$\boxed{1}$ Proceeding from $\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V + \mu\,\mathrm{d}N$ we first get

$$\left(\frac{\partial F}{\partial V}\right)_{S,N} = -S\left(\frac{\partial T}{\partial V}\right)_{S,N} - P$$

and then use the Maxwell relation (1.10.4) to arrive at

$$\left(\frac{\partial F}{\partial V}\right)_{S,N} = S\left(\frac{\partial P}{\partial S}\right)_{V,N} - P\,.$$

For the photon gas there is no "constant N" condition, so that

$$\left(\frac{\partial F}{\partial V}\right)_{S} = S\left(\frac{\partial P}{\partial S}\right)_{V} - P$$

applies. Now, in Section 3.4, we have the statements $P = \dfrac{1}{3}u = \dfrac{\pi^2}{45}\dfrac{(k_\mathrm{B}T)^4}{(\hbar c)^3}$, which we combine with $P = -\left(\dfrac{\partial F}{\partial V}\right)_T$ to conclude that $F = -\dfrac{\pi^2}{45}V\dfrac{(k_\mathrm{B}T)^4}{(\hbar c)^3} \propto -VT^4$ with a positive proportionality factor. It follows first that $S = -\left(\dfrac{\partial F}{\partial T}\right)_V = -4\dfrac{F}{T} \propto VT^3$, then that $F \propto -V(S/V)^{4/3}$ and $\left(\dfrac{\partial F}{\partial V}\right)_S = -\dfrac{F}{3V} = \dfrac{1}{3}P \propto (S/V)^{4/3}$, so that $\left(\dfrac{\partial P}{\partial S}\right)_V = \dfrac{4P}{3S}$. Accordingly, we have $S\left(\dfrac{\partial P}{\partial S}\right)_V - P = \dfrac{1}{3}P = \left(\dfrac{\partial F}{\partial V}\right)_S$, indeed.

$\boxed{2}$ In $C_V = -T\left(\dfrac{\partial^2 F}{\partial T^2}\right)_{V,N}$ we use $-\beta F = \log Q = \log(q(\beta,V,N)^N/N!)$ to establish

$$C_V = Nk_\mathrm{B}T\left(\frac{\partial}{\partial T}\right)^2 T\log(q(\beta,V,N)) = Nk_\mathrm{B}\beta^2\left(\frac{\partial}{\partial \beta}\right)^2 \log(q(\beta,V,N))$$

where

$$\begin{aligned} q(\beta,V,N) = \sum_k \mathrm{e}^{-\beta\varepsilon_k} &= \sum_{a,b,c} \mathrm{e}^{-\beta\left(\varepsilon_a^{(\mathrm{rot})} + \varepsilon_b^{(\mathrm{vib})} + \varepsilon_c^{(\mathrm{el})}\right)} \\ &= \sum_a \mathrm{e}^{-\beta\varepsilon_a^{(\mathrm{rot})}} \sum_b \mathrm{e}^{-\beta\varepsilon_b^{(\mathrm{vib})}} \sum_c \mathrm{e}^{-\beta\varepsilon_c^{(\mathrm{el})}} \\ &= q^{(\mathrm{rot})}(\beta,V,N)\, q^{(\mathrm{vib})}(\beta,V,N)\, q^{(\mathrm{el})}(\beta,V,N) \end{aligned}$$

is a product of three factors. Therefore, $\log(q(\beta,V,N))$ is a sum of three terms, and so is $C_V = C_V^{(\mathrm{rot})} + C_V^{(\mathrm{vib})} + C_V^{(\mathrm{el})}$.

$\boxed{3}$ From (3.5.13) we here get

$$U = 3N\frac{\hbar\omega_0}{\mathrm{e}^{\beta\hbar\omega_0} - 1}$$

and then, as in (3.5.20)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial\beta}{\partial T}\frac{\partial}{\partial\beta}\frac{3N\hbar\omega_0}{\mathrm{e}^{\beta\hbar\omega_0} - 1} = 3Nk_\mathrm{B}\left(\frac{\beta\hbar\omega_0\mathrm{e}^{\frac{1}{2}\beta\hbar\omega_0}}{\mathrm{e}^{\beta\hbar\omega_0} - 1}\right)^2$$

or

$$\frac{C_V}{Nk_\mathrm{B}} = 3\left(\frac{\frac{1}{2}\beta\hbar\omega_0}{\sinh(\frac{1}{2}\beta\hbar\omega_0)}\right)^2 .$$

For low temperatures, we have $k_\mathrm{B}T \ll \hbar\omega_0$ or $\beta\hbar\omega_0 \gg 1$ and $\sinh(\frac{1}{2}\beta\hbar\omega_0) \cong \frac{1}{2}\mathrm{e}^{\frac{1}{2}\beta\hbar\omega_0}$, so that

$$\frac{C_V}{Nk_\mathrm{B}} \cong 3(\beta\hbar\omega_0)^2\mathrm{e}^{-\beta\hbar\omega_0} .$$

For high temperatures, we have $k_\mathrm{B}T \gg \hbar\omega_0$ or $\beta\hbar\omega_0 \ll 1$ and $\sinh(\frac{1}{2}\beta\hbar\omega_0) \cong \frac{1}{2}\beta\hbar\omega_0 + \frac{1}{6}(\frac{1}{2}\beta\hbar\omega_0)^3$, so that

$$\frac{C_V}{Nk_\mathrm{B}} \cong 3 - \frac{1}{4}(\beta\hbar\omega_0)^2 .$$

$\boxed{4}$

(a) There are as many as $\binom{M}{N}$ ways of distributing N constituents over M sites. Each configuration has the canonical partition function of (2.5.30), so that we have

$$Q^{(M)}(\beta, N) = \binom{M}{N}[2\cosh(\tfrac{1}{2}\beta E_0)]^N$$

for the canonical partition function.

(b) The binomial factor $\binom{M}{N}$ has no bearing on the expected value of the energy, nor its spread, so that the expressions in (2.5.31) and (2.5.33) apply,

$$\langle E\rangle = -\frac{1}{2}NE_0\tanh(\tfrac{1}{2}\beta E_0) , \quad \sqrt{\langle\delta E^2\rangle} = \frac{1}{2}NE_0\cosh(\tfrac{1}{2}\beta E_0)^{-1} .$$

(c) In accordance with (3.1.6), we have

$$Z^{(M)}(\beta, z) = \sum_{N=0}^{\infty} z^N Q^{(M)}(\beta, N) = [1 + 2z\cosh(\tfrac{1}{2}\beta E_0)]^M .$$

(d) We find

$$\langle N\rangle = z\frac{\partial}{\partial z}\log(Z^{(M)}(\beta,z)) = \frac{2z\cosh(\frac{1}{2}\beta E_0)}{1+2z\cosh(\frac{1}{2}\beta E_0)}M$$

and thus first

$$2z\cosh(\tfrac{1}{2}\beta E_0) = \frac{\langle N\rangle}{M-\langle N\rangle} \cong \frac{\langle N\rangle}{M} \ll 1$$

and then

$$\langle \delta N^2\rangle = z\frac{\partial}{\partial z}\langle N\rangle = \frac{2z\cosh(\frac{1}{2}\beta E_0)}{\left[1+2z\cosh(\frac{1}{2}\beta E_0)\right]^2}M = \langle N\rangle\frac{M-\langle N\rangle}{M} \cong \langle N\rangle\,,$$

so that the spread of N is $\sqrt{\langle\delta N^2\rangle} \cong \sqrt{\langle N\rangle}$.

Note: The recognition that $2z\cosh(\frac{1}{2}\beta E_0) \ll 1$ permits the simplifying approximations

$$Z^{(M)}(\beta,z) = \mathrm{e}^{2Mz\cosh\left(\frac{1}{2}\beta E_0\right)}\,,\quad Q^{(M)}(\beta,N) = \frac{M^N}{N!}\left[2\cosh(\tfrac{1}{2}\beta E_0)\right]^N$$

from which we learn that $\binom{M}{N} \cong \frac{M^N}{N!}$ when $M \gg N$.