



# Computational Physics (PHYS6350)

*Lecture 14: Classical molecular dynamics*

$$m\ddot{\mathbf{r}}_i = - \sum_j \nabla_i V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$$

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**Instructor:** Volodymyr Vovchenko ([vvovchenko@uh.edu](mailto:vvovchenko@uh.edu))

**Course materials:** <https://github.com/vlvovch/PHYS6350-ComputationalPhysics/tree/spring2025>

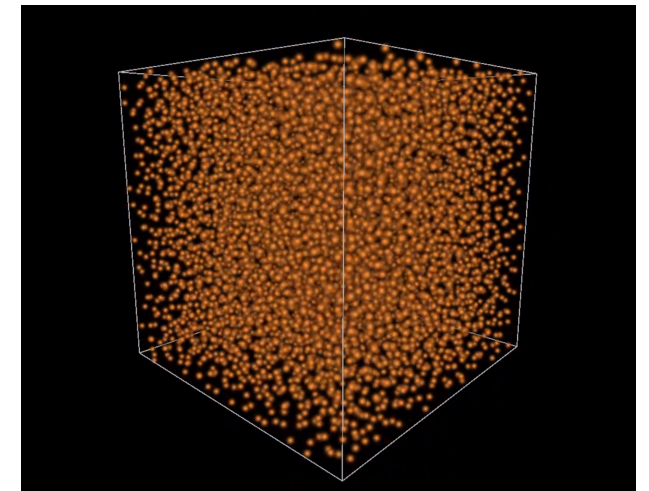
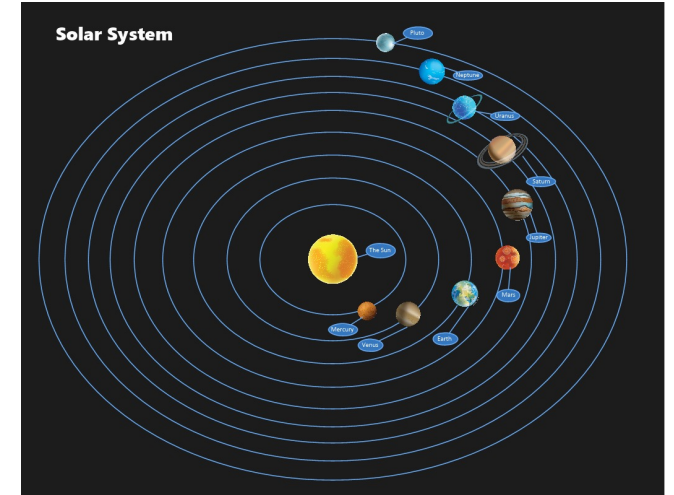
# Molecular dynamics (MD)

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- System of  $N$  particles with a pair potential
- Newton's equations of motion (classical  $N$ -body problem)

$$m\ddot{\mathbf{r}}_i = - \sum_j \nabla_i V_{ij}^{\text{LJ}}(|\mathbf{r}_i - \mathbf{r}_j|)$$

- Planetary motion
  - Solar system simulation
- Statistical mechanics properties and the **equation of state**
  - Finite simulation box with periodic boundary conditions



# Molecular dynamics equations

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Have to solve Newton's equations of motion

$$m_i \ddot{\mathbf{r}}_i = - \sum_{j \neq i} \nabla_i V(\mathbf{r}_i, \mathbf{r}_j)$$

- Desired properties
  - Stability (long simulations)
  - Energy conservation
  - Time-reversibility
- Rewrite as a system of first-order ODEs

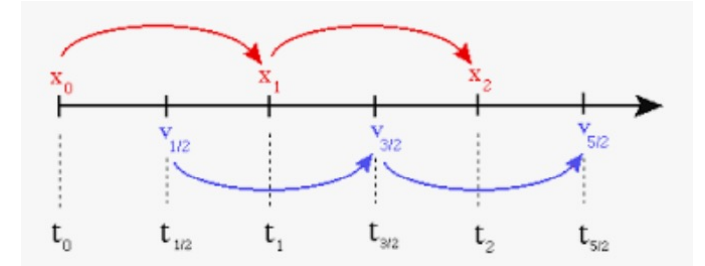
$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{v}_i, \\ \dot{\mathbf{v}}_i &= -(m_i)^{-1} \sum_{j \neq i} \nabla_i V(\mathbf{r}_i, \mathbf{r}_j), \end{aligned}$$

and use the **leapfrog method**

# Velocity Verlet method

We have system of equations

$$\begin{aligned}\frac{dx}{dt} &= v, \\ \frac{dv}{dt} &= f(x, t).\end{aligned}$$



The **leapfrog scheme** applied to this system of equations:

$$\begin{aligned}x(t+h) &= x(t) + hv(t+h/2), \\ v(t+3h/2) &= v(t+h/2) + hf[x(t+h), t+h],\end{aligned}$$

- Coordinates are evaluated at full steps
- Velocities are evaluated at half-steps

Leapfrog method applied to molecular dynamics problem is called **Velocity Verlet method**.

**Velocity Verlet:**

$$\begin{aligned}v(t+h/2) &= v(t) + \frac{h}{2}f[x(t), t], \\ x(t+h) &= x(t) + hv(t+h/2), \\ v(t+h) &= v(t+h/2) + \frac{h}{2}f[x(t+h), t+h].\end{aligned}$$

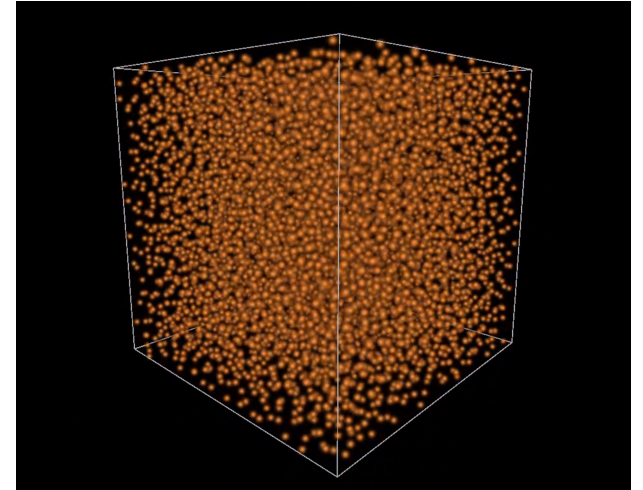
# Box simulation and statistical mechanics

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- Statistical mechanics: system with large number of particles
- Microscopically: Newton's equations of motion

$$m\ddot{\mathbf{r}}_i = - \sum_j \nabla_i V_{\text{LJ}}^{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$$

- Perform box simulation to emulate infinite system
  - Periodic boundary conditions (create images of the system)
  - Minimum-image convention (consider only closest image for all pairs)
- If  $N$  is large enough, system can be characterized by macroscopic parameters
  - Energy-Volume-Number (UVN): **microcanonical ensemble** describing closed system with fixed energy
  - Temperature-Volume-Number (TVN): **canonical ensemble** where the system is coupled to a thermostat to maintain constant temperature
- MD simulations give access to the **equation of state**



# Velocity Verlet method for box simulation

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$$\begin{aligned}\dot{\mathbf{r}}_i &= \mathbf{v}_i, \\ \dot{\mathbf{v}}_i &= -(m_i)^{-1} \sum_{j \neq i} \nabla_i V(\mathbf{r}_i, \mathbf{r}_j),\end{aligned}$$

```
# Apply the velocity verlet time step
# Returns the tuple of new positions, velocities, accelerations (forces), potential energy and pressure
def velocity_verlet(positions, velocities, accelerations,
                    time_step, potential, potential_gradient):
    # Update positions
    positions += velocities*time_step + 0.5*accelerations*time_step**2
    positions = positions - box_length*np.floor(positions/box_length)
    # Update velocities
    velocities_half = velocities + 0.5*accelerations*time_step
    # Compute new forces and potential energy
    accelerations, potential_energy, pressure = compute_forces(accelerations, positions, potential, potential_gradient)
    # Update velocities using new accelerations
    velocities = velocities_half + 0.5*accelerations*time_step
    # Add ideal gas contribution to the pressure
    kinetic_temperature = compute_kinetic_temperature(velocities)
    pressure += density * kinetic_temperature
    return positions, velocities, accelerations, potential_energy, pressure
```

# Forces

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We will assume all masses are equal to unity,  $m_i = 1$  (dimensionless) and that the pair potential depends on the distance only. Then

$$\ddot{\mathbf{r}}_i = - \sum_{j \neq i} \frac{dV(r_{ij})}{dr_{ij}} \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}} .$$

```
# Computes forces for a given vector of positions, interaction potential and its gradient
# Return a tuple: positions, total potential energy, and the virial part of the pressure
def compute_forces(forces, positions, potential, potential_gradient):
    # forces = np.zeros_like(positions)
    forces.fill(0.)
    potential_energy = 0.0
    virial = 0.0
    for i in range(n_particles):
        for j in range(i+1, n_particles):
            # Vector of relative distance
            r_ij = positions[i] - positions[j]
            # Periodic boundary conditions (minimum-image convention)
            r_ij = r_ij - box_length*np.round(r_ij/box_length)

            r_sq = np.sum(r_ij**2)
            f_ij = -potential_gradient(r_sq) * r_ij

            forces[i] += f_ij
            forces[j] -= f_ij
            potential_energy += potential(r_sq)
            virial += np.dot(f_ij, r_ij)

    virial = virial/(3.0*box_length**3)
    return forces, potential_energy, virial
```

# Example: Lennard-Jones fluid

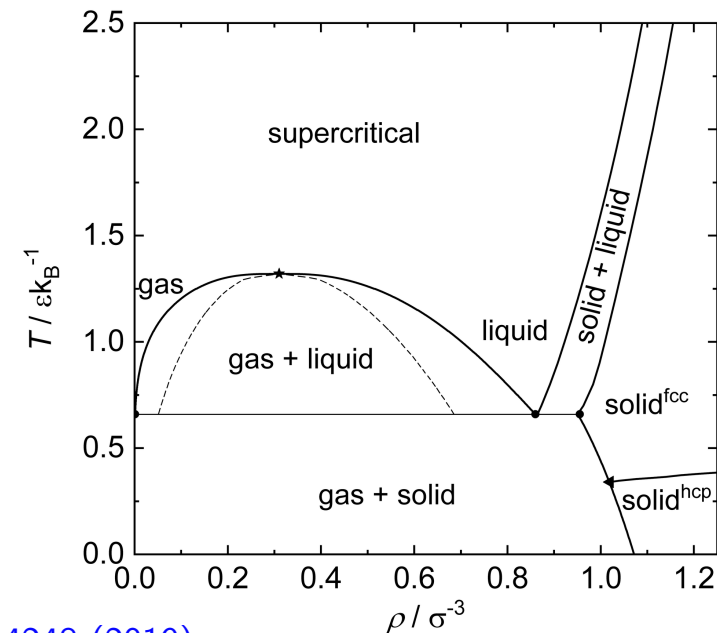
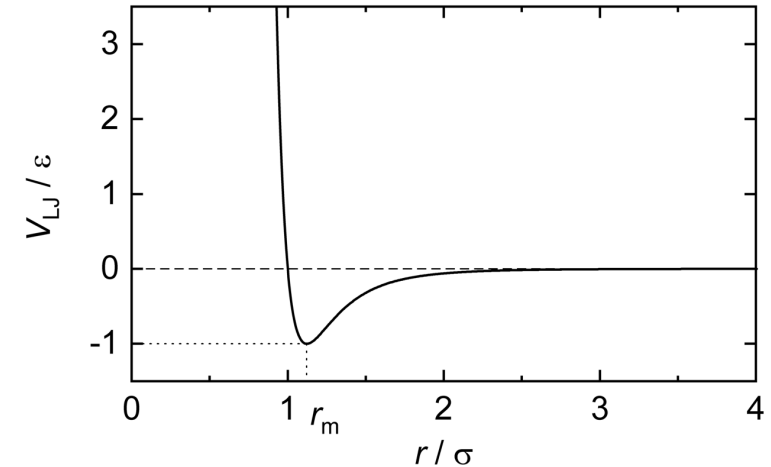
$$V_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

Reduced variables:

$$\tilde{r} = r/\sigma \quad \tilde{T} = T/(k_B\epsilon) \quad \tilde{n} = n\sigma^3$$

Properties:

- Multiple phase transitions, including critical point
- Cannot be solved analytically
- Tractable with molecular dynamics simulations





# Example: Lennard-Jones fluid

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$$\ddot{\mathbf{r}}_i = - \sum_{j \neq i} \frac{dV(r_{ij})}{dr_{ij}} \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}} .$$

```
# Lennard-Jones potential as a function of squared distance
def lj_potential(r_sq):
    r6 = r_sq**3
    r12 = r6**2
    return 4.0*(1./r12 - 1./r6)

# The grandient term dV/dr / r in the rhs of Newton's equations
# for the LJ potential
def lj_potential_gradient(r_sq):
    r6 = r_sq**3
    r12 = r6**2
    return -24.0*(2./r12 - 1./r6) / r_sq
```

Both the potential and the gradient term can be expressed in terms of  $|\mathbf{r}_i - \mathbf{r}_j|^2$ ,  
saves the unnecessary computation of the square root

# Simulation: Initial conditions

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We have to initialize the system with initial positions and velocities

- Coordinates
  - Put particles in a grid
  - Avoids particle overlap (mind the  $r^{-12}$  term)
- Velocities
  - Sample each component from Gaussian (Maxwell-Boltzmann) distribution

```
def initial_positions():  
    ret = np.zeros((n_particles,3))  
    Nsingle = np.ceil(n_particles**(1/3.))  
    dL = box_length / Nsingle  
    for i in range(n_particles):  
        ix = i % Nsingle  
        iy = (np.trunc(i / Nsingle)) % Nsingle  
        iz = np.trunc(i / (Nsingle * Nsingle))  
        ret[i][0] = (ix + 0.5) * dL;  
        ret[i][1] = (iy + 0.5) * dL;  
        ret[i][2] = (iz + 0.5) * dL;  
    return ret
```

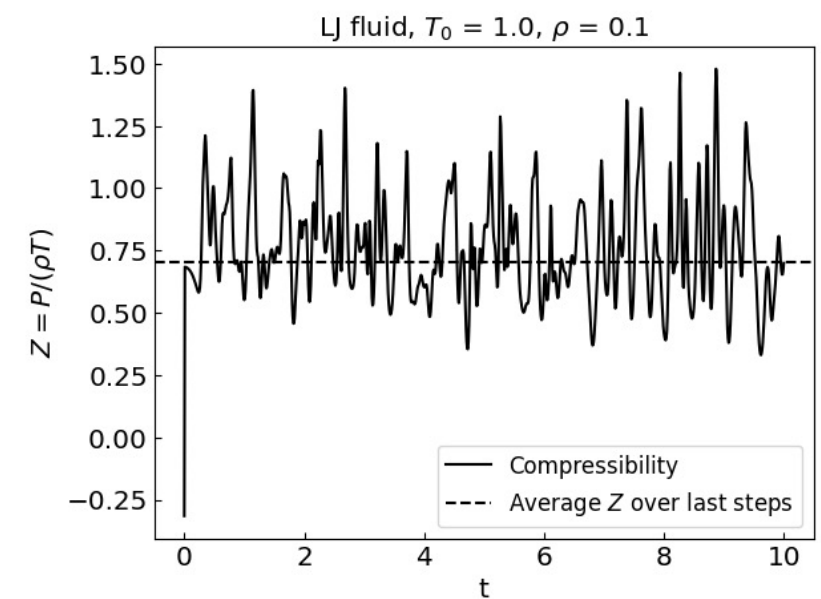
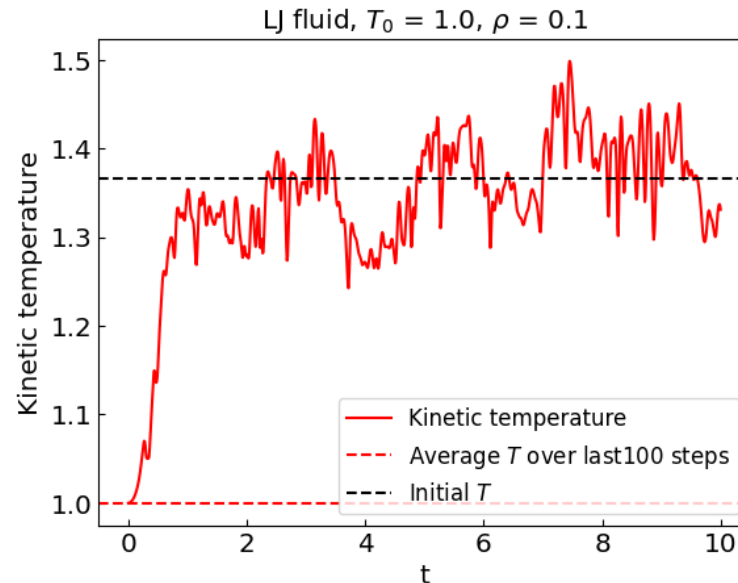
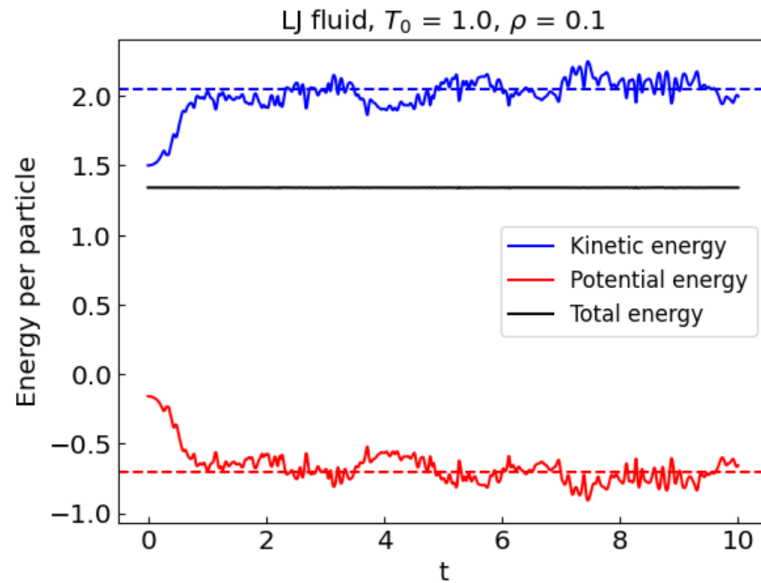
```
positions = initial_positions()  
velocities = np.random.normal(loc=0.0, scale=np.sqrt(temperature0), size=(n_particles, 3))
```

# Simulation

$$T = 1, \rho = 0.1, N = 64$$

$$T_{\text{kin}} = \langle \mathbf{v}_i^2 \rangle / 3$$

$$Z = p / (\rho T)$$



Kinetic temperature drifts away from initial value!

Reason: system takes time to equilibrate, and temperature is not conserved in microcanonical ensemble

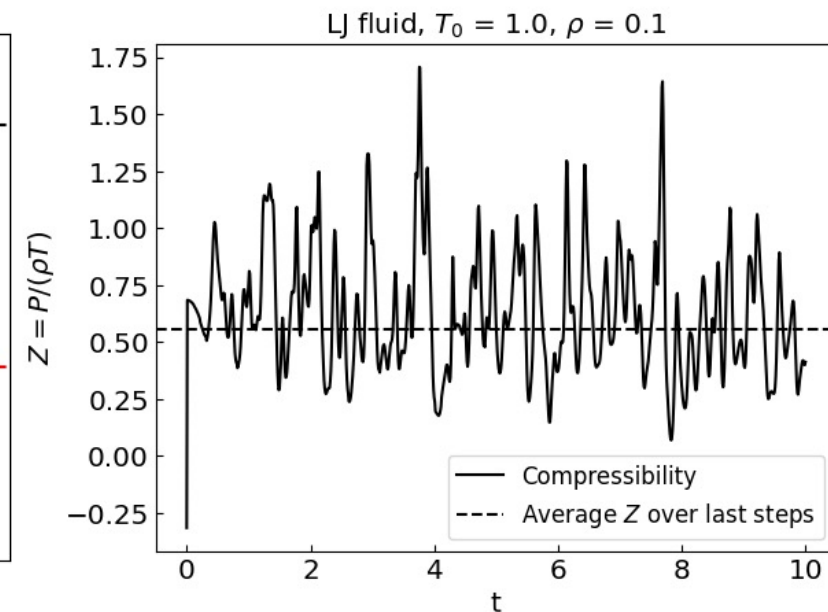
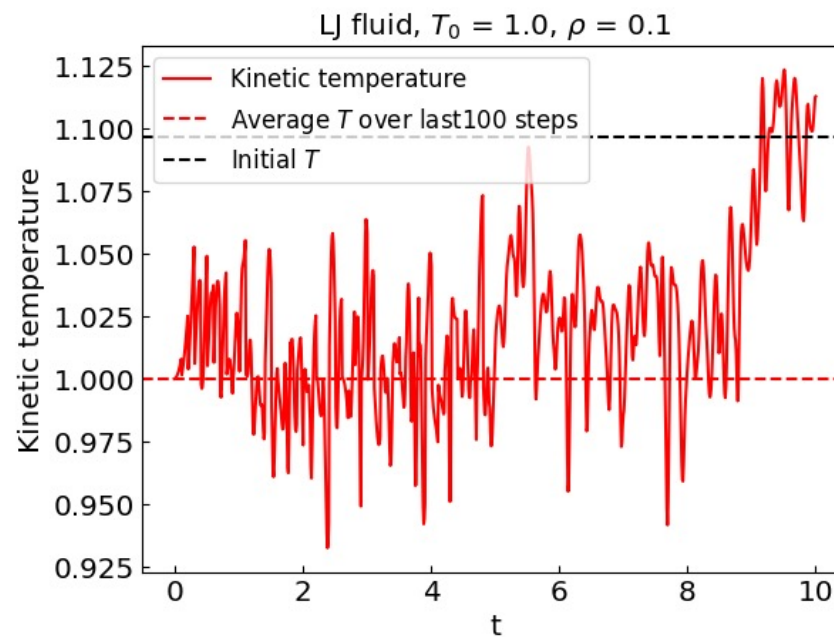
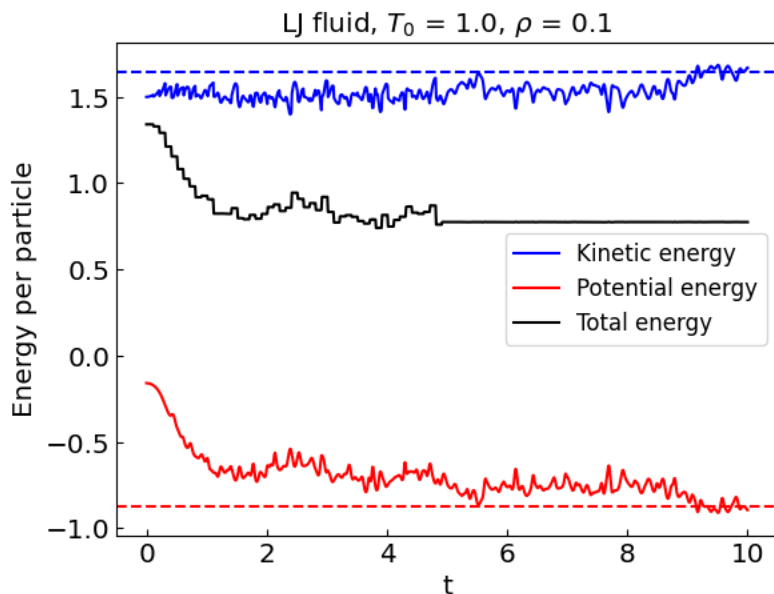
# Simulation: Keep the temperature fixed

Keep the temperature fixed during the equilibration phase by periodically rescaling the velocities to have desired temperature

$$T = 1, \rho = 0.1, N = 64$$

$$T_{\text{kin}} = \langle \mathbf{v}_i^2 \rangle / 3$$

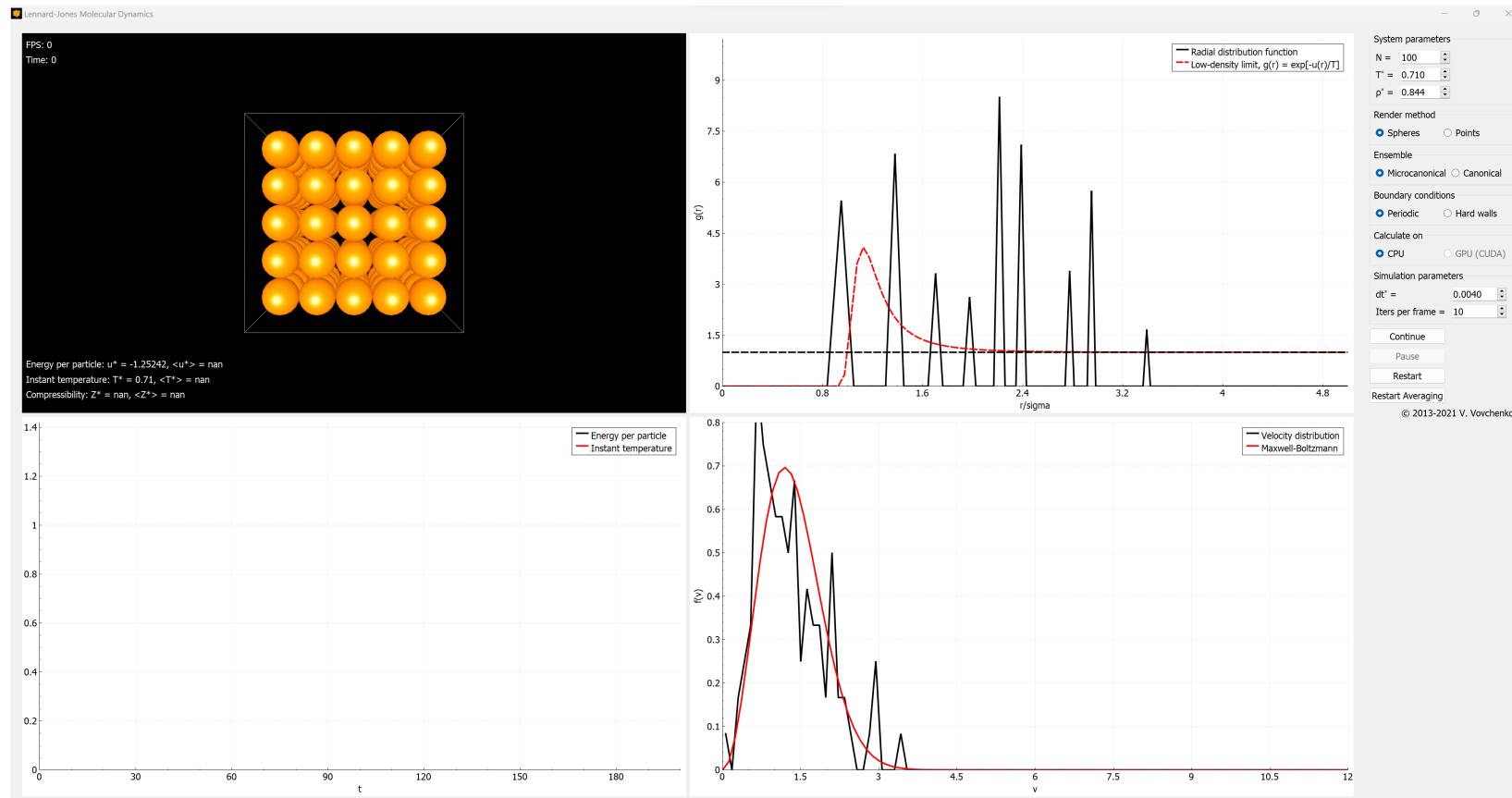
$$Z = p/(\rho T)$$



More involved approaches: thermostat degrees of freedom (Berendsen, Nose-Hoover, ...)

*final project idea(?)*

# Lennard-Jones fluid: C++/GPU implementation



## Implementation:

Velocity Verlet integration scheme implemented on CUDA-GPU (x100-200 speed-up\*)

open source: <https://github.com/vlvovch/lennard-jones-cuda>

