10.40 Thermodynamics **Fall 2003**
Problem Set 7

Problem 10.1 Text

Solution:

In general, the Laplace transform of a general function $f(x)$ is

$$£(f(x)) \equiv \int_0^{\infty} e^{-st} f(t)dt \quad (1)$$

Using Eq. (10-11) to define the probability distribution, we can rewrite $P_N = P_N(\mathbf{r}^N, \mathbf{p}^N)$ as

$$P_N = \frac{C}{\Psi(\underline{E})} \delta(\mathbf{H} - \underline{E}) \quad (2)$$

where $\mathbf{H}$ = Hamiltonian and $\delta(\mathbf{H} - \underline{E})$ is the Kronecker delta function that is zero everywhere except at $\mathbf{H} = \underline{E}$. The inverse of Eq. (2) gives the microcanonical density of states $\Omega(\underline{E})$:

$$P_N^{-1} = \frac{\Psi(\underline{E})}{C} \delta(\mathbf{H} - \underline{E}) \quad (3)$$

where $C = h^{3N} N!$

$$\Psi(\underline{E}) = \int \cdots \int dr^N dp^N \quad (4)$$

Using Eq. (1) with $t = \underline{E}$ and $s = \beta = 1/kT$

$$£(P_N^{-1}) = \frac{1}{h^{3N}N!} \int_0^{\infty} \int \cdots \int \exp[-\underline{E}/kT]\ \delta(\mathbf{H} - \underline{E}) dr^N dp^N\, d\underline{E} \quad (5)$$

using the property of the Kronecker delta:

$$£(P_N^{-1}) = \frac{1}{h^{3N}N!} \int \ldots \int \exp[-\mathbf{H}/kT]\ dr^N\, dp^N \quad (6)$$

which is exactly Q_N, the canonical partition function given in Eq. (10-20). We also note that the relationship between $\Omega(\underline{E})$ and P_N^{-1} can easily be seen by using the classical continuum approximation to evaluate Q_N by its definition in Eq. (10-15)

$$Q_N \equiv \sum_i \exp(-\underline{E}/kT) \rightarrow \int_0^{\infty} \Omega(\underline{E}) \exp[-\underline{E}/kT]\ d\underline{E} \quad (7)$$

where $\Omega(\underline{E})$ is the density of states of energy $\underline{E}$ in phase space treated as a continuum. Thus, Eq. (3) gives $\Omega(\underline{E})$ directly.

Given the uniqueness properties of Laplace transform generally, the information content of both ensembles is identical. For a large system ($N \to \infty$), the microcanonical probability density $\boldsymbol{P}_N$ is expressed in terms of the Kronecker delta function that is finite only at $\underline{E} = \mathbf{H}$ where $\delta(\mathbf{H} - \underline{E}) = 1$

$$\Omega(\underline{E}) = P_N^{-1} = \frac{\Psi(\underline{E})\ \delta(\mathbf{H} - \underline{E})}{C} \equiv Q_{\underline{E}\,\underline{V}\,N}$$

which defines the microcanonical partition function $Q_{\underline{E}\,\underline{V}\,N}$. From above we learned that as N gets large

$$\pounds(Q_{\underline{E}\,\underline{V}\,N}) = Q_N = Q_{N\underline{V}T}$$

so we can see that the information encoded in $Q_{\underline{E}\,\underline{V}\,N}$ is sufficient to replicate $Q_N = Q_{N\,\underline{V}\,T}$ exactly. In a very analogous way to Legendre transforms, converting from microcanonical ($\underline{E}\ \underline{V}\ N$) to canonical ($T\underline{V}N$) ensembles is equivalent to the Fundamental Equation variable changes given in Chapter 5.