

- (c) The system temperature is changed to a new value T_2 such that $T_2 = 2T_1$. Quantify the effect of this change on the probability determined in part (b) (i.e. By what factor will the probability determined in part (b) change because of this temperature change?).

$$\begin{aligned}
 \text{New, } T_2 &= 2T_1 \\
 (P_A)_{T_2} &= e^{-\frac{4EA}{kT_2}} \\
 &= e^{-\frac{4EA}{k \cdot 2T_1}} \\
 &= e^{-\frac{1}{2} \cdot \frac{4EA}{kT_1}} \\
 &= e^{-\frac{1}{2}} \cdot e^{-\frac{4EA}{kT_1}} \\
 &= e^{-1/2} \cdot (P_A)_{T_1}
 \end{aligned}$$

$(P_A)_{T_1}$ will change by the factor of $e^{-1/2}$ because,

$$\begin{aligned}
 (P_A)_{T_1} &= \frac{(P_A)_{T_2}}{e^{-1/2}} \\
 &= (P_A)_{T_2} e^{-1/2}
 \end{aligned}$$

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2. For the grand canonical ensemble, consider fluctuations in the number of particles. The relative magnitude of these fluctuations in the number of particles is given by the expression:

$$\frac{\sigma_N}{\bar{N}} = \left(\frac{k_B T \kappa}{V} \right)^{1/2}$$

where \bar{N} is the average number of particles, k_B is the Boltzmann constant, T is the temperature, κ is the isothermal compressibility, and V is the volume of the system.

- (a) Derive an expression for the relative fluctuations in the number of particles in an ideal gas system (Hint: Use the ideal gas equation of state).

For ideal gas system, $PV = NkT$

$$\Rightarrow V = \frac{NkT}{P}$$

$$\Rightarrow \frac{dV}{dP} = -\frac{NkT}{P^2}$$

$$= -\frac{PV}{P^2} = -\frac{V}{P}$$

$$\kappa = -\frac{1}{V} \left(\frac{\delta V}{\delta P} \right)$$

$$\Rightarrow \frac{\delta P}{\delta V} = -\frac{1}{\kappa V}$$

For isothermal compressibility, we know that,

$$\begin{aligned}
 \kappa &= -\frac{1}{V} \cdot \left(\frac{\delta V}{\delta P} \right)_{N,T} \\
 &= -\frac{1}{V} \cdot \left(-\frac{V}{P} \right) \\
 &= \frac{1}{P}
 \end{aligned}$$

$$\left[\because \frac{dV}{dP} = -\frac{V}{P} \Rightarrow \frac{\delta V}{\delta P} = -\frac{V}{P} \right]$$

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