Microscopic expression for heat: Feynman-Hibbs equation (10-19)

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Derivation of equation (10-19) in *Quantum Mechanics and Path Integrals* by Richard P. Feynman and Albert R. Hibbs (McGraw-Hill, New York, 1965).

According to equation (10-18), during an infinitesimal expansion

$$\frac{dQ}{dV} = \beta \frac{dF}{dV} \sum_i E_i e^{-\beta(E_i - F)} - \beta \sum_i E_i \frac{dE_i}{dV} e^{-\beta(E_i - F)}.$$

And according to equation (10-19), this equals

$$\frac{dQ}{dV} = -T \frac{\partial^2 F}{\partial T\, \partial V}.$$

Begin with the second form. We have

$$F(T, V) = -k_B T \ln Z, \qquad \text{where} \qquad Z = \sum_i e^{-\beta E_i} = e^{-\beta F}.$$

Then

$$\begin{aligned}
\frac{\partial F}{\partial V} = -k_B T \frac{\partial \ln Z}{\partial V} &= -k_B T \frac{1}{Z} \frac{\partial Z}{\partial V} \\
&= \frac{1}{Z} \sum_i \frac{dE_i}{dV} e^{-\beta E_i} \\
&= e^{\beta F} \sum_i \frac{dE_i}{dV} e^{-\beta E_i} \\
&= \sum_i \frac{dE_i}{dV} e^{-\beta(E_i - F)}.
\end{aligned}$$

A second differentiation gives

$$\begin{aligned}
\frac{\partial^2 F}{\partial \beta\, \partial V} &= \sum_i \frac{dE_i}{dV} e^{-\beta(E_i - F)} \left[-(E_i - F) + \beta \frac{\partial F}{\partial \beta} \right] \\
-\frac{T}{\beta} \frac{\partial^2 F}{\partial T\, \partial V} &= \sum_i \frac{dE_i}{dV} e^{-\beta(E_i - F)} \left[-(E_i - F) - \beta \frac{T}{\beta} \frac{\partial F}{\partial T} \right] \\
-\frac{T}{\beta} \frac{\partial^2 F}{\partial T\, \partial V} &= -\sum_i E_i \frac{dE_i}{dV} e^{-\beta(E_i - F)} + \left[F - T \frac{\partial F}{\partial T} \right] \sum_i \frac{dE_i}{dV} e^{-\beta(E_i - F)}
\end{aligned}$$

We recognize the expression for U in square brackets, and for dF/dV just to its right:

$$-T \frac{\partial^2 F}{\partial T\, \partial V} = -\beta \sum_i E_i \frac{dE_i}{dV} e^{-\beta(E_i - F)} + \beta\, [U]\, \frac{dF}{dV}.$$

And this is the desired relation.