Problem 1. **Average energy in the canonical ensemble.** In this assignment you will show that the average energy can be obtained from the canonical partition function as: 
\[
\langle E \rangle = -\frac{\partial \log(Z(T,V,N))}{\partial \beta}
\]

**Question 1.1:** Which expression shows the average energy within the canonical ensemble?

a) \[
\langle E \rangle = \sum_{\text{microstates } i} E_i e^{-\beta E_i}
\]

b) \[
\langle E \rangle = \frac{1}{Z(N,V,T)} \sum_{\text{microstates } i} E_i
\]

c) \[
\langle E \rangle = \frac{1}{Z(N,V,T)} \sum_{\text{microstates } i} E_i e^{-\beta E_i}
\]
Question 1.2: Based on the definition of partition function, which of

\[ \frac{\partial Z(T, V, N)}{\partial \beta} \]

the expression below represents?

\[ \sum_{\text{microstates}\,-i} -E_i e^{-\beta E_i} \]

a)

\[ \sum_{\text{microstates}\,-i} E_i e^{-\beta E_i} \]

b)

\[ \sum_{\text{microstates}\,-i} e^{-\beta E_i} \]

c)
Question 1.3. Which of the expressions below represents a correct use of the chain rule to solve our problem?

\[
- \frac{\partial \log(Z(T, V, N))}{\partial \beta} = -\frac{1}{Z} \frac{\partial Z(T, V, N)}{\partial \beta}
\]

a)

\[
\frac{\partial \log(Z(T, V, N))}{\partial \beta} = \frac{1}{Z} \frac{\partial Z(T, V, N)}{\partial \beta}
\]

b)

\[
- \frac{\partial \log(Z(T, V, N))}{\partial \beta} = -\log \left( \frac{\partial Z(T, V, N)}{\partial \beta} \right)
\]

c)

Combining the answers from questions 1.1, 1.2 and 1.3 we arrive at the desired result. An expression for the average number of atoms from the grand canonical partition function can be obtained similarly.
**Problem 2. Fluctuations in the canonical ensemble.** In this assignment you will prove that energy fluctuations in the canonical ensemble are related to the specific heat.

**Question 2.1.** Starting with the definition of specific heat $C_v = \frac{\partial \langle E(N,V,T) \rangle}{\partial T}$ and the canonical expression for average energy, select the correct expression:

\[
\frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \beta}{\partial T} \left( \frac{1}{Z} \sum_{\text{microstates} - i} E_i e^{-\beta E_i} + \frac{1}{Z} \sum_{\text{microstates} - i} -E_i^2 e^{-\beta E_i} \right)
\]

a) $\frac{\partial \langle E \rangle}{\partial T} = -\frac{1}{kT^2} \left( -\frac{1}{Z^2} \frac{\partial Z}{\partial \beta} \sum_{\text{microstates} - i} E_i e^{-\beta E_i} - \frac{1}{Z} \sum_{\text{microstates} - i} E_i^2 e^{-\beta E_i} \right)$

b) $\frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \beta}{\partial T} \left( \frac{\partial}{\partial \beta} \frac{1}{Z} + \frac{1}{Z} \sum_{\text{microstates} - i} -E_i^2 e^{-\beta E_i} \right)$

c) $\frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \beta}{\partial T} \left( \frac{\partial}{\partial \beta} \frac{1}{Z} + \frac{1}{Z} \sum_{\text{microstates} - i} -E_i^2 e^{-\beta E_i} \right)$

d) All of the above

e) a) and b)

To relate energy fluctuations to specific heat we start by remembering that variance in energy (the square of the standard deviation) is defined as: $\delta E^2 = \langle (E - \langle E \rangle)^2 \rangle$ where $\langle \cdots \rangle$ indicates canonical averages. This expression can be expanded and re-written as: $\delta E^2 = \langle E^2 \rangle - \langle E \rangle^2$. 
Question 2.2. Select the correct expression relating $C_V$ and variance in energy:

\[ C_V = \frac{1}{kT^2} \left( \langle E^2 \rangle - \langle E \rangle^2 \right) \]

a) \[ C_V = -\frac{1}{kT^2} \left( \langle E^2 \rangle - \langle E \rangle^2 \right) \]

b) \[ C_V = \left( \langle E^2 \rangle - \langle E \rangle^2 \right) \]

c) \[ C_V = \frac{1}{kT^2} \left( \langle E^2 \rangle - \langle E \rangle^2 \right) \]