REDUCED UNITS

Simulations are usually performed using reduced units

Suppose $U(r_1 \dots r_N) = \sum_{i<j} V(r_{ij})$

$V(r_{ij}) = \epsilon f\left(\frac{r}{\sigma}\right)$ $\qquad \epsilon$ = energy scale
σ = length scale

In the MC we use adimentional units:

$\{x_1 \dots x_N\}$ with $\bar{x}_i = \frac{\bar{r}_i}{\sigma}$

The variables x_i live in a box of size $\left(\frac{L}{\sigma}\right)^3$

CANONICAL ENSEMBLE:

The basic variables are $N, V, T \longrightarrow \boxed{N, \frac{V}{\sigma^3}, \frac{kT}{\epsilon}}$

We do not compute energies but energies$/\epsilon$

PRESSURE: dimensionally $p = \frac{\text{energy}}{(\text{length})^3}$ $\qquad \left(p = \frac{NkT}{V}\right)$

we compute $\frac{p\sigma^3}{\epsilon}$ which is dimensionless.

EXAMPLES :

$$\langle U \rangle = \frac{\int d^{3N}r \; U \, e^{-\beta U}}{\int d^{3N}r \; e^{-\beta U}} \qquad \beta_r = \beta\epsilon = \frac{\epsilon}{kT}$$

$$\int d^{3N}r \, U e^{-\beta U} = \int \sigma^{3N} d^{3N}x \; \epsilon \left[\sum_{i<j} f(x_{ij})\right] \exp\left(-\frac{\epsilon}{kT} \sum_{i<j} f(x_{ij})\right)$$

$$= \epsilon \sigma^{3N} \int d^{3N}x \left[\sum_{i<j} f(x_{ij})\right] \exp\left(-\beta_r \sum_{i<j} f(x_{ij})\right)$$

$$\int d^{3N}r \, e^{-\beta U} = \sigma^{3N} \int d^{3N}x \, \exp\left(-\beta_r \sum_{i<j} f(x_{ij})\right)$$

$$\left\langle \frac{U}{\epsilon} \right\rangle = \underbrace{\frac{\int d^{3N}x \left(\sum_{i<j} f(x_{ij})\right) \exp\left(-\beta_r \sum_{i<j} f(x_{ij})\right)}{\int d^{3N}x \, \exp\left(-\beta_r \sum_{i<j} f(x_{ij})\right)}}_{\text{canonical-ensemble average in adimensional units}}$$

PRACTICALLY: SET $\epsilon = \sigma = 1$ and use β_r, L/σ as input data.

For the pressure prove that

$$\left\langle -\sum_{i<j} r_{ij} \frac{\partial V}{\partial r_{ij}} \right\rangle = \epsilon \left\langle -\sum_{i<j} x_{ij} \frac{\partial f}{\partial x_{ij}} \right\rangle_{\text{computed in adimensional units}}$$

It follows

$$\frac{p^{exc}\sigma^3}{\epsilon} = \frac{1}{3\left(\frac{V}{\sigma^3}\right)} \left\langle -\sum_{i<j} x_{ij} \frac{\partial f}{\partial x_{ij}} \right\rangle_{\text{adim units}}$$