

# 0. Introduction

These notes will describe five different methods, 1 through 5, for doing simulations of a gas of interacting particles.

First some introductory points:

- Adding interactions to the ideal gas.
- The Lennard-Jones interaction.
- Length and time scales.
- Simulation units.
- The Boltzmann distribution.
- Expression for the pressure.

# Adding interactions to the ideal gas

## The ideal gas—no interactions

$$pV = Nk_B T,$$

relates pressure times volume to the number of particles, Boltzmann's constant, and the temperature (measured in Kelvin).

Approximate the interaction energy by a sum of pair interactions:

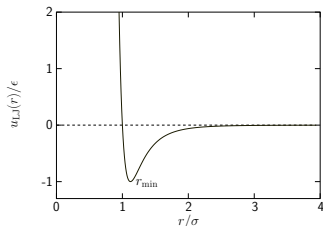
$$\begin{aligned} U(\{\mathbf{r}\}) &= \frac{1}{2} \sum_i \sum_j u(|\mathbf{r}_i - \mathbf{r}_j|) \\ &= \sum_i \sum_{j>i} u(|\mathbf{r}_i - \mathbf{r}_j|). \end{aligned}$$

Note: two different ways to avoid double counting.  
In the code we should use the second!

# The Lennard-Jones interaction

The Lennard-Jones interaction:

- attractive at large distances,  $\sim -r^{-6}$ ,
- repulsive at short distances,  $\sim r^{-12}$ .



Taken together this gives the Lennard-Jones potential,

$$u_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right],$$

where  $\sigma$  and  $\epsilon$  are the length and energy scales of the interaction.

The minimum of the potential:

$$r_{\min} = 2^{1/6}\sigma, \quad u_{LJ}(r_{\min}) = -\epsilon.$$

## Length and time scales

What are the characteristic length, time, and energy scales of a real gas?

The parameters of the LJ interaction for Neon atoms are

$$\epsilon = 4.18 \times 10^{-22} \text{ J} \quad \text{and} \quad \sigma = 3.12 \times 10^{-10} \text{ m}.$$

The typical velocity from  $m\langle \mathbf{v}^2 \rangle = 3k_B T$ , where “3” is the dimensionality.

With

- $m \approx 28 \times 1.67 \times 10^{-26} \text{ kg}$  for  $N_2$  molecules (typical of air),
- $T = 300 \text{ K}$  (which is  $27^\circ \text{C}$ ),  $k_B \approx 1.38 \times 10^{-23} \text{ J/K}$ ,

$$\sqrt{\langle \mathbf{v}^2 \rangle} \approx 10^3 \text{ m/s}.$$

Time scale of  $10^{-13} \text{ s} = 0.1 \text{ ps}$ , since  $\sigma \sim 10^{-10} \text{ m}$ .

# Simulation units

To use simulation units, let

$$\frac{r}{\sigma/\mathbf{m}} \rightarrow r \quad \text{and} \quad \frac{u_{\text{LJ}}(r)}{\epsilon/\mathbf{J}} \rightarrow u_{\text{LJ}}(r) \quad \text{and} \quad k_B T / (\epsilon/\mathbf{J}) \rightarrow T,$$

where  $\sigma/\mathbf{m}$  (meter) and  $\epsilon/\mathbf{J}$  (Joule) are pure numbers.

Note:

- $r$  and  $u_{\text{LJ}}$  still have dimensions of length and energy,
- $r = \sigma$  in ordinary units is now  $r = 1$ .
- The temperature now has dimension of energy.
- We often take  $m = 1$  (instead of something  $\times 10^{-26}$  kg).

# The Boltzmann distribution

Two different ensembles:

- Microcanonical ensemble—only states with a given energy,
- Canonical ensemble—all energies are possible, controlled by the temperature.

(Including states irrespective of energy often simplifies both analytical calculations and numerical computations.)

A key quantity in the canonical ensemble: the Boltzmann factor,  $e^{-E_\nu/T}$ .

The probability of a state is proportional to the Boltzmann factor,

$$P_\nu \propto e^{-E_\nu/T}.$$

## Expression for the pressure

- Molecular dynamics—pressure from the change of momentum the particles bounce off the walls.
- Monte Carlo (no dynamics)—determine pressure from a correlation function!

Starting point:  $dF = -SdT - pdV + \mu dN$  gives  $p = -\left(\frac{\partial F}{\partial V}\right)_{N,T}$ .

From  $\beta F = -\ln Z$  we get

$$\beta p = \left(\frac{\partial \ln Z}{\partial V}\right)_{N,\beta}, \quad Z = Z_{\text{kin}} Z_{\text{conf}},$$

where

$$Z_{\text{conf}} = \frac{1}{N!} \int_V d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta U(\mathbf{r}^N)}.$$

Differentiate with respect to the integration volume?!

## Expression for the pressure... cont'd

Changing coordinates to  $\mathbf{x} = \mathbf{r}/V^{1/d} \Rightarrow d\mathbf{r}^N = V^N d\mathbf{x}^N$  gives

$$\begin{aligned}\beta p &= \frac{\partial}{\partial V} \ln \left[ V^N \int d\mathbf{x}^N e^{-\beta \sum_{i<j} u(V^{1/d} x_{ij})} \right] \\ &= \frac{d}{dV} \ln V^N + \frac{\partial}{\partial V} \ln \left[ \int d\mathbf{x}^N e^{-\beta U} \right] \\ &= \frac{N}{V} + \left[ \int d\mathbf{x}^N \left( -\beta \frac{\partial U}{\partial V} \right) e^{-\beta U} \right] / \left[ \int d\mathbf{x}^N e^{-\beta U} \right].\end{aligned}$$

Putting things together we get the virial theorem

$$\beta p = \frac{N}{V} - \frac{\beta}{Vd} \left\langle \sum_i \sum_{j>i} r_{ij} u'(r_{ij}) \right\rangle,$$

which in terms of the interparticle force becomes

$$pV = Nk_B T + \frac{1}{d} \left\langle \sum_i \sum_{j>i} r_{ij} F_{ij} \right\rangle. \quad (1)$$



## Different kinds of simulations

Five different methods that may be used for simulating a gas.

i–iii: Different ways to *describe* the system.

1–5: Different kinds of *dynamics*.

i) Describe the gas in terms of  $\{\mathbf{r}\}$  and  $\{\mathbf{v}\}$ .

1) Molecular dynamics: ODE – deterministic.

2) Langevin dynamics: ODE with a stochastic term.

ii) Describe the gas with  $\{\mathbf{r}\}$ , only.

3) Brownian dynamics:  $\Delta\mathbf{r}_i = c\mathbf{F}_i + \text{noise}$ .

4) Monte Carlo: No real dynamics. For each particle  $i$  iterate:

★ suggest a change  $\Delta\mathbf{r}_i$  by random,

★ calculate the change in energy,  $\Delta E_i$ ,

★ accept this change with a probability that depends on  $\Delta E_i/T$ .

iii) Use a discrete space with positions

$\mathbf{r}_\ell = (0, 0, 0), (0, 0, 1), \dots (0, 0, L - 1), \dots (L - 1, L - 1, L - 1)$ .

5) The lattice gas: Each position either occupied or empty,  $n_\ell = 0, 1$ .

Monte Carlo with fluctuating numbers of particles.

## Considerations for MD—Elementary physics

The behavior of a classical gas is fully specified by the Hamiltonian,

$$\mathcal{H}(\{\mathbf{r}\}, \{\mathbf{v}\}) = U(\{\mathbf{r}\}) + K(\{\mathbf{v}\}), \quad \text{given by}$$

$$U = \frac{1}{2} \sum_{i,j} u(\mathbf{r}_i - \mathbf{r}_j) \quad \text{and} \quad K = \sum_i \frac{m_i \mathbf{v}_i^2}{2}.$$

The dynamics is given by Newton's second law:

$$m_i \dot{\mathbf{v}}_i = \mathbf{F}_i \equiv -\nabla_i U(\{\mathbf{r}\}), \quad \text{where } \nabla_i \text{ is differentiation w.r.t. } \mathbf{r}_i.$$

For each velocity component the probability distribution is

$$P(v) \propto e^{-mv^2/2T}, \quad \text{normal distribution—central limit theorem.}$$

and accordingly

$$m \langle v^2 \rangle = T \quad \text{in terms of energy: } \frac{m}{2} \langle v^2 \rangle = \frac{T}{2}. \quad (2)$$

The total energy is a constant.  $U$  and  $K$  fluctuate during the simulation.

## Cutoff in the interaction potential

In an “exact” simulation of a Lennard-Jones gas we would use the potential out to arbitrary distances—very inefficient!

Introduce a cutoff  $r_c$

$$u_s(r) = \begin{cases} u_{\text{LJ}}(r) - u_{\text{LJ}}(r_c), & r < r_c, \\ 0, & r > r_c. \end{cases}$$

We can then neglect particles at big distances.

If one also needs a well-behaved second derivative:

$$u_s(r) = \begin{cases} u_{\text{LJ}}(r) - u_{\text{LJ}}(r_c) + (r_c - r) \left. \frac{du_{\text{LJ}}}{dr} \right|_{r_c}, & r < r_c, \\ 0, & r > r_c. \end{cases}$$

## How handle the walls? Periodic boundary conditions!

Think of several identical simulation cells placed one after the other with the same particles. Only a mental picture!



- Dynamics: When a particle leaves the system through a wall it simultaneously enters the system through the opposite wall. Each time a particle coordinate changes, check if the new position is outside the cell,  $x < 0$  or  $x > L$ . If so  $x + L \rightarrow x$  or  $x - L \rightarrow x$ .
- Forces: Only consider the interaction with the nearest image. To find the nearest image, for directions  $x$ ,  $y$ , and  $z$ :  $x_{ij} = x_i - x_j$ . If  $|x_{ij}| > L/2$  either add or subtract  $L$  such that  $|x_{ij}| < L/2$ .

The distance vector is  $\mathbf{r}_{ij} = (x_{ij}, y_{ij}, z_{ij})$ .

- The nearest image convention has implications for the smallest possible size of the simulation cell. We need  $L \geq 2r_c$ .

# Integration method

Our basic equations:

$$\dot{\mathbf{r}} = \mathbf{v}, \quad m\dot{\mathbf{v}} = \mathbf{F}.$$

Two good methods with time reversal symmetry:

- The leap from method.
- The velocity Verlet method.

The leap-frog method has positions and forces defined at times  $t = n\Delta_t$  whereas velocities are defined at the intermediate times,  $t = (n + 1/2)\Delta_t$ .

With the notation  $\mathbf{r}_n \equiv \mathbf{r}(n\Delta_t)$ :

$$\begin{aligned}\mathbf{v}_{n+1/2} &= \mathbf{v}_{n-1/2} + (1/m)\mathbf{F}_n\Delta_t, \\ \mathbf{r}_{n+1} &= \mathbf{r}_n + \mathbf{v}_{n+1/2}\Delta_t.\end{aligned}$$

Note: in the code we always write over the old values with the new ones.

# Integration time step

Two considerations when it comes to the time step:

- Stability—otherwise the solution will go to infinity.
- Good precision!

*We can only expect a good precision if the steps are small enough that the change in interaction potential in a single step is small.*

If the interaction potential changes on the scale  $\ell$ ,

$$\sqrt{\langle v^2 \rangle} \Delta_t \ll \ell, \quad \text{or} \quad \Delta_t \ll \ell \sqrt{\frac{m}{T}}.$$

In practice: test different time steps and choose one in the range where the measured results only depend very weakly on  $\Delta_t$ .

# Langevin dynamics

- Mostly used as an ODE with a thermostat.
- Originally invented to simulate bigger molecules in a solvent with a large number of smaller molecules. (Big biological molecules in water.)

Idea: include the effect of the smaller molecules in an average way. Good for two reasons:

- A large fraction of the molecules may be eliminated from the calculations.
- The heavier molecules typically move more slowly—we can do with a bigger time step!

## Langevin dynamics. . . cont'd

Add two terms:

- a random force,  $\zeta$ , adds energy,
- a friction term  $-\alpha\mathbf{v}$ , dissipates energy.

The equations of motion then become

$$m\dot{\mathbf{v}} = \mathbf{F} - \alpha\mathbf{v} + \zeta.$$

How should the magnitude of  $\zeta$  be chosen to do a simulation at a desired temperature?

We first need to consider how the noise should be treated.