Problem 1 (**15** marks)
For a system that can be characterized by entropy S, volume V, and particle number N, show that

$$N\left(\frac{\partial\mu}{\partial V}\right)_{T,N} = V\left(\frac{\partial P}{\partial V}\right)_{T,N} .$$

Problem 2 (**20**=10+10 marks)
The so-called Dieterici model of a real gas is specified by the equation of state

$$P(T,v) = \frac{RT}{v-b}\exp\left(-\frac{a}{vRT}\right)$$

with positive material constants a and b. Just like the van der Waals gas and the Berthelot gas, the Dieterici gas has a gas-to-liquid phase transition for temperatures below the critical temperature $T_{\rm cr}$.

(a) Express the critical temperature $T_{\rm cr}$ and also the critical values of the molar volume ($v_{\rm cr}$) and the pressure ($P_{\rm cr}$) in terms of a, b, and the gas constant R. What is the value of $P_{\rm cr}v_{\rm cr}/T_{\rm cr}$?

(b) Find the coexistence pressure $P(T)$ for temperatures just below the critical temperature, $0 \lesssim T_{\rm cr} - T \ll T_{\rm cr}$.

Problem 3 (**25**=10+15 marks)
We denote the energy and the particle number in the kth microstate by $E_k(V)$ and N_K, respectively. Then the partition functions for the canonical and grand canonical ensembles are

$$Q(\beta,V,N) = \sum_k \mathrm{e}^{-\beta E_k}\delta_{N,N_k} \quad \text{and} \quad Z(\beta,V,z) = \sum_k \mathrm{e}^{-\beta(E_k\,-\,\mu N_k)}$$

with the fugacity $z = \mathrm{e}^{\beta\mu}$,

(a) Show that these partition functions are related to each other by

$$Z(\beta,V,z) = \sum_{N=0}^{\infty} z^N\,Q(\beta,V,N) .$$

(b) For the single-component classical ideal gas, we have $\log Z(\beta,V,z) = Vz/\lambda^3$ with the thermal de Broglie wavelength $\lambda = \hbar\sqrt{2\pi\beta/m}$. What is $Q(\beta,V,N)$?

Problem 4 (**40**=5+15+10+10 marks)
Consider an ideal classical gas of N particles with the energy

$$H(\boldsymbol{r}_1,\boldsymbol{p}_1;\boldsymbol{r}_2,\boldsymbol{p}_2;\ldots;\boldsymbol{r}_N,\boldsymbol{p}_N)=\sum_{j=1}^{N}\left[\frac{\boldsymbol{p}_j^2}{2m}+Fr_j\right],$$

where $r_j=|\boldsymbol{r}_j|$ is the length of the position vector of the jth particle and $F>0$ is a force constant.

(a) Is F an extensive or an intensive variable? Why?

(b) Find the canonical partition function $Q(\beta,F,N)$.

(c) Then determine the average energy per particle in units of $k_{\mathrm{B}}T$.

(d) Determine also the average kinetic energy and the average potential energy and verify that their sum equals the average energy.

Here are some mathematical identities that could be useful:

$$\int_0^\infty \mathrm{d}x\, x^\nu \mathrm{e}^{-ax}=2\int_0^\infty \mathrm{d}x\, x^{2\nu+1}\mathrm{e}^{-ax^2}=\frac{\nu!}{a^{\nu+1}}\quad \text{for } a>0 \text{ and } \nu>-1\,;$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^j x^k\bigg|_{x=0}=\delta_{j,k}\,k!\quad \text{for } j,k=0,1,2,3,\ldots\,;$$

$$0!=1\,,\quad \left(-\frac{1}{2}\right)!=\sqrt{\pi}\,,\quad (\nu+1)!=\nu!\,(\nu+1)\,.$$