Assignment 8

Parth Bhargava · A0310667E

PC2135

Thermodynamics and Statistical Mechanics

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Problem 1

[**15 pts**] In class, we have learnt that the van der Waals model of fluids can be used to qualitatively describe the liquid-gas transition. Near the critical point of the transition, universal physics emerges, and important quantities associated with the universal physics are various critical exponents. In this problem, we will use the van der Waals model to calculate some of the critical exponents. Although the final results we get are not exact, this exercise helps us better understand the van der Waals model and the concepts of critical exponents.

For your convenience, the van der Waals equation of state is copied here:

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \tag{1}$$

where a and b are positive constants. In terms of the reduced variables, this equation of state takes the dimensionless form

$$p = \frac{8t}{3v - 1} - \frac{3}{v^2} \tag{2}$$

where $p = P/P_c$, $v = V/V_c$ and $t = T/T_c$, with $V_c = 3Nb$, $P_c = a/(27b^2)$ and $kT_c = 8a/(27b)$.

(1) (2 points) Expand the van der Waals equation Equation 2 in a Taylor series in $\delta v = v - 1$, keeping terms through order δv^3. For now, we assume that for T sufficiently close to T_c, the term quadratic in δv becomes negligible compared to the others and may be dropped. We will justify this assumption in part (3).

(2) (2 points) The resulting expression for $p(v)$ is anti-symmetric about the point $\delta v = 0$. Use this fact to find an approximate formula for the vapor pressure as a function of temperature. Evaluate the slope of the phase boundary, $\mathrm{d}p/\mathrm{d}t$, at the critical point.

(3) (3 points) Still working in the same limit, find an expression for the difference in volume between the gas and liquid phases at the vapor pressure. You should find $v_g - v_l \propto \delta t^\beta$ for $\delta t > 0$, where $\delta t = 1 - t$ and β is known as a critical exponent. Experiments show that β has a universal value of about 1/3, but the van der Waals model predicts a larger value. Use this result to justify the assumption made in part (1), where the term quadratic in δv can be ignored.

(4) (2 points) Use the previous result to calculate the predicted latent heat of the liquid-gas transition as a function of temperature, and sketch this function.

(5) (3 points) The shape of the $T = T_c$ isotherm defines another critical exponent, called δ: $\delta p \propto \delta v^\delta$, where $\delta p = p - 1$. Calculate δ in the van der Waals model.

(6) (3 points) A third critical exponent describes the temperature dependence of the isothermal compressibility right at P_c:

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial P}_T \tag{3}$$

> This quantity diverges at the critical point, in proportion to a power of δt that in principle could differ depending on whether one approaches the critical point from higher or lower temperature. Therefore, the critical exponents γ and γ' are defined by the relation
>
> $$\kappa \propto \begin{cases} \delta t^{-\gamma} & \text{as } \delta t \to 0^+ \\ |\delta t|^{-\gamma'} & \text{as } \delta t \to 0^- \end{cases} \tag{4}$$
>
> Calculate γ and γ' in the van der Waals model and show that $\gamma = \gamma'$ in this model.

Solution

Part (1): Taylor expansion of reduced equation

Write $v = 1 + \delta v$ and expand each term of Equation 2 to third order.

For the first term, $3v - 1 = 2 + 3\delta v$:

$$\frac{1}{3v-1} = \frac{1}{2} \cdot \frac{1}{1 + \frac{3\delta v}{2}} \approx \frac{1}{2}\left[1 - \frac{3}{2}\delta v + \frac{9}{4}\delta v^2 - \frac{27}{8}\delta v^3\right] \tag{5}$$

For the second term, $v^2 = (1 + \delta v)^2$:

$$\frac{1}{v^2} \approx 1 - 2\delta v + 3\delta v^2 - 4\delta v^3 \tag{6}$$

Substituting and collecting powers of δv (using $\delta t = 1 - t$, so $t = 1 - \delta t$):

$$p \approx (1 - 4\delta t) + 6\delta t\, \delta v - 9\delta t\, \delta v^2 - \frac{3}{2}\delta v^3 \tag{7}$$

Dropping the quadratic term (justified in part (3)):

$$p \approx (1 - 4\delta t) + 6\delta t\, \delta v - \frac{3}{2}\delta v^3 \tag{8}$$

Part (2): Vapor pressure and phase boundary slope

Write Equation 8 as $p = p_0 + f(\delta v)$, where $p_0 = 1 - 4\delta t$ and $f(\delta v) = 6\delta t\, \delta v - \frac{3}{2}\delta v^3$ is an odd function of δv. By Maxwell's equal-area rule, the horizontal tie-line at the vapor pressure must have equal areas above and below. Since $f(\delta v)$ is odd, the line $p = p_0$ satisfies this automatically by symmetry. Therefore the vapor pressure is

$$p_{\text{vap}} = 1 - 4\delta t = 4t - 3 \tag{9}$$

The slope of the phase boundary at the critical point ($t = 1$):

$$\frac{\mathrm{d}p_{\text{vap}}}{\mathrm{d}t} = 4 \tag{10}$$

Part (3): Volume difference and critical exponent β

At $p = p_{\text{vap}}$, the δv-dependent part vanishes:

$$6\delta t\, \delta v - \frac{3}{2}\delta v^3 = 0 \quad \Longrightarrow \quad \delta v\left(6\delta t - \frac{3}{2}\delta v^2\right) = 0 \tag{11}$$

The non-trivial solutions are $\delta v^2 = 4\delta t$, giving $\delta v = \pm 2\sqrt{\delta t}$. Therefore

$$v_g - v_l = 4\sqrt{\delta t} \propto \delta t^{1/2} \tag{12}$$

The critical exponent is $\beta = 1/2$ (the experimental value $\beta \approx 1/3$ is smaller).

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Justification for dropping the quadratic term: at the phase boundary, $\delta v \propto \delta t^{1/2}$, so $\delta v^2 \propto \delta t$ and the quadratic term scales as $\delta t \cdot \delta v^2 \propto \delta t^2$. The retained terms scale as $\delta t \cdot \delta v \propto \delta t^{3/2}$ and $\delta v^3 \propto \delta t^{3/2}$. Since $\delta t^2 \ll \delta t^{3/2}$ as $\delta t \to 0$, the quadratic term is indeed negligible.

Part (4): Latent heat

From the Clausius–Clapeyron relation in reduced variables:

$$\frac{\mathrm{d}p_{\text{vap}}}{\mathrm{d}t} = \frac{l}{t(v_g - v_l)} \tag{13}$$

where l is the latent heat in reduced units ($l = L/(P_c V_c)$). Using Equation 9 and Equation 12:

$$l = t(v_g - v_l) \cdot \frac{\mathrm{d}p_{\text{vap}}}{\mathrm{d}t} = t \cdot 4\sqrt{\delta t} \cdot 4 = 16t\sqrt{1-t} \tag{14}$$

Near $t = 1$: $l \approx 16\sqrt{1-t} \propto (T_c - T)^{1/2}$. The latent heat vanishes at the critical point and grows as the square root of the distance below T_c.

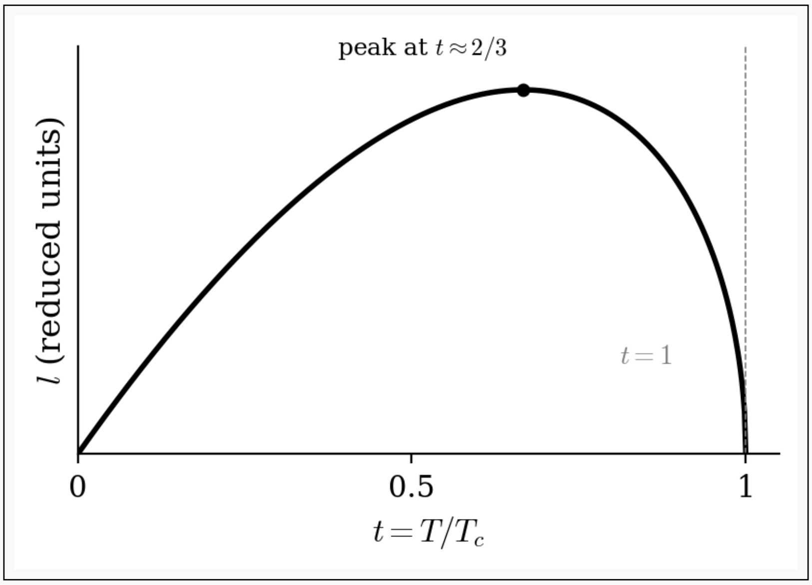

Figure 1: Latent heat l in reduced units as a function of $t = T/T_c$. The latent heat vanishes at the critical point ($t = 1$) and peaks near $t \approx 2/3$.

Part (5): Critical exponent δ

On the critical isotherm $t = 1$ ($\delta t = 0$), Equation 8 reduces to

$$\delta p = p - 1 = -\frac{3}{2}\delta v^3 \tag{15}$$

Therefore $\delta p \propto |\delta v|^3 \operatorname{sgn}(\delta v)$, giving

$$\delta = 3 \tag{16}$$

(Experimental values are typically $\delta \approx$ 4–5.)

Part (6): Critical exponents γ and γ' for compressibility

The isothermal compressibility in reduced variables is $\kappa = -(1/(P_c v)) \frac{\partial v}{\partial p}_t = -(1/(P_c v)) \left(\frac{\partial p}{\partial v}_t\right)^{-1}$.

From Equation 8:

$$\frac{\partial p}{\partial v}_t = \frac{\partial p}{\partial (\delta v)}_t = 6\delta t - \frac{9}{2}\delta v^2 \tag{17}$$

Approaching from above ($t > 1$, $\delta t < 0$): at $v = 1$ ($\delta v = 0$), the single-phase fluid exists. From Equation 17:

$$\frac{\partial p}{\partial v} = 6\delta t = -6\ |\delta t| \quad \Longrightarrow \quad \kappa = \frac{1}{P_c \cdot 6\ |\delta t|} \propto |\delta t|^{-1} \tag{18}$$

Therefore $\gamma = 1$.

Approaching from below ($t < 1$, $\delta t > 0$): the system phase-separates. Evaluate the compressibility of either phase at the coexistence volume $\delta v = \pm 2\sqrt{\delta t}$:

$$\frac{\partial p}{\partial v} = 6\delta t - \frac{9}{2} \cdot 4\delta t = 6\delta t - 18\delta t = -12\delta t \tag{19}$$

$$\kappa = \frac{1}{P_c \cdot 12\delta t} \propto \delta t^{-1} \tag{20}$$

Therefore $\gamma' = 1$, and $\gamma = \gamma' = 1$ in the van der Waals model. ■

Problem 2

[**15 pts**] In class, when we discuss the energy of mixing of non-ideal mixtures, we took the energy to be proportional to $x(1-x)$, where x is the fraction of one of the two substances in the mixture. In this problem, we consider a concrete model that indeed gives such an energy of mixing. From this model, we will also better understand the notion of solubility gap.

Consider a mixture of A and B molecules that is ideal in every way but one: the potential energy due to the interaction of neighbouring molecules depends upon whether the molecules are like or unlike. Let n be the average number of nearest neighbours of any given molecule (perhaps 6 or 8 or 10). Let u_0 be the average potential energy associated with the interaction between neighbouring molecules that are the same (A–A or B–B), and let u_{AB} be the potential energy associated with the interaction of a neighbouring unlike pair (A–B). There are no interactions beyond the range of the nearest neighbours; the values of u_0 and u_{AB} are independent of the amounts of A and B; the entropy of mixing is the same as for an ideal solution; and without mixing the Gibbs free energy density is the same for pure A and pure B systems.

(1) (2 points) Show that when the system is unmixed, the total potential energy due to all neighbour–neighbour interactions is $Nnu_0/2$. (Hint: Be sure to count each neighbouring pair only once.)

(2) (2 points) Find a formula for the total potential energy when the system is mixed, in terms of x, the fraction of B. (Assume that the mixing is totally random.)

(3) (2 points) Subtract the results of parts (1) and (2) to obtain the change in energy upon mixing. Simplify the result as much as possible; you should obtain an expression proportional to $x(1-x)$. Sketch this function vs. x, for both possible signs of $u_{AB} - u_0$.

(4) (2 points) Show that the slope of the mixing energy function is finite at both end points, unlike the slope of the mixing entropy function.

(5) (3 points) Below we assume $u_{AB} > u_0$. Sketch a graph of the Gibbs free energy of this system vs. x at several temperatures. Find the maximal temperature at which this system has a solubility gap.

(6) (2 points) Make a very rough estimate of $u_{AB} - u_0$ for a liquid mixture that has a solubility gap below 100 °C.

(7) (2 points) Sketch the phase diagram (T vs. x) for this system.

Solution

Part (1): Potential energy of the unmixed system

Each of the N molecules has n nearest neighbours. Summing over all molecules counts each pair twice (once from each end), so the number of distinct pairs is $Nn/2$. In the unmixed system, every neighbour pair is like–like with energy u_0. Therefore

$$U_{\text{unmixed}} = \frac{Nnu_0}{2} \tag{21}$$

Part (2): Potential energy of the mixed system

With fraction x of B and $(1-x)$ of A, assuming random mixing, the probability that a given neighbouring pair is of each type is

A–A: $(1-x)^2$ with energy u_0
B–B: x^2 with energy u_0
A–B: $2x(1-x)$ with energy u_{AB}

The total potential energy is

$$U_{\text{mixed}} = \frac{Nn}{2}[(1-x)^2u_0 + x^2u_0 + 2x(1-x)u_{AB}] \tag{22}$$

$$= \frac{Nn}{2}[u_0(1-2x(1-x)) + 2x(1-x)u_{AB}] \tag{23}$$

$$= \frac{Nn}{2}[u_0 + 2x(1-x)(u_{AB}-u_0)] \tag{24}$$

Part (3): Energy of mixing

$$\Delta U = U_{\text{mixed}} - U_{\text{unmixed}} = Nnx(1-x)(u_{AB}-u_0) \tag{25}$$

The function $x(1-x)$ is a symmetric parabola with maximum $1/4$ at $x = 1/2$. If $u_{AB} > u_0$, $\Delta U > 0$ (mixing is energetically unfavourable). If $u_{AB} < u_0$, $\Delta U < 0$ (mixing is favourable).

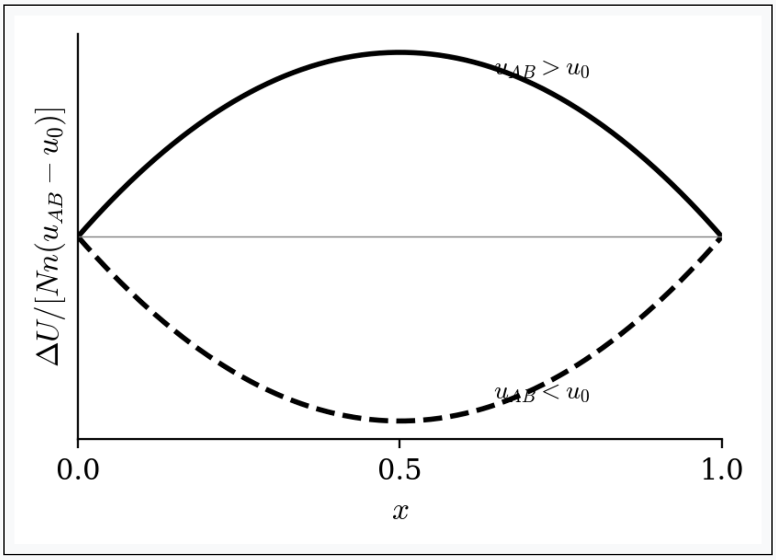

Figure 2: Energy of mixing ΔU vs. composition x for both signs of $u_{AB} - u_0$.

Part (4): Finite slope at the endpoints

$$\frac{\mathrm{d}\Delta U}{\mathrm{d}x} = Nn(u_{AB}-u_0)(1-2x) \tag{26}$$

At $x = 0$: slope $= Nn(u_{AB}-u_0)$ (finite). At $x = 1$: slope $= -Nn(u_{AB}-u_0)$ (finite).

By contrast, the ideal mixing entropy is $\Delta S = -Nk[x\ln x + (1-x)\ln(1-x)]$, with derivative

$$\frac{\mathrm{d}\Delta S}{\mathrm{d}x} = -Nk[\ln x - \ln(1-x)] \tag{27}$$

which diverges as $x \to 0^+$ or $x \to 1^-$. The entropy slope is infinite at both endpoints while the energy slope remains finite.

Part (5): Gibbs free energy and maximum solubility-gap temperature

The Gibbs free energy of mixing (at constant P, with $\Delta V \approx 0$) is

$$\frac{\Delta G}{N} = n(u_{AB}-u_0)x(1-x) + kT[x\ln x + (1-x)\ln(1-x)] \tag{28}$$

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At high T, the entropy term (concave) dominates and ΔG is concave everywhere: one phase. At low T, the energy term creates a local maximum near $x = 1/2$: a solubility gap.

The critical temperature occurs when the curvature at $x = 1/2$ changes sign. Taking the second derivative of Equation 28:

$$\frac{1}{N}\frac{\mathrm{d}^2\Delta G}{\mathrm{d}x^2} = -2n(u_{AB} - u_0) + kT\left[\frac{1}{x} + \frac{1}{1-x}\right] \tag{29}$$

At $x = 1/2$:

$$\frac{1}{N}\frac{\mathrm{d}^2\Delta G}{\mathrm{d}x^2} = -2n(u_{AB} - u_0) + 4kT \tag{30}$$

Setting this to zero:

$$T_c = \frac{n(u_{AB} - u_0)}{2k} \tag{31}$$

For $T > T_c$ the system is fully miscible; for $T < T_c$ a solubility gap exists.

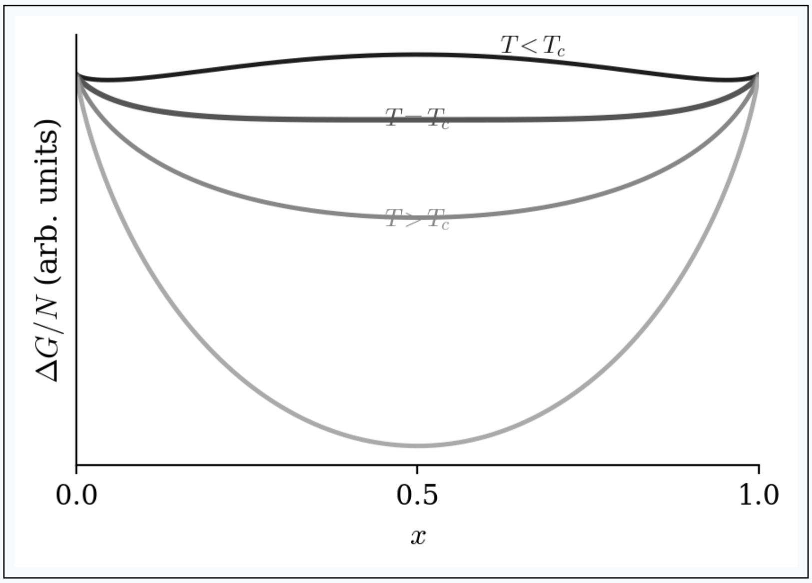

Figure 3: Gibbs free energy of mixing $\Delta G/N$ vs. x at several temperatures. Below T_c, the curve develops a local maximum at $x = 1/2$ indicating a solubility gap.

Part (6): Rough estimate of $u_{AB} - u_0$

A solubility gap below 100 °C means $T_c \approx 373$ K. Using Equation 31 with $n \approx 6$:

$$u_{AB} - u_0 = \frac{2kT_c}{n} = \frac{2(1.381 \times 10^{-23})(373)}{6} \approx 1.7 \times 10^{-21} \ \text{ J} \approx 0.01 \ \text{ eV} \tag{32}$$

This is a small fraction of a typical bond energy, consistent with the fact that the A–B interaction is only slightly different from A–A and B–B.

Part (7): Phase diagram

The model treats A and B symmetrically, so the phase diagram is symmetric about $x = 1/2$. Below T_c, there is a miscibility gap (two-phase region) bounded by a coexistence curve. The two branches meet at $(x, T) = (1/2, T_c)$ and curve outward towards $(0, 0)$ and $(1, 0)$.

At each $T < T_c$, the phase boundary compositions x_1 and $x_2 = 1 - x_1$ are found from the common tangent construction on $\Delta G(x)$. By the symmetry of the model, they satisfy $x_1 + x_2 = 1$, and they approach $x = 1/2$ as $T \to T_c$ from below, forming an inverted-parabola-shaped coexistence dome.

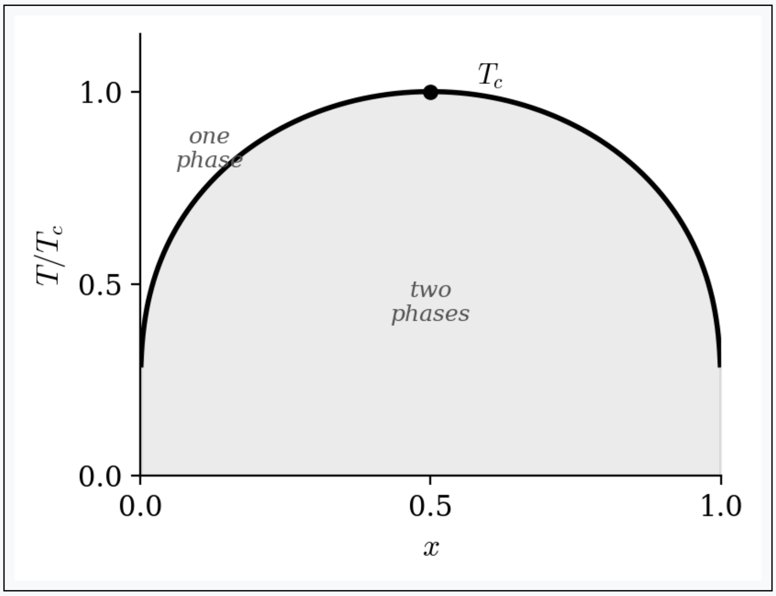

Figure 4: Phase diagram (T/T_c vs. x) showing the coexistence dome. The critical point sits at $(x, T/T_c) = (1/2, 1)$.

Problem 3

[**10 pts**] Seawater has a salinity of 3.5%, meaning that if you boil away a kilogram of seawater, when you are finished you will have 35 g of solids (mostly NaCl) left in the pot. When dissolved, sodium chloride dissociates into separate $\mathrm{Na}\{\}^+$ and $\mathrm{Cl}\{\}^-$ ions.

(1) (5 points) Calculate the osmotic pressure difference between a kilogram of seawater and freshwater at temperature 300 K. Assume for simplicity that all the dissolved salts in seawater are NaCl, and that 1 kilogram of seawater has a volume of 1 litre.

(2) (5 points) If you apply a pressure difference greater than the osmotic pressure to a solution separated from pure solvent by a semipermeable membrane, you get reverse osmosis: a flow of solvent out of the solution. This process can be used to desalinate seawater. Calculate the minimum work required to desalinate one litre of seawater. Discuss some reasons why the actual work required would be greater than the minimum.

Solution

Part (1): Osmotic pressure

Mass of NaCl per kilogram of seawater: 35 g. Molar mass of NaCl: $M = 58.44$ g/mol. Moles of NaCl:

$$n_{\text{NaCl}} = \frac{35}{58.44} \approx 0.599 \ \ \text{mol} \tag{33}$$

Each NaCl dissociates into $\mathrm{Na}\{\}^+$ and $\mathrm{Cl}\{\}^-$, giving 2 solute particles per formula unit:

$$n_{\text{solute}} = 2 \times 0.599 \approx 1.20 \ \ \text{mol} \tag{34}$$

The van ‘t Hoff formula gives the osmotic pressure for a dilute solution:

$$\Pi = \frac{n_{\text{solute}} RT}{V} \tag{35}$$

With $V = 1 \ \ \text{L} = 10^{-3}\ \text{m}^3$, $T = 300$ K, and $R = 8.314 \ \ \text{J/(mol·K)}$:

$$\Pi = \frac{1.20 \times 8.314 \times 300}{10^{-3}} \approx 2.99 \times 10^6 \ \ \text{Pa} \approx 29.5 \ \ \text{atm} \tag{36}$$

Part (2): Minimum desalination work

The minimum work to push a volume V of pure water through the membrane against the osmotic pressure is

$$W_{\text{min}} = \Pi V = 2.99 \times 10^6 \times 10^{-3} \approx 3.0 \times 10^3 \ \ \text{J} \approx 3.0 \ \ \text{kJ} \tag{37}$$

This is the thermodynamic lower bound for desalinating one litre of seawater.

In practice, significantly more work is required because:

- As water permeates out, the remaining brine becomes more concentrated and Π increases, so the applied pressure must exceed the initial osmotic pressure.
- Frictional losses and pressure drops across the membrane dissipate energy.
- Pumping systems have finite mechanical efficiency.
- Pre-treatment (filtration, chemical conditioning) requires additional energy input.

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