10.40 Thermodynamics **Fall 2003**
Problem Set 6

Problem 2

Given a 3D lattice model, 10x10x10, which is connected to a bath at 298 K and in which there are 100 non-interacting gas particles having no internal structure, each of which are located only at the lattice points, calculate $\underline{U}$, $\underline{S}$, $\underline{G}$, and $\underline{C}_v$.

Solution:

The system operates at constant temperature (T), number of particles (N), volume ($\underline{V}$) since the lattice is not changing with time, and energy ($\underline{E}$) since we assume that the energy of a particle at any lattice point is the same and independent of how many other particles are also at that lattice point. Thus, the system fulfills the criteria for a microcanonical ensemble and a canonical ensemble.

The partition function for the microcanonical ensemble, $\Omega(N,\underline{V},\underline{E})$, is the total number of possible states of the system. The particles are indistinguishable (there is no way to tell them apart in the lattice) and non-interacting (more than one particle can reside at each site). From combinatorics:

$$\Omega = \frac{(M+N-1)!}{N!(M-1)!} = \frac{1099!}{100!999!} \qquad \text{where } M = \text{\# of sites} = 1000,\ N = \text{\# of particles} = 100$$

The large factorial operations are calculated using Stirling's approximation: $\ln y! \approx y \ln y - y$

$\ln \Omega = 335$ and is independent of temperature, volume, and energy.

For the microcanonical ensemble:

$\underline{S} = k \ln \Omega$

$\underline{U} = \underline{E} = \text{constant}$

$\underline{G} = \underline{U} + P\underline{V} - T\underline{S}$

$$\underline{C}_v = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = 0$$

Since the energy is constant, we can give it any value we want by defining it with respect to some arbitrary reference state. Therefore, we can say that $\underline{U} = 0$. Also noting that $P = 0$ for a lattice gas, then $\underline{G} = -T\underline{S}$.

We can also use the equations developed for the canonical ensemble to evaluate $\underline{U}$, $\underline{S}$, $\underline{G}$, and $\underline{C}_v$ since this system is both a microcanonical and a canonical ensemble. For the canonical ensemble:

$$Q = \sum_i e^{-\beta \underline{E}_i} = \Omega e^{-\beta \underline{E}}$$

If we let $\underline{E}$ = constant = 0 again, then we get $Q = \Omega$. Hence:

$\underline{G} = \underline{A} + P\underline{V}$

Since Q is not a function of $\underline{V}$, pressure does not have any real physical meaning for our system. Thus P = 0 and

$\underline{G} = \underline{A}$

The relation between our thermodynamic properties and Ω is as follows:

$$\underline{A} = -kT \ln \Omega = \underline{G}$$

$$\underline{S} = kT \underbrace{\left(\frac{\partial \ln Q}{\partial T}\right)_{\underline{V},N}}_{=0 \text{ since } Q \neq f(T)} + k \ln Q = k \ln Q$$

$$\underline{U} = \underline{A} + T\underline{S} = -kT \ln \Omega + kT \ln \Omega = 0$$

$$\underline{C}_v = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = 0$$

Plugging in for k, T and lnΩ yields:

$$\underline{G} = -1.38 \times 10^{-18}\ J$$

$$\underline{S} = 4.63 \times 10^{-21}\ J/K$$

$$\underline{U} = 0$$

$$\underline{C}_v = 0$$