Mathematical Methods for Molecular Physics Coursework #1

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Contents

Problem 1

Question

Polynomial expansions

1.1. To the accuracy of the first three non-vanishing terms, write down the Maclaurin expansion of the functions (near the point $x = 0$):

a) $e^{-\alpha x^2}$, b) $\ln\left(1+\alpha x^2\right)$, c) $(1+\alpha\sqrt{x})^\mu$

1.2. Plot separately each function against its polynomial approximation for $\alpha = 1$ and $\alpha = -1$, $= 0.5$ and $= 2$. Plot a) and b) in the interval of $0 \le x \le 2$ and plot c) in the interval $0 \le x \le 1$

1.3. Using the plots from part 1.2, comment on where the polynomial approximations of a), b) and c) are good and where they stop reproducing the given functions.

Solution

1.1 Since all three functions are to be approximated near $x = 0$ and are analytic in a neighbourhood of the origin (for suitable α), it is natural to use the Maclaurin expansion, which has the form

$$f(x) = \sum_{n=0}^{+\infty} \frac{f^{(n)}(0)}{n!} x^n.$$

a) For $e^{-\alpha x^2}$, it is convenient to introduce the substitution $t = -\alpha x^2$, so that the function becomes $f(t) = e^t$. This reduces the problem to the well–known Maclaurin series of the exponential, which can be written without recomputing derivatives:

$$\begin{aligned} f(t) &= \frac{e^t\big|_{t=0}}{0!}t^0 + \frac{e^t\big|_{t=0}}{1!}t^1 + \frac{e^t\big|_{t=0}}{2!}t^2 + \mathcal{O}(t^3) \\ &= 1 + t + \frac{1}{2}t^2 + \mathcal{O}(t^3). \end{aligned}$$

Since we only need the first three non-vanishing terms and $t = -\alpha x^2$ is small whenever x is small, truncating after t^2 is justified for $|x| \ll 1$. Therefore,

$$f(x) = 1 - \alpha x^2 + \frac{1}{2}\alpha^2 x^4 + \mathcal{O}(x^6).$$

b) For $\ln\left(1+\alpha x^2\right)$ we again set $t = \alpha x^2$, so that $f(t) = \ln(1+t)$. This choice isolates the small parameter t and allows us to use the standard Taylor series of $\ln(1+t)$ about $t = 0$, which converges for $|t| < 1$ (i.e. $|\alpha x^2| < 1$):

$$\begin{aligned} f(t) &= \frac{\ln(1+t)\big|_{t=0}}{0!}t^0 + \frac{\frac{1}{1+t}\big|_{t=0}}{1!}t^1 + \frac{-\frac{1}{(1+t)^2}\big|_{t=0}}{2!}t^2 + \frac{\frac{2}{(1+t)^3}\big|_{t=0}}{3!}t^3 + \mathcal{O}(t^4) \\ &= t - \frac{1}{2}t^2 + \frac{1}{3}t^3 + \mathcal{O}(t^4). \end{aligned}$$

Keeping only the first three non-vanishing terms is consistent with the required accuracy and is valid as long as $|\alpha x^2| \ll 1$. Substituting back $t = \alpha x^2$ gives

$$f(x) = \alpha x^2 - \frac{1}{2}\alpha^2 x^4 + \frac{1}{3}\alpha^3 x^6 + \mathcal{O}(x^8).$$

c) For $(1+\alpha\sqrt{x})^\mu$, we set $t = \alpha\sqrt{x}$, so that $f(t) = (1+t)^\mu$. This allows us to use the generalized binomial expansion around $t = 0$, which is appropriate because the problem asks for behaviour near $x = 0$, i.e. $|\alpha\sqrt{x}| \ll 1$:

$$\begin{aligned} f(t) &= \frac{(1+t)^\mu\big|_{t=0}}{0!}t^0 + \frac{\mu(1+t)^{\mu-1}\big|_{t=0}}{1!}t^1 + \frac{\mu(\mu-1)(1+t)^{\mu-2}\big|_{t=0}}{2!}t^2 + \mathcal{O}(t^3) \\ &= 1 + \mu t + \frac{\mu(\mu-1)}{2}t^2 + \mathcal{O}(t^3). \end{aligned}$$

Truncating after the t^2–term gives the first three non-vanishing contributions and is valid provided $|\alpha\sqrt{x}|$ remains small. Substituting $t = \alpha\sqrt{x}$ yields

$$f(x) = 1 + \mu\alpha\sqrt{x} + \frac{\mu(\mu-1)}{2}\alpha^2 x + \mathcal{O}(x^{3/2}).$$

In all cases, the truncation is justified because we expand around $x = 0$ and keep only the lowest powers of x that contribute.

1.2

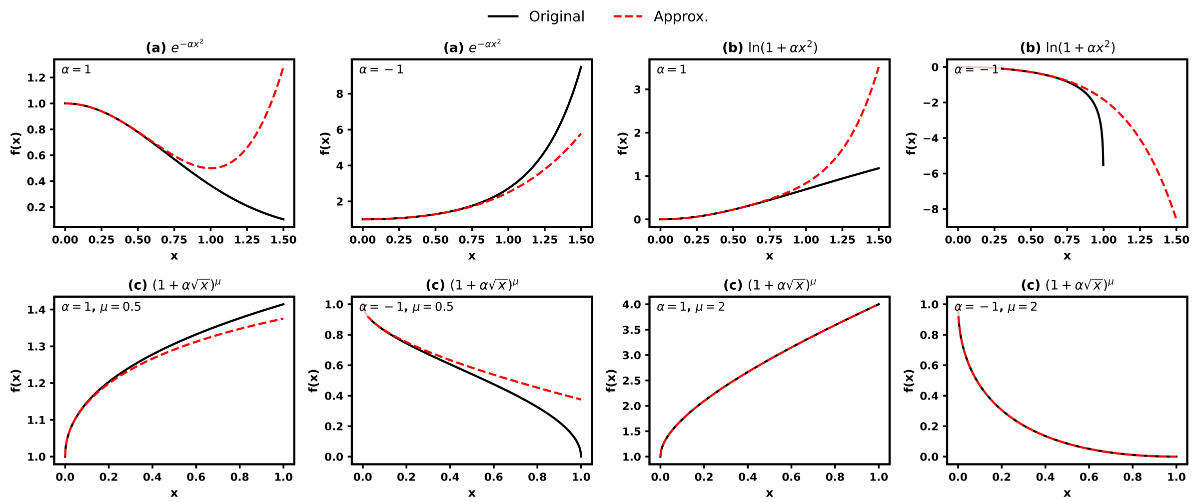

Figure 1: Function Plots. Solid lines: the original function. Dashed lines: the approximated function.

1.3 From the plots, the Maclaurin (polynomial) approximations reproduce the given functions accurately only for small values of x (i.e. near $x = 0$), where higher-order terms such as x^4 or x^6 remain negligible. For $e^{-\alpha x^2}$, the truncated series follows the exact curve well up to about $x \approx 1$, but diverges afterwards—the error grows rapidly for large x because the exponential decays or increases faster than the polynomial. For $\ln(1 + \alpha x^2)$, the approximation is valid within $|\alpha x^2| < 1$; beyond this region the series either diverges ($\alpha = -1$) or drifts from the true curve. For $(1 + \alpha\sqrt{x})^\mu$, the polynomial is reliable only for small x where $|\alpha\sqrt{x}| < 1$; when x approaches 1, the deviation becomes visible as higher-order terms in $\sqrt{x}$ become significant. However, when $\mu = 2$, the binomial expansion terminates after a finite number of terms—$(1 \pm \sqrt{x})^2 = 1 \pm 2\sqrt{x} + x$—so the Maclaurin polynomial exactly equals the true function, resulting in a perfect fit across the entire interval. In summary, the majority of the approximations work well near the expansion point but lose accuracy once x is no longer small.

Problem 2

Question

Sketching functions using your understanding of its asymptotic properties
Sketch the graph of a Fermi-like-function,

$$F(x, \alpha) = \frac{1}{1 + \exp\{\alpha(x - x_0)\}}$$

In the interval of $0 \leq x < +\infty$ *as a function of* x *for the case of* $\alpha > 1, \alpha x_0 \gg 1$*:*

a) Approximate this function near the point x_0 *(using Taylor expansion).*
b) What does $F(x, \alpha)$ *simplify to, at* $x \gg x_0$*?*
c) Sketch the whole function.

Solution

a) To approximate $F(x, \alpha)$ near $x = x_0$, we use a Taylor expansion about the point where the function changes most rapidly. Since $F(x, \alpha)$ is a smooth sigmoid and $\alpha > 1$, the steepest variation occurs at $x = x_0$, where the exponent $\alpha(x - x_0)$ vanishes. Expanding around this point gives an accurate local description of the transition region.
We first compute derivatives evaluated at $x = x_0$:

$$F^{(1)}(x, \alpha)\Big|_{x=x_0} = \frac{\alpha e^{\alpha(x-x_0)}}{(1 + e^{\alpha(x-x_0)})^2} \Rightarrow F'(x_0, \alpha) = -\frac{\alpha}{4},$$

$$F^{(2)}(x, \alpha)\Big|_{x=x_0} = -\frac{\alpha^2(e^{\alpha(x-x_0)} - 1)e^{\alpha(x-x_0)}}{(e^{\alpha(x-x_0)} + 1)^3} \Rightarrow F''(x_0, \alpha) = 0,$$

$$F^{(3)}(x, \alpha)\Big|_{x=x_0} = -\frac{\alpha^3 e^{\alpha(x-x_0)}\left(e^{2\alpha(x-x_0)} - 4e^{\alpha(x-x_0)} + 1\right)}{(e^{\alpha(x-x_0)} + 1)^4} \Rightarrow F'''(x_0, \alpha) = \frac{1}{8}\alpha^3.$$

Because $F''(x_0) = 0$, the Taylor expansion contains no quadratic term, making the cubic term the next non-vanishing contribution. This is typical for symmetric sigmoidal functions expanded at their mid-point.
Keeping only the first three non-vanishing terms gives:

$$F(x, \alpha) \approx F(x_0) + F'(x_0)(x - x_0) + \frac{1}{6}F^{(3)}(x_0)(x - x_0)^3.$$

Substituting the evaluated derivatives:

$$F(x, \alpha) = \frac{1}{2} - \frac{1}{4}\alpha(x - x_0) + \frac{1}{48}\alpha^3(x - x_0)^3.$$

This truncation is justified because we are approximating the function only in a small neighbourhood of $x = x_0$, where higher-order terms in $(x - x_0)$ become negligible, and because $\alpha x_0 \gg 1$ ensures that the steep transition occurs sharply around this point.

b) At $x \gg x_0$, the function can be reduced to:

$$\lim_{x \gg x_0} F(x, \alpha) = \frac{1}{1 + e^{\alpha(x-x_0)}} \sim e^{-\alpha(x-x_0)},$$

since $e^{\alpha(x-x_0)} \gg 1$ at $x \gg x_0$.

c)

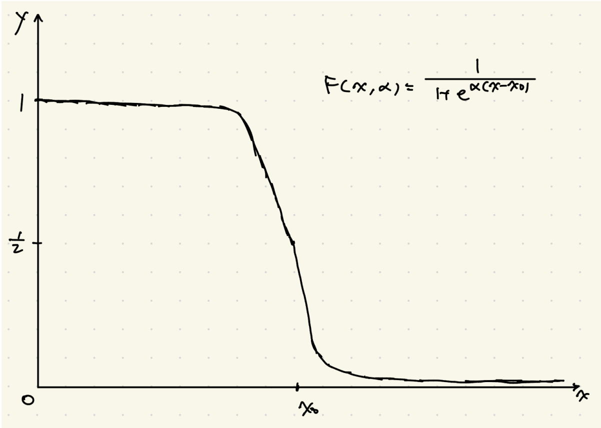

Figure 2: Sketch of the Fermi-like function.

Problem 3

Question

Approximate solution of transcendental equations
A popular equation appearing in the mean-field theory of critical phenomena has the form: $\alpha x = \tanh(x)$. Its solution(s) determines x as a function of α.

a) How many solutions this equation has? Under which circumstances this equation has only one solution?

b) Find all approximate solutions, i.e. expression for, $x(\alpha)$, when $0 < \alpha \ll 1$.

c) Find all approximate solutions, i.e. expression for, $x(\alpha)$, when $\alpha < 1,\ \alpha \to 1$.

Solution

a) The first derivative of $f(x) = \tanh(x) - \alpha x$ is:

$$f'(x) = \operatorname{sech}^2(x) - \alpha.$$

i) For $\alpha \geq 1$, since $\forall x \in R,\ \operatorname{sech}^2 x \leq 1$,

$$f'(x) = \operatorname{sech}^2 x - \alpha \leq 1 - \alpha \leq 0.$$

Hence $f(x)$ is a non-increasing function (flat when $\alpha = 1$), crossing 0 at $x = 0$. There is only one solution, which is $x = 0$.
ii) For $\alpha \leq 0$,

$$f'(x) = \operatorname{sech}^2 x - \alpha \geq -\alpha \geq 0.$$

Hence the function is monotonically increasing function, crossing 0 at $x = 0$. There is only one solution, which is $x = 0$.
iii) For $0 < \alpha < 1$, when near 0, $\tanh(x)$ can be expanded into:

$$\tanh(x) = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 + \mathcal{O}(x^7).$$

Hence,

$$f(x) = (1-\alpha)x - \frac{1}{3}x^3 + \mathcal{O}(x^5).$$

$f(x)$ is therefore greater than 0 for a small value of x, and $f(x) = -\infty$ as $x \to +\infty$. Since the function is smooth, there will be a positive root $x^* > 0$. By odd symmetry of $f(x)$, $-x^*$ is also a solution to the equation. The function will also have a solution at $x = 0$. Therefore, there are three solutions.

b) When $0 < \alpha \ll 1$, the line $y = \alpha x$ has a very small slope, while the curve $y = \tanh x$ rises rapidly near $x = 0$ and quickly saturates to $y = \pm 1$. Hence, the intersections occur near $x = 0$ and at points where $\tanh x \to \pm 1$.
For large positive x, $\tanh x$ can be approximated by expanding in powers of e^{-2x}:

$$\tanh x = \frac{1 - e^{-2x}}{1 + e^{-2x}} = 1 - 2e^{-2x} + 2e^{-4x} - 2e^{-6x} + ...$$

Since for large x, $e^{-2x} \ll 1$, the higher-order terms are negligible and we can keep only the leading two terms:

$$\tanh x \approx 1 - 2e^{-2x}.$$

Substituting this into the original equation $\alpha x = \tanh x$ gives:

$$\alpha x = 1 - 2e^{-2x}.$$

Rearranging:

$$e^{-2x} = \frac{1-\alpha x}{2}.$$

For small α, the intersection occurs at large x, so we assume $x \approx 1/\alpha$ and add a small correction s, i.e. $x = \frac{1}{\alpha} - s,$ where $s \ll \frac{1}{\alpha}$.
Substituting this into the prior equation gives:

$$e^{-2(1/\alpha - s)} = \frac{1-\alpha(1/\alpha - s)}{2} \Rightarrow e^{-2/\alpha}e^{2s} = \frac{\alpha s}{2}.$$

Multiply both sides by $\frac{2}{\alpha}e^{-2s}$:

$$\frac{2}{\alpha}e^{-2/\alpha} = se^{-2s}.$$

Multiply by -2 to match the standard Lambert W form $ue^u = z$:

$$(-2s)e^{-2s} = -\frac{4}{\alpha}e^{-2/\alpha}.$$

Then, by definition of W(z):

$$-2s = W\left(-\frac{4}{\alpha}e^{-2/\alpha}\right) \Rightarrow s = -\frac{1}{2}W\left(-\frac{4}{\alpha}e^{-2/\alpha}\right).$$

Substituting $x = \frac{1}{\alpha} - s$, we obtain

$$x_+(\alpha) = \frac{1}{\alpha} + \frac{1}{2}W\left(-\frac{4}{\alpha}e^{-2/\alpha}\right).$$

However, since the argument of W is exponentially small when $\alpha \ll 1$, we can use the leading approximation $W(z) \approx z$, yielding

$$x_+(\alpha) \approx \frac{1}{\alpha} - \frac{2}{\alpha}e^{-2/\alpha}.$$

Because the full equation $\alpha x = \tanh x$ is odd, the negative solution is simply $x_-(\alpha) = -x_+(\alpha)$, and together with the trivial intersection at $x = 0$, the approximate set of solutions is

$$x(\alpha) = 0, \ \pm\left(\frac{1}{\alpha} - \frac{2}{\alpha}e^{-2/\alpha}\right).$$

c) We can approximate $\tanh x$ by its Taylor series around $x = 0$ in this regime where the non-zero solutions are expected to be small when $\alpha < 1$ and $\alpha \to 1$, i.e. close to the critical value where the non-trivial solutions merge into $x = 0$:

$$\alpha x = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 ...$$

Substituting this into the equation $\alpha x = \tanh x$ and keeping the first three non-vanishing terms gives

$$(1-\alpha)x - \frac{1}{3}x^3 + \frac{2}{15}x^5 = 0.$$

We can introduce a small parameter $\varepsilon = 1 - \alpha \to 0$ and multiply by 15 to give:

$$15\varepsilon x - 5x^3 + 2x^5 = 0.$$

One obvious solution is $x = 0$, which corresponds to the central intersection of the curves. To find the non-trivial solutions, we assume $x \neq 0$ and divide by x:

$$2t^2 - 5t + 15\varepsilon = 0.$$

The solutions of the quadratic equation are:

$$t = \frac{5 \pm \sqrt{25 - 120\varepsilon}}{4}.$$

Since $t = x^2$, the corresponding solutions for the original variable are:

$$x = \sqrt{\frac{5 \pm \sqrt{25 - 120(1-\alpha)}}{4}}.$$

However, the Taylor expansion of $\tanh x$ is valid only for sufficiently small $|x|$. For $\varepsilon \ll 1$, the "+" root in t is of order 1 and leads to $|x|$ that is not small, violating the small-x assumption used in the expansion. The "$-$" root, on the other hand, tends to zero as $\varepsilon \to 0$ and thus remains within the regime where the truncated Taylor series is accurate.
Therefore, within the validity of the approximation, the physically relevant non-zero solutions are given by

$$x \approx \pm\sqrt{\frac{5 - \sqrt{25 - 120(1-\alpha)}}{4}},$$

together with the trivial solution $x = 0$.

Problem 4

Question

Integrals as functions

4.1 Function $F(p)$ is defined as an integral: $F(p) = \int_0^\infty dx \frac{\exp(-px^2)}{1+x}$.

a) To the accuracy of two non-vanishing terms, approximate this function at $p \gg 1$.

b) Plot numerically $F(p)$ (using Excel for the numerical calculation of integrals) and the approximate result, comment on where the approximation is valid and where it breaks down.

4.2 Function $f(p)$ is defined as an integral: $f(p) = \int_0^p \frac{\sin(kx)}{x} dx$.

a) Find its small p-expansion to the accuracy of the first two non-vanishing terms.

b) Put $k = 1$ and plot $f(p, 1)$ numerically; compare it with the approximation obtained. Comment on where the approximation is valid and where it obviously breaks down.

Solution

4.1

a) The Maclaurin expansion of $(1 + x)^{-1}$ is used here since, for $p \gg 1$, the integral $F(p)$ is dominated by the region of *small* x. And when p is large, the factor e^{-px^2} decays extremely rapidly, hence the main contribution to the integral is in the region where $x \ll 1$, so it is therefore justified to replace

$$\begin{aligned}(1+x)^{-1} &= 1 + \frac{-1}{1!}x + \frac{-1(-1-1)}{2!}x^2 + \frac{-1(-1-1)(-1-2)}{3!}x^3 + ... \\ &= 1 - x + x^2 - x^3 + ...\end{aligned}$$

by the first two non-vanishing terms:

$$(1 + x)^{-1} \approx 1 - x.$$

Thus the integral is:

$$\begin{aligned}F(p) &= \int_0^\infty dx \frac{\exp(-px^2)}{1+x} \\ &= \int_0^\infty dx \ \exp(-px^2)(1-x) \\ &= \underbrace{\int_0^\infty dx \ \exp(-px^2)}_{I_1} - \underbrace{\int_0^\infty dx \ x\exp(-px^2)}_{I_2}.\end{aligned}$$

For I_1, let $y = \sqrt{p}x \Rightarrow dy = \sqrt{p}\ dx$. Substitution gives:

$$I_1 = \int_0^\infty dy \ \frac{e^{-y^2}}{\sqrt{p}} = \frac{1}{\sqrt{p}} \cdot \frac{\sqrt{\pi}}{2}.$$

For I_2, let $u = -px^2 \Rightarrow du = 2px\ dx$. Substitution gives:

$$I_2 = \int_0^\infty e^{-u} \frac{du}{2p} = \frac{1}{2p}.$$

Hence,

$$F(p) = I_1 - I_2 = \frac{\sqrt{\pi}}{2\sqrt{p}} - \frac{1}{2p}.$$

b)

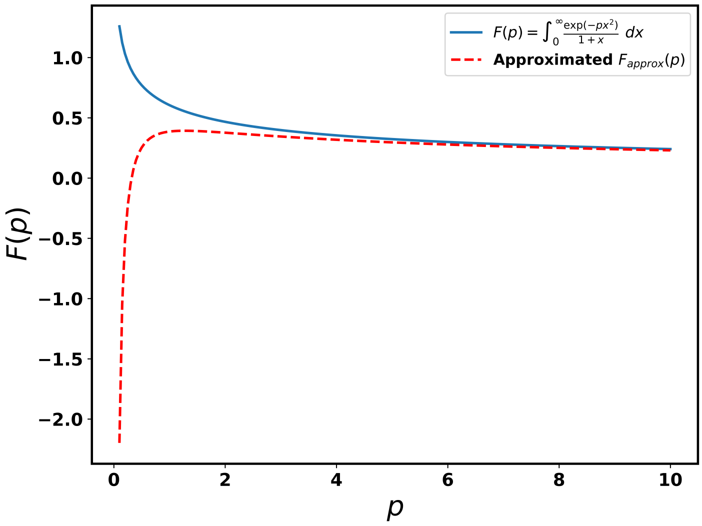

Figure 3: Comparison of numerical and approximate F(p). Solid lines: the original function. Dashed lines: the approximated function.

The approximate expression

$$F_{\text{approx}}(p) = \frac{\sqrt{\pi}}{2\sqrt{p}} - \frac{1}{2p}$$

is derived from expanding the integrand $(1+x)^{-1}$ as $1 - x + \cdots$, and is therefore valid when the integral is dominated by small x values. This occurs for large p, where the exponential factor e^{-px^2} decays rapidly with increasing x, and the first two terms of the Taylor expansion provide an excellent approximation. Hence $F_{\text{approx}}(p)$ reproduces the numerical result almost exactly. As p decreases, the Gaussian broadens and the contribution from larger x becomes more significant. In this case, higher-order terms in the expansion of $(1+x)^{-1}$ are no longer negligible, and the two-term approximation begins to deviate from the numerical curve. Specifically, for $p \lesssim 4, F_{\text{approx}}(p)$ starts to underestimate the true integral, and the discrepancy grows rapidly as p approaches zero.

4.2

a) We use the Maclaurin expansion of $\sin(kx)$ because, for small p, the upper integration limit in $f(p)$ ensures that the integrand is evaluated only for $0 \le x \le p$, where $x \ll 1$. In this regime, the argument kx is also small, and the Taylor series

$$\sin kx = \sum_{n=0}^{\infty} \frac{(-1)^n (kx)^{2n+1}}{(2n+1)!} = kx - \frac{(kx)^3}{3!} + \frac{(kx)^5}{5!} - \frac{(kx)^7}{7!} + \ldots$$

converges rapidly, where we can only retain the first two non-vanishing terms

$$kx - \frac{(kx)^3}{3!}.$$

Therefore,

$$\begin{aligned} f(p,k) &= \int_0^p \frac{\sin kx}{x}\, dx \\ &= \int_0^p \frac{kx - \frac{(kx)^3}{3!}}{x}\, dx \\ &= \int_0^p k - \frac{k^3x^2}{6}\, dx \\ &= \left[kx - \frac{k^3x^3}{18}\right]_0^p \\ &= kp - \frac{k^3p^3}{18}. \end{aligned}$$

b) Let $k = 1$, then

$$f(p,1) = \int_0^p \frac{\sin x}{x}\, dx.$$

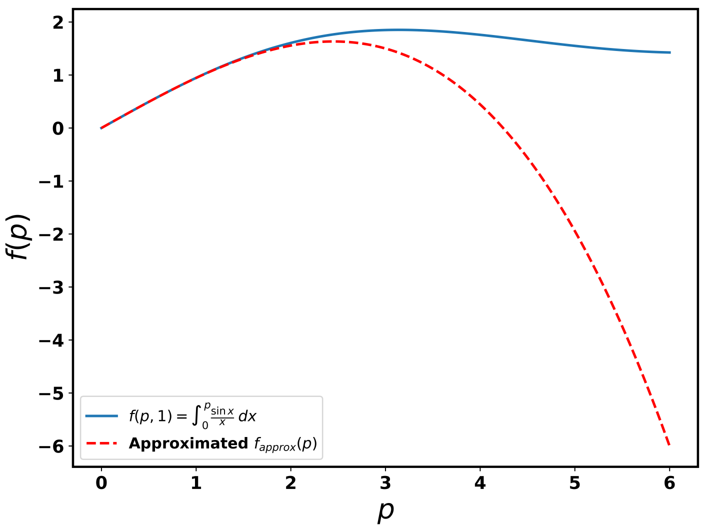

Figure 4: Comparison of numerical and approximate f(p). Solid line: the original function. Dashed line: the approximated function.

The approximate expression

$$f_{\text{approx}}(p) = p - \frac{p^3}{18}$$

is derived from the Maclaurin expansion of $\sin x$ and is therefore accurate only for small arguments (i.e., $p \ll 1$, where $\frac{\sin x}{x} \approx 1 - \frac{x^2}{6}$).

In the plot, the approximation (orange) agrees closely with the numerical result (blue) up to about $p \approx 1.5$, where the cubic term still captures the curvature of the true function. Beyond this region, the approximation begins to deviate: it starts to underestimate $f(p, 1)$ after the peak and eventually decreases rapidly, while the true function slowly approaches the asymptotic value $\frac{\pi}{2}$. This breakdown occurs because higher-order terms in the series become non-negligible, and a low-order polynomial cannot reproduce the oscillatory or saturating behaviour of the sine integral at large p.

Problem 5

Question

Using approximations to answer physical questions
The Lennard-Jones potential $U(R) = U_0[(\frac{a}{R})^{12} - (\frac{a}{R})^6]$
Approximates interactions of neutral species, most suitable for atoms of noble gases, where R is the distance between the atomic centres, a is the characteristic size of atoms, U_0 is the constant determining the energy scale. For Ar, $U_0 \approx 0.08\ eV,\ a = 0.36\ nm$.

5.1. Explain the meaning of the two terms in this equation, which effects they represent?

5.2. Find an expression for the vibration frequency of Ar_2 dimer that may be kept by this potential.

5.3. Compare the result with the vibration frequency of the H_2 molecule (which you should estimate following the corresponding pages of the handouts of Lecture 2).

5.4 Estimate for which temperatures the Ar_2 dimer will dissociate? Explain why at room temperature there is no such thing as an Ar_2 molecule.

Solution

5.1 The potential energy function consists of two competing terms with distinct physical meanings:
The first term, $U_0\left(\frac{a}{R}\right)^{12}$, represents the short-range repulsive interaction, which becomes dominant when the atoms are very close to each other ($R < a$). It originates from the Pauli exclusion principle, preventing the overlap of electron clouds belonging to different atoms.

The second term, $-U_0\left(\frac{a}{R}\right)^{6}$, corresponds to the long-range attractive interaction. It arises from the London dispersion forces (induced dipole–induced dipole interactions) between neutral atoms. The R^{-6} dependence comes from quantum mechanical treatment of these van der Waals forces.

The competition between the attractive and repulsive terms gives rise to a potential minimum at an equilibrium distance where the net force between the atoms is zero and the configuration is most stable.

5.2 The first derivative of the Lennard-Jones potential can be expressed as:

$$\frac{dU}{dR} = U_0\Big[-12a^{12}R^{-13} + 6a^6R^{-7}\Big].$$

Let $\frac{dU}{dR} = 0$, the equilibrium distance R_0 can be solved as follows:

$$-12\cdot a^{12}R_0^{-13} + a^6R_0^{-7} = 0 \ \Rightarrow\ R_0 = 2^{1/6}a.$$

The second derivative of the Lennard Jones potential can be expressed as:

$$\frac{d^2U}{dR^2} = U_0\Big[156a^{12}R^{-14} - 42a^6R^{-8}\Big].$$

The spring constant k can be found as follows:

$$k = \frac{d^2U}{dR^2} = U_0\Big[156a^{12}R^{-14} - 42a^6R^{-8}\Big].$$

Let $a^6R^{-6} = \frac{1}{2}$, the spring constant is:

$$k = U_0\Big[156a^{12}(2^{1/6}a)^{-14} - 42a^6(2^{1/6}a)^{-8}\Big] \ \Rightarrow\ k = 18\cdot 2^{-1/3}U_0a^{-2}.$$

Since the reduced mass of Ar_2 is:$\mu_{\mathrm{Ar}_2} = \frac{m_{\mathrm{Ar}}}{2} = 20m_p$, the vibrational frequency of Ar_2 is:

$$\begin{aligned}\omega &= \sqrt{\frac{k}{m}} \\ &= \sqrt{\frac{18 \cdot 2^{-1/3} U_0 a^{-2}}{20m_p}} \\ &= \sqrt{\frac{9 \cdot 2^{-1/3} U_0}{10 m_p a^2}}.\end{aligned}$$

Using the parameters, the vibration frequency is:

$$\begin{aligned}\omega &= \sqrt{\frac{9 \cdot 2^{-1/3} \cdot 0.08 \cdot 1.6 \times 10^{-19}\ \mathrm{J}}{10 \cdot 1.67377 \times 10^{-27}\ \mathrm{kg}\ \cdot (0.36 \times 10^{-9}\ \mathrm{m})^2}} \\ &= 6.49 \times 10^{12}\ \mathrm{s}^{-1}\ \text{(to 3 s.f.)}.\end{aligned}$$

5.3 The vibrational frequency of H_2 given in Lecture 2 is $8.3 \times 10^{14}\ \mathrm{s}^{-1}$, which is higher than that of the supposed Ar_2 in two orders of magnitude.
This difference is due to the fact that H_2 has a strong covalent bond (i.e., large force constant $k \sim 500$–$600\ \mathrm{N\,m^{-1}}$) and a very small reduced mass $\mu_{\mathrm{H}_2} = m_{\mathrm{H}}/2$. On the contrary, along with a much greater reduced mass, Ar_2 is only very weakly bound by Van der Waals forces, leading to a very long bond distance and low bond strength, hence much lower vibrational frequency.
5.4 The dissociation temperature T_{diss} can be estimated by the formula below:

$$k_B T_{\mathrm{diss}} \sim D_0.$$

The lowest dissociation energy D_0 can be calculated as:

$$\begin{aligned}D_0 &= E_{\text{free atoms}} - E_{v=0} \\ &= \varepsilon - \tfrac{1}{2}\hbar\omega.\end{aligned}$$

Using $\varepsilon = U_0/4 = 0.02$ eV, D_0 is:

$$\begin{aligned}D_0 &= 0.02 \cdot 1.6 \times 10^{-19}\ \mathrm{J} - 0.5 \cdot 1.055 \times 10^{-34}\ \mathrm{J \cdot s} \cdot 6.49 \times 10^{12}\ \mathrm{s}^{-1} \\ &= 2.86 \times 10^{-21}\ \mathrm{J}\ \text{(to 3 s.f.)}.\end{aligned}$$

Therefore,

$$T_{\mathrm{diss}} \geq \frac{D_0}{k_B} = \frac{2.86 \times 10^{-21}\ \mathrm{J}}{1.38 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}} = 207\ \mathrm{K}\ \text{(to 3 s.f.)}.$$

At room temperature (295 K), the thermal energy from random motion of Ar_2 would exceed the binding energy. Any transiently formed dimer will be immediately broken apart by collisions, leading to monoatomic structure.

Problem 6

Question

Functions of more than one variables

6.1 The ideal gas equation $pV = nRT$ relates pressure p, volume V, and absolute temperature, T (n is the number of moles occupying the given volume, R is the gas constant).

a) Derive the expression for isothermal compressibility, $\frac{\partial V}{\partial p}\Big|_T$, for the ideal gas. Interpret its pressure-dependence.

b) Derive the expression for isobaric thermal expansion coefficient, $\frac{\partial V}{\partial T}\Big|_p$, for the ideal gas.

6.2. van der Waals equation (Johannes Diderik van der Waals, 1837-1923) extends the ideal gas equation to include attractive interaction between atoms and molecules (van der Waals forces) and the so called 'excluded volume' due to hard core repulsion between atoms/molecules due to collisions in compressed state. VdW-equation even describe in a qualitative way the transition to a liquid state at high pressures and reduced temperatures. If we are not going that far, it just corrects the ideal gas equation. The VdW equation reads

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Here a is a constant characterizing the attraction between atoms/molecules, and b is the volume excluded by one mole of atoms/molecules due to their physical volume (so that $V - nb$ is the 'free volume of the space between the atoms/molecules) . The parameters a and b are generally substance dependent.

a) Show in which limiting case in terms of volume the ideal gas equation is recovered. Show in which particular case in terms of parameters a and b the ideal gas equation is recovered. Interpret your results.

b) Find the parametric dependence of isothermal compressibility on pressure.

c) Find a saddle point on the surface defined by equation $S(x, y) = x^2 - y^2$

Solution

6.1 a)

$$pV = nRT$$
$$\Rightarrow V = \frac{nRT}{p}$$
$$\Rightarrow \frac{\partial V}{\partial p}\Big|_T = -\frac{nRT}{p^2} = -\frac{V}{p}.$$

The rate of change of volume with pressure is inversely proportional to p, i.e., the volume becomes less sensitive to further increases in pressure.

6.1 b)

$$pV = nRT$$
$$\Rightarrow V = \frac{nRT}{p}$$
$$\Rightarrow \frac{\partial V}{\partial T}\Big|_p = \frac{nR}{p}.$$

6.2 a) At very large V, both correction terms in the Van der Waals equation become negligible:

$$\frac{n^2 a}{V^2} \to 0, \qquad nb \ll V.$$

Substituting these limits into

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

gives

$$pV \approx nRT.$$

From a physical understanding, in the limit of large volume (low density), intermolecular attractions and excluded volume effects vanish, and the ideal gas law is recovered.
The ideal gas equation $pV = nRT$ is recovered for all $p,\ V,\ T$ if

$$a = 0 \quad \text{and} \quad b = 0.$$

From a physical understanding, $a = 0$ means there is no attractive (van der Waals) forces between particles, and $b = 0$ means particles have no finite size (no excluded volume), i.e. point particles. Together, this is exactly the ideal-gas model: non-interacting point particles.
6.2 b)

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\Rightarrow p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$\begin{aligned}\Rightarrow \frac{\partial p}{\partial V}\bigg|_T &= \frac{d}{dV}\left(\frac{nRT}{V - nb}\right) - \frac{d}{dV}\left(\frac{n^2 a}{V^2}\right) \\ &= -\frac{nRT}{(V - nb)^2} + \frac{2n^2 a}{V^3}.\end{aligned}$$

$$\Rightarrow \frac{\partial V}{\partial p}\bigg|_T = \frac{1}{\frac{\partial p}{\partial V}\big|_T} = \frac{1}{-\frac{nRT}{(V-nb)^2} + \frac{2n^2 a}{V^3}}.$$

6.3

$$S(x,y) = x^2 - y^2 \Rightarrow \begin{cases} \dfrac{\partial S(x,y)}{\partial x} = 2x \\ \dfrac{\partial S(x,y)}{\partial y} = -2y \end{cases} \Rightarrow \begin{cases} \dfrac{\partial^2 S(x,y)}{\partial x^2} = 2 > 0 \\ \dfrac{\partial^2 S(x,y)}{\partial y^2} = -2 < 0 \\ \dfrac{\partial^2 S(x,y)}{\partial x \partial y} = 0 \end{cases}$$

where

$$\frac{\partial S(x,y)}{\partial x} = \frac{\partial S(x,y)}{\partial y} = 0 \text{ at } (0,0).$$

Therefore,

$$S = \frac{\partial^2 S(x,y)}{\partial x^2}\frac{\partial^2 S(x,y)}{\partial y^2} - \left(\frac{\partial^2 S}{\partial x \partial y}\right)^2 = -4 < 0.$$

Since $S < 0$, and

$$\frac{\partial^2 S(x,y)}{\partial x^2} \cdot \frac{\partial^2 S(x,y)}{\partial y^2} < 0,$$

it is determined that (0,0) is a saddle point on the surface.