, \mathbf{p}_i$ and $M_i, \mathbf{R}_i, \mathbf{P}_i$. The N -particle Hamiltonian is

$$H = \sum_{i=1}^N \left(\frac{p_i^2}{2m_i} + \frac{P_i^2}{2M_i} + \frac{k}{2} (|\mathbf{r}_i - \mathbf{R}_i| - d)^2 \right) + \text{interactions.}$$

As the spring becomes increasingly stiff ($k \rightarrow \infty$), the Hooke's law contribution remains finite only because deviations from the equilibrium length d become negligible.

In that limit, the motion along the line of connection is quenched, and we are left with a "ball and stick" model of the molecule. The number of degrees of freedom has thus been reduced, and the total phase space is correspondingly smaller. In principle, we can eliminate the constrained variables by a suitable coordinate transformation. For two particles, there are $3 \times 4 = 12$ real variables associated with $\mathbf{r}, \mathbf{v}, \mathbf{R}$, and \mathbf{V} . But for the rigid rod, there are $3 \times 2 = 6$ variables associated with the position and velocity of the center of mass, and there are $2 \times 2 = 4$ variables associated with the position and velocity of the rod end's intersection with a 2-sphere. The dimension of the phase space is reduced from $12N$ to $10N$.

Rigid constraints

Unfortunately, interactions between particles are difficult to express in terms of internal coordinates. The reduction in phase space comes at the cost of formal complexity, and it is typically better to remain in cartesian coordinates and to impose a rigid bond constraint $|\mathbf{r}_i - \mathbf{R}_i| = d$ for all $i = 1, 2, \dots, N$.

We proceed by introducing a Lagrange multiplier λ_i for each bond. The Hamiltonian now reads

$$H = \sum_{i=1}^N \left(\frac{p_i^2}{2m_i} + \frac{P_i^2}{2M_i} - \lambda_i [(\mathbf{r}_i - \mathbf{R}_i)^2 - d^2] \right) + \text{interactions.}$$

The resulting equations of motion are explicitly λ_i -dependent. Their values are fixed by imposing

$$\frac{\partial H}{\partial \lambda_i} = (\mathbf{r}_i - \mathbf{R}_i)^2 - d^2 = 0.$$