PS 3 Solutions

1. The states are: $\begin{cases} \text{unoccupied} \\ \text{energy } 0 \text{ state occupied} \\ \text{energy } \varepsilon \text{ " " } \end{cases}$

so $$\mathcal{Z} = 1 + e^{\mu/kT} + e^{(\mu-\varepsilon)/kT}$$

The average # of particles is
$$\langle N \rangle = \left(e^{\mu/kT} + e^{(\mu-\varepsilon)/kT}\right)/\mathcal{Z}$$
because the 3 terms in $\mathcal{Z}$ are the relative probabilities and the 2nd + 3rd states have a particle.

Alternatively, $\langle N \rangle = kT \frac{\partial}{\partial \mu} \log \mathcal{Z}$ = same thing

Likewise $\langle E \rangle = \varepsilon e^{(\mu-\varepsilon)/kT}/\mathcal{Z}$ "by inspection"

or else $$\langle E - N\mu \rangle = kT^2 \frac{\partial}{\partial T} \log \mathcal{Z}$$
$$= \left(-\mu e^{\mu/kT} + (\varepsilon-\mu) e^{(\mu-\varepsilon)/kT}\right)/\mathcal{Z}$$
$\rightarrow$ same result.

If both states can be occupied simultaneously, there's a new state with 2 particles + energy ε, so
$$\mathcal{Z} \rightarrow \mathcal{Z} + e^{(2\mu-\varepsilon)/kT} = \left(1+e^{\mu/kT}\right)\left(1+e^{(\mu-\varepsilon)/kT}\right)$$
since the two states are independent.

2. Ideal gas above a surface with single-particle absorbing sites

The sites ~~are~~ are independent so

$$\mathcal{Z}_{surface} = \prod_{sites} \mathcal{Z}_{site} = \mathcal{Z}_{site}^{N_{sites}}$$

where $\mathcal{Z}_{site} = 1 + e^{(\mu+\varepsilon_0)/kT}$ (empty, or occupied at energy $-\varepsilon_0$)

so $$p(\text{site occupied}) = \frac{e^{(\mu+\varepsilon_0)/kT}}{\mathcal{Z}}$$

$$= \frac{1}{1+e^{-(\mu+\varepsilon_0)/kT}}$$

This is also the fraction of occupied sites, f.

In equilibrium $\mu = \mu_{gas} = kT \log(n/n_Q)$ $\quad n_Q = \lambda_{TH}^{-3}$

so $$e^{-\mu/kT} = \frac{n_Q}{n}$$

and $$f = \frac{n}{n + e^{-\varepsilon_0/kT}} = \text{"Langmuir isotherm"}$$

3. Since the 4 sites are independent, $\mathcal{Z} = \mathcal{Z}_1^{\,4}$ where

$$\mathcal{Z}_1 = \sum_{n=0}^{\infty} e^{n\mu/kT} \sum_{\{\varepsilon_n\}} e^{-\varepsilon_n/kT} = 1 + e^{(\mu+\varepsilon)/kT}$$

Each term in $\mathcal{Z}$ = relative probability of that state

$$\mathcal{Z}_1 : \text{ empty} = 1/\mathcal{Z}_1 \, , \text{ occupied} = e^{(\mu+\varepsilon)/kT}/\mathcal{Z}_1$$

$$\text{In } \mathcal{Z} = \underset{\substack{\uparrow \\ \text{all empty}}}{1} + \underset{\substack{\uparrow \\ \text{1 site occupied}}}{4e^{(\mu+\varepsilon)/kT}} + \underset{\substack{\uparrow \\ \text{2 sites occupied}}}{6e^{2(\mu+\varepsilon)/kT}} + \cdots$$

so $p_0 = 1/\mathcal{Z}$, $p_1 = 4e^{(\mu+\varepsilon)/kT}/\mathcal{Z}$ etc.

$T \to 0$ or ∞? Hard to say because $\mu = \mu(T)$, depends on the material & other conditions

e.g. ideal gas $\mu = kT \log \frac{n}{n_Q}$

$$= kT \left[\log \frac{N}{V} + \log T^{3/2} + \text{const.} \right]$$