

2. Establish that the probability density of finding a system in the canonical ensemble with energy  $E$ ,  $p(E) = \frac{1}{Z} g(E) e^{-\beta E}$  has a Gaussian shape in the vicinity of its most

likely value  $E^*$ , i.e., that  $p(E) = p(E^*) \exp\left\{-\frac{(E - E^*)^2}{2kT^2 C_V}\right\}$ , near  $E^*$ .

In class, we established that the first and 2nd moments were respectively,  $E^*$ , and  $kT^2 C_V$ . For the third moment, we have  $\langle (E - E^*)^3 \rangle$

$$\begin{aligned} &= \langle E^3 - 3E^2 E^* + 3E(E^*)^2 \rangle = \langle E^3 \rangle - 3E^* \langle E^2 - EE^* \rangle - (E^*)^3 \\ &= \langle E^3 \rangle - (E^*)^3 - 3E^* \sigma^2. \end{aligned}$$

In class we also found

$$\frac{\partial U}{\partial \beta} = -\frac{1}{Z} \left[ \frac{1}{h^{3N}} \int_0^\infty E^2 g(E) e^{-\beta E} dE \right] + \frac{\langle E \rangle}{Z} \left[ \frac{1}{h^{3N}} \int_0^\infty E g(E) e^{-\beta E} dE \right] = -\sigma^2.$$

Taking the derivative again with respect to  $\beta$ ,

$$\begin{aligned} \frac{\partial^2 U}{\partial \beta^2} &= \frac{1}{Z} \left[ \frac{1}{h^{3N}} \int_0^\infty E^3 g(E) e^{-\beta E} dE \right] - \frac{\langle E \rangle}{Z} \left[ \frac{1}{h^{3N}} \int_0^\infty E^2 g(E) e^{-\beta E} dE \right] \\ &\quad - \frac{\langle E \rangle}{Z} \left[ \frac{1}{h^{3N}} \int_0^\infty E^2 g(E) e^{-\beta E} dE \right] + \frac{\langle E \rangle^2}{Z} \left[ \frac{1}{h^{3N}} \int_0^\infty E g(E) e^{-\beta E} dE \right] \end{aligned}$$

$= \langle E^3 \rangle - 2\langle E \rangle \langle E^2 \rangle + \langle E \rangle^3$ . Regrouping terms, we have

$$= \langle E^3 \rangle - \langle E \rangle^3 - 2\langle E \rangle \langle E^2 \rangle + 2\langle E \rangle \langle E \rangle^2 = \langle E^3 \rangle - \langle E \rangle^3 - 2\langle E \rangle \sigma^2. \text{ So, the third}$$

moment can be written as  $\langle (E - \langle E \rangle)^3 \rangle = \frac{\partial^2 U}{\partial \beta^2} - \langle E \rangle \sigma^2$ .

Using  $\frac{\partial}{\partial \beta} = -kT^2 \frac{\partial}{\partial T}$ , and the result from class,

$$\langle (E - \langle E \rangle)^3 \rangle = k^2 T^3 \left( 2C_V + T \frac{\partial C_V}{\partial T} \right) - \langle E \rangle kT^2 C_V = \left( 2kT + \frac{kT^2}{C_V} \frac{\partial C_V}{\partial T} - \langle E \rangle \right) kT^2 C_V.$$

We also showed that  $\frac{\sigma^2}{\langle E \rangle^2} \sim \frac{C_V}{N^2}$ , so that  $\frac{\sigma}{\langle E \rangle} \sim \frac{1}{\sqrt{N}}$ , since  $C_V \sim N$ . For the

case of the third moment, similarly, the term  $\frac{\langle (E - \langle E \rangle)^3 \rangle}{\langle E \rangle^3} \sim \frac{C_V}{N^3} \sim \frac{1}{N^2}$ . So, for

large enough ensembles, the distribution is approximately Gaussian.