9. *Statistical Mechanics and Thermodynamics* (Spring 2006)

A researcher claims that a particular substance in thermal equilibrium exhibits the following total-number-of-states function

$$\Omega(E) = c(E - E_0)^\alpha V^\gamma \exp\left(-\frac{g}{V}\right)$$

where E_0, c, α, γ, and g are positive coefficients independent of the energy E, the volume V, and the temperature T.

(a) Find the equation of state for this substance.

(b) What is the relationship between the average energy and the temperature?

(c) Does this substance satisfy the third law of thermodynamics? Why?

(d) What values should E_0, c, α, γ, and g take for this substance to behave as an ideal gas?

a. $dE = TdS - pdV \Rightarrow dS = \frac{1}{T}dE + \frac{p}{T}dV$

$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV \Rightarrow \left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$ and $\left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T}$

The most typical equation of state here is

$$p = T\left(\frac{\partial S}{\partial V}\right)_E \text{ and } S = k\ln(\Omega(E)) = k\ln\left[c(E-E_0)^\alpha V^\gamma \exp\left(-\frac{g}{V}\right)\right]$$

$$= T\left(\frac{\partial}{\partial V}\right)_E\left(k\ln\left[c(E-E_0)^\alpha\right] + k\ln\left[V^\gamma \exp\left(-\frac{g}{V}\right)\right]\right)$$

$$= kT\frac{1}{V^\gamma \exp(-g/V)}\left(\gamma V^{\gamma-1}\exp\left(-\frac{g}{V}\right) + V^\gamma(-g)\left(-\frac{1}{V^2}\right)\exp\left(-\frac{g}{V}\right)\right)$$

$$= kT\left(\frac{\gamma}{V} + \frac{g}{V^2}\right)$$

$$\Rightarrow pV = kT\left(\gamma + \frac{g}{V}\right)$$

b. $$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \left(\frac{\partial}{\partial E}\right)_V\left(k\ln\left[(E-E_0)^\alpha\right] + k\ln\left[cV^\gamma\exp\left(-\frac{g}{V}\right)\right]\right)$$

$$= \left(\frac{\partial}{\partial E}\right)_V\left(\alpha k\ln(E-E_0)\right)$$

$$= \frac{\alpha k}{E-E_0}$$

$$\Rightarrow T = \frac{E-E_0}{\alpha k}$$

c. The 3rd Law states $S \xrightarrow{T\to 0} S_0$ and as $T\to 0$ we have $E \to E_0$ and $S \to k\ln(0) = -\infty$, which is not some constant S_0, so the answer is no.

Note: The ideal gas also does not satisfy the 3rd Law because it is not a valid approximation for low temperatures.

d. For an ideal gas, $E = \frac{3}{2}NkT$ and $pV = NkT$

$E \to 0$ as $T \to 0$ $\Rightarrow$ $\underline{E_0 = 0}$, $E = \frac{3}{2}NkT = \alpha kT \Rightarrow \underline{\alpha = \frac{3}{2}N}$,

$pV = NkT = kT\left(\gamma + \frac{g}{V}\right) \Rightarrow N = \gamma + \frac{g}{V} \Rightarrow \underline{g = 0}$ and $\underline{\gamma = N}$

Now $\Omega(E) = c\left(VE^{3/2}\right)^N \Rightarrow \underline{\underline{c = 1}}$ since $S(N=0) \to 0$.