Assignment 7

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PC2135
Thermodynamics and Statistical Mechanics

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Problem 1

[**20 pts**] In class, we have learnt the Gibbs–Duhem relation, i.e., $S\,\mathrm{d}T - V\,\mathrm{d}P + N\,\mathrm{d}\mu = 0$. To better understand the meaning of this relation, in this problem, we explicitly check this relation for a monatomic ideal gas. Denote the particle number of this gas by N, the energy of the gas by U and the volume of the gas by V. The entropy of this gas as a function of N, U and V is

$$S(N,U,V) = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right] \tag{1}$$

where m is the mass of a particle.

(1) (2 points) Calculate the temperature T, pressure P and chemical potential μ of this gas. Express the answer in terms of N, U and V.

(2) (4 points) Calculate the three differentials $\mathrm{d}T$, $\mathrm{d}P$ and $\mathrm{d}\mu$. Express the answer in terms of N, U and V as well as their differentials $\mathrm{d}N$, $\mathrm{d}U$ and $\mathrm{d}V$.

(3) (4 points) Explicitly show that $S\,\mathrm{d}T - V\,\mathrm{d}P + N\,\mathrm{d}\mu = 0$ using the results of part (2).

(4) (2 points) In the above, we express everything in terms of N, U and V and their differentials. Below we would like to express everything in terms of P, T and V and their differentials. Write down the expressions of S, N and μ in terms of P, T and V.

(5) (4 points) Calculate the differential $\mathrm{d}\mu$. Express the answer in terms of P, T and V and their differentials.

(6) (4 points) Explicitly show that $S\,\mathrm{d}T - V\,\mathrm{d}P + N\,\mathrm{d}\mu = 0$ using the results of part (5).

Solution

Part (1): T, P, μ from the Sackur–Tetrode equation

Expand Equation 1 by separating logarithms:

$$S = Nk\left[\ln V + \frac{3}{2}\ln\frac{4\pi mU}{3h^2} - \frac{5}{2}\ln N + \frac{5}{2}\right] \tag{2}$$

Temperature via $1/T = \frac{\partial S}{\partial U}_{V,N}$:

$$\frac{1}{T} = Nk\cdot\frac{3}{2}\cdot\frac{1}{U} = \frac{3Nk}{2U} \implies T = \frac{2U}{3Nk} \tag{3}$$

Pressure via $P/T = \frac{\partial S}{\partial V}_{U,N}$:

$$\frac{P}{T} = \frac{Nk}{V} \implies P = \frac{NkT}{V} = \frac{2U}{3V} \tag{4}$$

Chemical potential via $\mu = -T\frac{\partial S}{\partial N}_{U,V}$. Differentiating Equation 2:

$$\left.\frac{\partial S}{\partial N}\right|_{U,V} = k\left[\ln V + \frac{3}{2}\ln\frac{4\pi mU}{3h^2} - \frac{5}{2}\ln N + \frac{5}{2}\right] + Nk\left(-\frac{5}{2N}\right) \tag{5}$$

$$= k\left[\ln V + \frac{3}{2}\ln\frac{4\pi mU}{3h^2} - \frac{5}{2}\ln N\right] = \frac{S}{N} - \frac{5}{2}k \tag{6}$$

Therefore

$$\mu = -T\left(\frac{S}{N} - \frac{5}{2}k\right) = -\frac{TS}{N} + \frac{5}{2}kT = -kT\ln\left[\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right] \tag{7}$$

Part (2): Differentials $\mathrm{d}T$, $\mathrm{d}P$, $\mathrm{d}\mu$

From Equation 3, $T = 2U/(3Nk)$:

$$\mathrm{d}T = \frac{2}{3Nk}\,\mathrm{d}U - \frac{2U}{3N^2k}\,\mathrm{d}N \tag{8}$$

From Equation 4, $P = 2U/(3V)$:

$$\mathrm{d}P = \frac{2}{3V}\,\mathrm{d}U - \frac{2U}{3V^2}\,\mathrm{d}V \tag{9}$$

For $\mathrm{d}\mu$, write $\mu = -\frac{2U}{3N}f$ where $f = \ln V + \frac{3}{2}\ln U + \frac{3}{2}\ln\frac{4\pi m}{3h^2} - \frac{5}{2}\ln N$.

Note that $S = Nk(f + 5/2)$, so $f = S/(Nk) - 5/2$. Taking the total differential of μ:

$$\left.\frac{\partial \mu}{\partial U}\right|_{N,V} = -\frac{2}{3N}f - \frac{2U}{3N}\cdot\frac{3}{2U} = -\frac{2f+3}{3N} \tag{10}$$

$$\left.\frac{\partial \mu}{\partial V}\right|_{N,U} = -\frac{2U}{3NV} \tag{11}$$

$$\left.\frac{\partial \mu}{\partial N}\right|_{U,V} = \frac{2U}{3N^2}f + \frac{2U}{3N}\cdot\frac{5}{2N} = \frac{2U}{3N^2}\left(f + \frac{5}{2}\right) = \frac{2US}{3N^3k} \tag{12}$$

Hence

$$\mathrm{d}\mu = -\frac{2f+3}{3N}\,\mathrm{d}U - \frac{2U}{3NV}\,\mathrm{d}V + \frac{2US}{3N^3k}\,\mathrm{d}N \tag{13}$$

Part (3): Verification of $S\,\mathrm{d}T - V\,\mathrm{d}P + N\,\mathrm{d}\mu = 0$

Substituting Equation 8, Equation 9, Equation 13:

Coefficient of $\mathrm{d}U$:

$$\frac{2S}{3Nk} - \frac{2V}{3V} + N\cdot\left(-\frac{2f+3}{3N}\right) = \frac{2S}{3Nk} - \frac{2}{3} - \frac{2f+3}{3} \tag{14}$$

Since $S/(Nk) = f + 5/2$, this becomes

$$\frac{2(f+5/2)}{3} - \frac{2}{3} - \frac{2f+3}{3} = \frac{2f+5}{3} - \frac{2}{3} - \frac{2f+3}{3} = 0 \quad \checkmark \tag{15}$$

Coefficient of $\mathrm{d}V$:

$$0 - V\left(-\frac{2U}{3V^2}\right) + N\left(-\frac{2U}{3NV}\right) = \frac{2U}{3V} - \frac{2U}{3V} = 0 \quad \checkmark \tag{16}$$

Coefficient of $\mathrm{d}N$:

$$S\left(-\frac{2U}{3N^2k}\right) - 0 + N\cdot\frac{2US}{3N^3k} = -\frac{2US}{3N^2k} + \frac{2US}{3N^2k} = 0 \quad \checkmark \tag{17}$$

All three coefficients vanish, so $S\,\mathrm{d}T - V\,\mathrm{d}P + N\,\mathrm{d}\mu = 0$. ∎

Part (4): S, N, μ in terms of P, T, V

From Equation 3 and Equation 4: $U = 3NkT/2$ and $N = PV/(kT)$. Substituting into the Sackur–Tetrode equation, the argument of the logarithm simplifies since $\frac{V}{N} = \frac{kT}{P}$ and $\frac{4\pi mU}{3Nh^2} = \frac{2\pi mkT}{h^2}$.

$$S = \frac{PV}{T}\left[\ln\frac{kT}{P} + \frac{3}{2}\ln\frac{2\pi mkT}{h^2} + \frac{5}{2}\right] \tag{18}$$

$$N = \frac{PV}{kT} \tag{19}$$

$$\mu = -kT\left[\ln\frac{kT}{P} + \frac{3}{2}\ln\frac{2\pi mkT}{h^2}\right] \tag{20}$$

Note that μ depends only on P and T, not on V.

Part (5): Differential $\mathrm{d}\mu$ in terms of $\mathrm{d}P$, $\mathrm{d}T$, $\mathrm{d}V$

Since $\mu(P,T)$ is independent of V, we need only $\frac{\partial\mu}{\partial T}_P$ and $\frac{\partial\mu}{\partial P}_T$.

Write $\mu = -kT\left[\frac{5}{2}\ln T + \ln\frac{k}{P} + \frac{3}{2}\ln\frac{2\pi mk}{h^2}\right]$. Let $\alpha = \ln\frac{k}{P} + \frac{3}{2}\ln\frac{2\pi mk}{h^2}$ (depends on P, not T). Then $\mu = -kT\left(\frac{5}{2}\ln T + \alpha\right)$.

$$\frac{\partial\mu}{\partial T}_P = -k\left(\frac{5}{2}\ln T + \alpha\right) - kT\cdot\frac{5}{2T} = -k\left(\frac{5}{2}\ln T + \alpha + \frac{5}{2}\right) \tag{21}$$

Comparing with Equation 18 and Equation 19, $S/N = k\left(\frac{5}{2}\ln T + \alpha + \frac{5}{2}\right)$, so

$$\frac{\partial\mu}{\partial T}_P = -\frac{S}{N} \tag{22}$$

$$\frac{\partial\mu}{\partial P}_T = -kT\cdot\left(-\frac{1}{P}\right) = \frac{kT}{P} = \frac{V}{N} \tag{23}$$

Therefore

$$\mathrm{d}\mu = -\frac{S}{N}\,\mathrm{d}T + \frac{V}{N}\,\mathrm{d}P \tag{24}$$

Part (6): Verification of $S\,\mathrm{d}T - V\,\mathrm{d}P + N\,\mathrm{d}\mu = 0$

Substituting Equation 24:

$$S\,\mathrm{d}T - V\,\mathrm{d}P + N\left(-\frac{S}{N}\,\mathrm{d}T + \frac{V}{N}\,\mathrm{d}P\right) = S\,\mathrm{d}T - V\,\mathrm{d}P - S\,\mathrm{d}T + V\,\mathrm{d}P = 0 \tag{25}$$

∎

Problem 2

[**20 pts**] In class we have considered various fluids and will consider more, including the ideal gas and van der Waals fluids, where the latter can be either a gas or liquid. In general, a fluid is a thermodynamic system that can be fully characterized by its temperature T, volume V and particle number N. For example, the pressure P can be written as a function of these variables, $P(T, V, N)$.

(1) (5 points) The equation of state for the ideal gas is $PV = NkT$. Calculate $V\frac{\partial P}{\partial V}_{T,N} + N\frac{\partial P}{\partial N}_{T,V}$ for an ideal gas.

(2) (10 points) The equation of state for the van der Waals fluid is

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NkT \tag{26}$$

with a and b two constants. Calculate $V\frac{\partial P}{\partial V}_{T,N} + N\frac{\partial P}{\partial N}_{T,V}$ for a van der Waals fluid.

(3) (5 points) Consider a general fluid that may not be an ideal gas or van der Waals fluid. Can the value of $V\frac{\partial P}{\partial V}_{T,N} + N\frac{\partial P}{\partial N}_{T,V}$ for this fluid be different from the answers you obtain in parts (1) and (2)? If yes, give an example of such a fluid and show that the value there is indeed different from both part (1) and part (2). If no, give a proof of why the value cannot be different.

Solution

Part (1): Ideal gas

From $P = NkT/V$:

$$\frac{\partial P}{\partial V}_{T,N} = -\frac{NkT}{V^2} \implies V\frac{\partial P}{\partial V}_{T,N} = -\frac{NkT}{V} = -P \tag{27}$$

$$\frac{\partial P}{\partial N}_{T,V} = \frac{kT}{V} \implies N\frac{\partial P}{\partial N}_{T,V} = \frac{NkT}{V} = P \tag{28}$$

Therefore

$$V\frac{\partial P}{\partial V}_{T,N} + N\frac{\partial P}{\partial N}_{T,V} = -P + P = 0 \tag{29}$$

Part (2): Van der Waals fluid

Solving for P:

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \tag{30}$$

$$\frac{\partial P}{\partial V}_{T,N} = -\frac{NkT}{(V - Nb)^2} + \frac{2aN^2}{V^3} \tag{31}$$

$$V\frac{\partial P}{\partial V}_{T,N} = -\frac{NkTV}{(V - Nb)^2} + \frac{2aN^2}{V^2} \tag{32}$$

$$\frac{\partial P}{\partial N}_{T,V} = \frac{kT}{V - Nb} + \frac{NkTb}{(V - Nb)^2} - \frac{2aN}{V^2} \tag{33}$$

$$N\frac{\partial P}{\partial N}_{T,V} = \frac{NkT}{V - Nb} + \frac{N^2kTb}{(V - Nb)^2} - \frac{2aN^2}{V^2} \tag{34}$$

Adding:

$$V\frac{\partial P}{\partial V} + N\frac{\partial P}{\partial N} = \frac{NkT}{V-Nb}\left[1 - \frac{V}{V-Nb} + \frac{Nb}{V-Nb}\right] + \frac{2aN^2}{V^2} - \frac{2aN^2}{V^2} \tag{35}$$

The bracket simplifies:

$$1 - \frac{V}{V-Nb} + \frac{Nb}{V-Nb} = 1 + \frac{-V+Nb}{V-Nb} = 1 - 1 = 0 \tag{36}$$

Hence

$$V\frac{\partial P}{\partial V}_{T,N} + N\frac{\partial P}{\partial N}_{T,V} = 0 \tag{37}$$

Part (3): General fluid — the answer is always zero

The result cannot differ from parts (1) and (2). The proof follows from the fact that pressure is an intensive quantity, so $P(T,V,N)$ is homogeneous of degree 0 in (V,N) at fixed T:

$$P(T,\lambda V,\lambda N) = P(T,V,N) \quad \forall\lambda > 0 \tag{38}$$

By Euler's theorem for homogeneous functions, a function $f(x_1,x_2)$ that is homogeneous of degree n satisfies $\sum_i x_i \frac{\partial f}{\partial x_i} = nf$. With $n=0$, $x_1 = V$, and $x_2 = N$:

$$V\frac{\partial P}{\partial V}_{T,N} + N\frac{\partial P}{\partial N}_{T,V} = 0 \cdot P = 0 \tag{39}$$

This holds for any fluid whose pressure is intensive. ■