Problem 1:

2 a) first law: energy is conserved
second law: heat flows only from hot to cold reservoirs
third law: the entropy difference between reversibly connected states vanishes as $T \to 0$.

2 b) The entropy is maximized in thermodynamic equilibrium.

c) A thermodynamic phase transition is a non-analyticity (1) in the Gibbs free energy of a system. At a first order phase transition the first derivative of G is not continuous. At a continuous phase transition all (1) first derivatives of G are continuous.

2 d) If $N(E)$ is the number of microscopic states $S = k_B \ln N(E)$ is the entropy of the corresponding macroscopic state

e) If $N(E)$ is the number of states with energy E, the probability for state i with energy E_i in the microcanonical ensemble ~~at~~ at energy E is

$$p_i = \begin{cases} \frac{1}{N(E)} & E_i = E \\ 0 & E_i \neq E \end{cases} \quad (1)$$

It corresponds to a closed and adiabatically isolated system. (1)

Problem 2

a) $H(\vec{x}^N) \leq E \Leftrightarrow \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2mE} + \sum_{i=1}^{N} \frac{(\vec{r}_i - \vec{r}_{0,i})^2}{2E/m\omega^2} \leq 1$

$\Rightarrow H(\vec{x}^N) \leq E$ describes a $6N$ dimensional ellipsoid with $3N$ axis $\sqrt{2mE}$ and $3N$ axis of length $\sqrt{2E/m\omega^2}$ 2

b) $\Omega(E, N) = \Omega_{6N} (2mE)^{\frac{3N}{2}} \left(\frac{2E}{m\omega^2}\right)^{\frac{3N}{2}} = \frac{\pi^{3N}}{3N\Gamma(3N)} (2mE)^{\frac{3N}{2}} \left(\frac{2E}{m\omega^2}\right)^{\frac{3N}{2}}$

$= \left(\frac{2\pi E}{\omega}\right)^{3N} \frac{1}{(3N)!}$ 1

$S = k_B \ln \frac{\Omega(E,N)}{C_N} \underset{\substack{\uparrow \\ \text{oscillators} \\ \text{distinguishable}}}{=} k_B \ln \left[\left(\frac{2\pi E}{\omega}\right)^{3N} \frac{1}{h^{3N}} \frac{1}{(3N)!} \right]$

$\approx 3N k_B \ln \frac{2\pi E}{h\omega} - k_B 3N \ln(3N) + 3N k_B$

$= 3N k_B \left[1 + \ln \frac{E}{3N\hbar\omega} \right]$ 2

c) QM result from lecture: $E = \hbar\omega M + \frac{3}{2}N\hbar\omega$

$S = k_B (3N + M) \ln(3N + M) - k_B M \ln M - k_B 3N \ln(3N)$

$= k_B \left(3N + \frac{E - \frac{3}{2}N}{\hbar\omega}\right) \ln\left(3N + \frac{E - \frac{3}{2}N}{\hbar\omega}\right) - k_B \frac{E - \frac{3}{2}N}{\hbar\omega} \ln \frac{E - \frac{3}{2}N}{\hbar\omega}$

$- k_B 3N \ln(3N)$

$= 3N k_B \Big[\cancel{\left(1 + \frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln 3N} + \left(1 + \frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln\left(\frac{1}{2} + \frac{E}{3N\hbar\omega}\right)$
$\qquad - \cancel{\left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln 3N} - \left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln\left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) - \cancel{\ln(3N)} \Big]$

$= 3N k_B \left[\left(\frac{E}{3N\hbar\omega} + \frac{1}{2}\right) \ln\left(\frac{1}{2} + \frac{E}{3N\hbar\omega}\right) - \left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \ln\left(\frac{E}{3N\hbar\omega} - \frac{1}{2}\right) \right]$

If the number of quanta is large compared to the number of oscillators, i.e., $\frac{E}{3N\hbar\omega} \gg \frac{1}{2}$

also accept $k_B T \gg \hbar\omega$

$$S \simeq 3Nk_B\Big[\left(\frac{E}{3N\hbar\omega}+\frac{1}{2}\right)\ln\frac{E}{3N\hbar\omega}+\left(\frac{E}{3N\hbar\omega}+\frac{1}{2}\right)\ln\left(1+\frac{3N\hbar\omega}{2E}\right)$$
$$-\left(\frac{E}{3N\hbar\omega}-\frac{1}{2}\right)\ln\frac{E}{3N\hbar\omega}-\left(\frac{E}{3N\hbar\omega}-\frac{1}{2}\right)\ln\left(1-\frac{3N\hbar\omega}{2E}\right)\Big]$$

$$\approx 3Nk_B\left[\ln\frac{E}{3N\hbar\omega}+\left(\frac{E}{3N\hbar\omega}+\frac{1}{2}\right)\frac{3N\hbar\omega}{2E}+\left(\frac{E}{3N\hbar\omega}-\frac{1}{2}\right)\frac{3N\hbar\omega}{2E}\right]$$

$$= 3Nk_B\left[1+\ln\frac{E}{3N\hbar\omega}\right] \quad (3)$$

d) If the oscillators were indistinguishable we have to use $C_N = N!\,h^{3N}$

Then $S \simeq 3Nk_B\left[1+\ln\frac{E}{3N\hbar\omega}\right] - Nk_B\ln N + k_B N$

$$= Nk_B\left[4+\ln\left(\frac{E}{3N\hbar\omega}\right)^3\frac{1}{N}\right] \quad (1)$$

This is not an extensive quantity. (1)

Problem 3:

a) $E = m\varepsilon \Rightarrow$ m right angle turns and $N-m$ straight

(1) There are $\binom{N}{m}$ ways to arrange the m turns.

Each right angle turn can go in two directions

$$\Rightarrow \quad N(E) = \binom{N}{E/\varepsilon} 2^{E/\varepsilon} \quad (1)$$

b) $S \overset{(1)}{=} k_B \ln N(E) = k_B \ln \binom{N}{E/\varepsilon} 2^{E/\varepsilon} \simeq k_B \frac{E}{\varepsilon} \ln 2$

$+ N k_B \ln N - \left(N - \frac{E}{\varepsilon}\right) k_B \ln\left(N - \frac{E}{\varepsilon}\right) - \frac{E}{\varepsilon} k_B \ln \frac{E}{\varepsilon}$

$$= k_B N \left[\frac{E}{N\varepsilon} \ln 2 + \cancel{\ln N} - \left(1 - \frac{E}{N\varepsilon}\right) \ln\left(1 - \frac{E}{N\varepsilon}\right) - \cancel{\left(1 - \frac{E}{N\varepsilon}\right) \ln N} \right.$$
$$\left. - \frac{E}{N\varepsilon} \ln \frac{E}{N\varepsilon} - \cancel{\frac{E}{N\varepsilon} k_B \ln N} \right]$$

$$= k_B N \left[\frac{E}{N\varepsilon} \ln 2 - \frac{E}{N\varepsilon} \ln \frac{E}{N\varepsilon} - \left(1 - \frac{E}{N\varepsilon}\right) \ln\left(1 - \frac{E}{N\varepsilon}\right) \right] \quad (1)$$

c) $\frac{1}{T} \overset{(1)}{=} \left(\frac{\partial S}{\partial E}\right)_N = \frac{k_B}{\varepsilon} \left[\ln 2 - \ln \frac{E}{N\varepsilon} \cancel{-1} + \ln\left(1 - \frac{E}{N\varepsilon}\right) \cancel{+1} \right] \quad (1)$

d) $\frac{\varepsilon}{k_B T} = \beta\varepsilon = \ln \dfrac{2 - 2\frac{E}{N\varepsilon}}{E/N\varepsilon}$

$$\Rightarrow e^{\beta\varepsilon} = \frac{2 - 2\frac{E}{N\varepsilon}}{E/N\varepsilon} \Rightarrow \frac{E}{N\varepsilon}\left(e^{\beta\varepsilon} + 2\right) = 2 \Rightarrow E = \frac{2N\varepsilon}{2 + e^{\beta\varepsilon}} \quad (2)$$

e) $C_N \overset{(1)}{=} \left(\frac{\partial E}{\partial T}\right)_N = \left(\frac{\partial \frac{1}{k_B T}}{\partial T}\right)_N \left(\frac{\partial E}{\partial \beta}\right)_N = + \frac{1}{k_B T^2} \frac{2N\varepsilon}{(2 + e^{\beta\varepsilon})^2} \varepsilon e^{\beta\varepsilon}$

$$= N k_B (\beta\varepsilon)^2 \frac{2 e^{\beta\varepsilon}}{(2 + e^{\beta\varepsilon})^2} \quad (1)$$