Exercise 8

The specific isochoric heat capacity of Ar fluid
Heat capacities are among the fundamental response functions often evaluated from the simulations. In this exercise you'll get to determine the isochoric heat capacity for argon via three routes.

For the sake of an argument, let's choose the following conditions:

$$\rho^* = 0.7 \text{ and } 0.96 < T^* < 2.23,$$

where the reduced density and temperature are $\rho^* = \rho\sigma^3 = \frac{N}{V}\sigma^3$, and $T^* = Tk_B/\epsilon$, respectively. The σ and ϵ are the familiar Lennard-Jones parameters you have been using before. To obtain the exact values, you need to look into the ar.top file, and do some arithmetics. Probably the easiest way to set up your system is to take one of your previous argon runs and modify the box size to obtain the desired density.

Perform a decent number of

(a) **NVE** simulations (1/3 of total points)

(b) **NVT** simulations (1/3 of total points)

within the asked temperature range and calculate the isochoric heat capacity for each temperature. Present your results in dimensionless form $C_V^* \equiv \frac{C_v}{Nk_B}$ in a nice graph as a function of the temperature.

Then, perform even more

(c) **NVE** simulations within the temperature range (1/3 of total points)

and obtain the internal energy as a function of the temperature, $U(T)$, from your simulation data. Calculate the specific heat capacity from the $U(T)$ and compare it to the values you got from (a) and (b).

Which of the methods, if any, would you trust the most – why? As usual, make sure that your simulations are meaningful.

Please return your solutions into the box in the second floor lobby by Thursday afternoon (07NOV2013) if you want some feedback. Alternatively, you can return your solutions at the exercise session on Friday (08NOV2013), starting at 11:15.

So... how to obtain the heat capacities from the simulations? Using some statistical physics, one can derive the following relations:

$$\langle(\delta E_{pot})^2\rangle_{NVE} = \langle(\delta E_{kin})^2\rangle_{NVE} = \frac{3}{2}Nk_B^2T^2\left(1 - \frac{3Nk_B}{2C_V}\right)$$

and

$$\langle(\delta E_{pot})^2\rangle_{NVT} = k_BT^2C_V,$$

where $\delta A = A - \langle A\rangle$.

Deriving *both* of these relations yields you an extra 1/3 of total points!