SHEET 9

(a) $[E] = kg \frac{m^2}{s^2}$ $\qquad [v] = \sqrt{\frac{[E]}{[m]}} = \frac{m}{s}$

$$\Rightarrow [v'] = \sqrt{\frac{[E']}{[m']}} = \sqrt{\frac{[E]/\varepsilon}{[m]/\alpha}} = \sqrt{\frac{\alpha}{\varepsilon}}\,[v] = \frac{[v]}{\sqrt{\frac{\varepsilon}{\alpha}}} = \frac{[v]}{\sigma}$$

where α is the mass unit and ε the energy unit

(h) $\frac{1}{2} m v^2 = \frac{1}{2} k_B T \Rightarrow v = \sqrt{\frac{k_B T}{m}}$

$$\Rightarrow \frac{v'}{v} = \sqrt{\frac{T'}{T}}$$

(i) $\langle x_i \frac{\partial H}{\partial x_i} \rangle = k_B T$ $\qquad x_i < \begin{matrix} q^i \\ p_i \end{matrix}$

$H = E_K + V$ $\qquad \frac{\partial H}{\partial q^i} = \frac{\partial V}{\partial q^i}$ $\qquad \frac{\partial H}{\partial p_i} = \frac{\partial E_K}{\partial p_i}$

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \frac{\partial E_K}{\partial p_i} \rangle = \langle \frac{p_i^2}{m} \rangle = k_B T$$

Summing over all particles and directions

$$\sum_{i=1}^{3N} k_B T = 3N k_B T = \sum_{i=1}^{3N} \langle \frac{p_i^2}{m} \rangle = \sum_{i=1}^{N} \langle \frac{p_{i,x}^2}{m} \rangle + \langle \frac{p_{i,y}^2}{m} \rangle + \langle \frac{p_{i,z}^2}{m} \rangle$$

Assuming $\langle p_x^2 \rangle = \langle p_y^2 \rangle = \langle p_z^2 \rangle$

$$\frac{3}{2} N k_B T = \frac{3}{2} \sum_{i=1}^{N} \frac{N}{N} \langle \frac{p_i^2}{m} \rangle = \langle E_K \rangle$$

Where I used that $N \left(\frac{1}{N} \sum_{i=1}^{N} 3 \langle \frac{p_i^2}{m} \rangle \right) = N \langle E_K^{Part} \rangle = \langle E_K \rangle$

Hence $C_v = \frac{1}{n} \frac{\partial U}{\partial T} = \frac{3}{2} R$ only when $U \approx E_K$

n = number of moles

Numerically, we can calculate C_v as follows:

$$C_v = \frac{\varepsilon}{n} \frac{U(T+\Delta T) - U(T)}{\Delta T} =$$

$$= \frac{120\,K \cdot k_B}{10\,K} \left(\frac{N_A}{N}\right)^{n} \Delta U =$$

$$= 12 \cdot \left(\frac{R}{N_A}\right)^{k_B} \frac{N_A}{N} \Delta U = \frac{12\,\Delta U\, R}{N}$$

We have $N = 8^3 = 512 \Rightarrow C_v / R = \frac{12\,\Delta U}{512} \simeq 0.0234\ \Delta U$

ΔU in natural units

$$\frac{C_v}{R}(T = 75\,K) \simeq 1.55$$

$$\frac{C_v}{R}(T = 400\,k) \simeq 1.51$$

As the temperature grows so it does the kinetic energy.
Hence the approximation $U \simeq E_K$ becomes more accurate
(remember tha $C_v = \frac{3}{2} R$ only if $V = 0$)

(j) The temperature is so low that the contribution to the total energy of the system comes almost only from the potential.
We expect the particles to lie at an average distance equal to the equilibrium ~~point~~ distance of the Lennard-Jones potential, since temperature does not provide enough excitation to jump away
we also expect C_v very different from $\frac{3}{2} R$