MATH327: StatMech and Thermo, Spring 2025
# Second homework assignment

Instructions

Complete all four questions below and submit your solutions by file upload on Canvas. Clear and neat presentations of your workings and the logic behind them will contribute to your mark. Use of resources beyond the module materials must be explicitly referenced in your submissions. This assignment is **due by 17:00 on Friday, 4 April 2025**. Anonymous marking is turned on and I will aim to return feedback by Monday, 21 April 2025.

You should already be familiar with the Department's academic integrity guidance for 2024–2025, which states that by submitting solutions to this assessment you affirm that you have read and understood the Academic Integrity Policy detailed in Appendix L of the Code of Practice on Assessment, and that you have successfully passed the Academic Integrity Tutorial and Quiz in the course of your studies. You also affirm that the work you are submitting is your own and you have not commissioned production of the work from a third party or used artificial intelligence (AI) software in an unacceptable manner to generate the work. (Generative AI software applications include, but are not limited to, ChatGPT, MS Copilot, and Gemini.) You also affirm that you have not plagiarized material from another person or source, nor fabricated, falsified or embellished data when completing this assignment. You also affirm that you have not colluded with any other student in the preparation or production of your work. The marks achieved on this assessment remain provisional until they are ratified by the Board of Examiners in June 2025.

Question 1: Diesel cycle

Consider the Diesel cycle defined by the PV diagram shown below, in which the 'compression' stage $1 \rightarrow 2$ and the 'power' stage $3 \rightarrow 4$ are both adiabatic, while the pressure is constant during the 'injection/ignition' stage $2 \rightarrow 3$, and the volume is constant during the 'exhaust' stage $4 \rightarrow 1$. The compression ratio is $r \equiv V_1/V_2 > 1$ and the cutoff ratio is $C \equiv V_3/V_2 > 1$, with $C < r$.
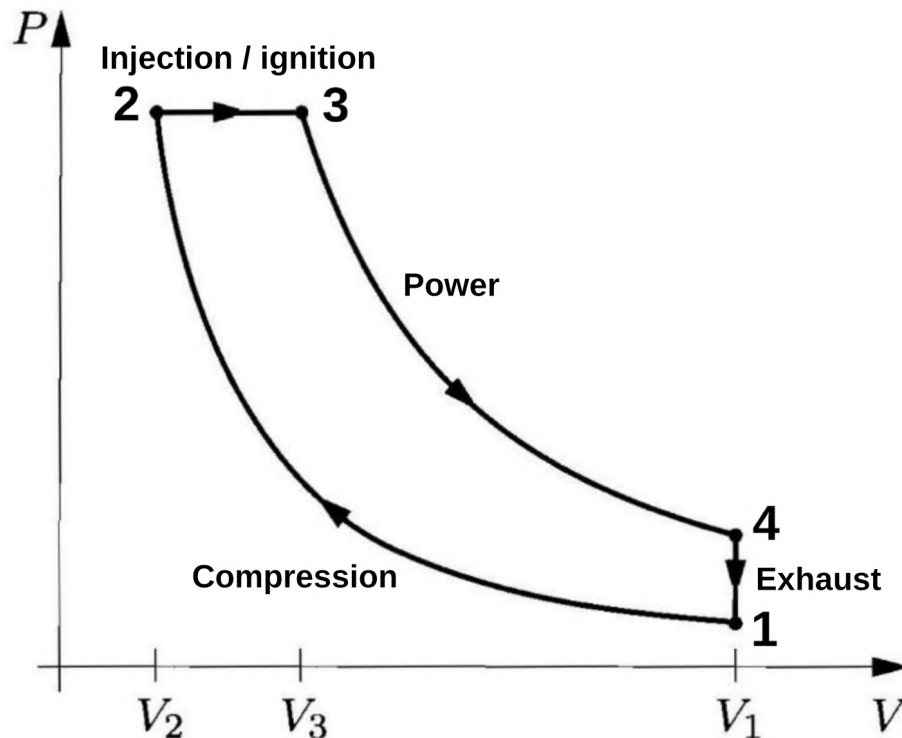
(a) By computing W_{out}, W_{in} and Q_{in}, show that the Diesel cycle's efficiency is

$$\eta_D = 1 - \frac{f(C)}{r^{2/3}}$$

and determine the function $f(C)$ that depends only on the cutoff ratio.

[18 marks]

(b) Show $f(C) > 1$ for $C > 1$. This indicates the Diesel cycle is less efficient than the Otto cycle with the same compression ratio r.

[6 marks]

Question 2: Mixed ideal gases

Consider a mixture of two classical ideal gases in thermodynamic equilibrium, in a container of volume V at temperature T, like that illustrated below. Let N_1 and N_2 be the particle numbers of the two gases. Within each gas the particles are indistinguishable, but particles of one gas are distinguishable from particles of the other gas. In particular, they have different masses m_1 and m_2, implying different thermal de Broglie wavelengths λ_1 and λ_2.
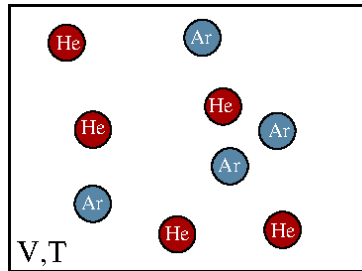
(a) First consider the case of fixed particle numbers. Calculate the partition function Z and the Helmholtz free energy of the $(N_1 + N_2)$-particle mixture, approximating $\log(N_i!) \approx N_i \log N_i - N_i$.

[4 marks]

(b) Calculate the internal energy $\langle E \rangle$ and the entropy S of the mixture. What is the condition of constant entropy?

[4 marks]

(c) Calculate the pressure P of the mixture, and relate it to the pressures P_1 and P_2 of each gas in isolation (as illustrated below).

[4 marks]

(d) Now allow the particle numbers to fluctuate, with distinct chemical potentials μ_1 and μ_2 for each type of particle. Calculate the grand-canonical partition function Z_g and the grand-canonical potential of the mixture, again approximating $\log(N_i!) \approx N_i \log N_i - N_i$.

[4 marks]

(e) Calculate the average particle number $\langle N \rangle = \langle N_1 \rangle + \langle N_2 \rangle$.

[5 marks]

(f) Re-calculate the internal energy $\langle E \rangle$ now that the particle numbers are allowed to fluctuate — explicitly evaluate the relevant derivatives to ensure you obtain what you expect; don't just write down an answer by inspection.

[5 marks]
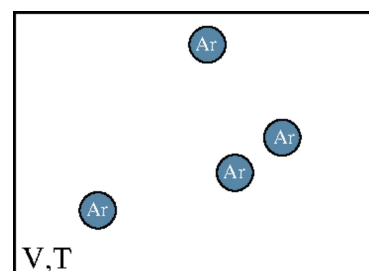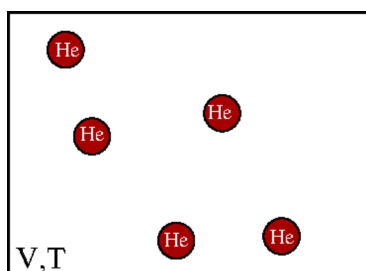
Question 3: Particle number fluctuations

Consider the fugacity expansion of the grand-canonical partition function (Eq. 82 in the lecture notes):

$$Z_g(T, \mu) = \sum_{N=0}^{\infty} \xi^N Z_N(T).$$

Here $\xi = e^{\beta\mu} = e^{\mu/T}$ is the fugacity and $Z_N(T)$ is the N-particle canonical partition function, which is independent of ξ. Recall that $\Phi(T, \mu) = -T \log Z_g(T, \mu)$ is the corresponding grand-canonical potential.

(a) Derive a relation between the average particle number $\langle N \rangle$ and the derivative $\dfrac{\partial}{\partial \log \xi} \Phi$.

[8 marks]

(b) Derive a relation between $\left\langle (N - \langle N \rangle)^2 \right\rangle$ and $\left(\dfrac{\partial}{\partial \log \xi} \right)^2 \Phi$.

[8 marks]

(c) Specialize to the case of Maxwell–Boltzmann statistics, for which the fugacity expansion simplifies to $Z_g^{\mathsf{MB}}(T, \mu) = \exp[\xi Z_1(T)]$, where Z_1 is the single-particle partition function. Use the relations you have derived to determine $\langle N \rangle$ and $\left\langle (N - \langle N \rangle)^2 \right\rangle$ for this case, and show

$$\frac{\sqrt{\left\langle (N - \langle N \rangle)^2 \right\rangle}}{\langle N \rangle} = \frac{1}{\sqrt{\langle N \rangle}}.$$

It may be useful to note $\dfrac{\partial}{\partial \log \xi} = \xi \dfrac{\partial}{\partial \xi}$.

[8 marks]

Question 4: Grand-canonical massive bosons

The grand-canonical potential for a gas of bosons with mass m in a box of volume V, with temperature $T = 1/\beta$ and chemical potential μ, is

$$\Phi(\beta, \mu) = \frac{V}{\beta} \frac{\sqrt{2m^3}}{2\pi^2 \hbar^3} \int_0^\infty \log\left[1 - e^{-\beta(E-\mu)}\right] \sqrt{E}\, dE \,.$$

Consider the case of vanishing chemical potential, $\mu = 0$.

(a) Calculate the particle density $\dfrac{\langle N \rangle}{V}$.

[6 marks]

(b) Calculate the internal energy density $\dfrac{\langle E \rangle}{V}$ to show $\langle E \rangle = \gamma \langle N \rangle T$ and determine the constant γ.

[7 marks]

(c) Calculate the entropy of the gas. What is the condition of constant entropy?

[6 marks]

(d) Calculate the pressure P to show $PV = \kappa \langle N \rangle T$ and determine the constant κ.

[7 marks]

Hints: You can look up derivatives or integrals, citing any sources you use. You can leave your answers in terms of the Riemann zeta function.