

Homework Assignment 1

Modeling Graphene Surface Properties and Derivation of the Van der Waals Equation of State

Due date: 7.Mar.2025

Q1 Surface tension of graphene and graphene stacks

Graphene, a two-dimensional, one-atom-thick hexagonal lattice of carbon atoms, has received considerable attention due to its extraordinary properties. Research on wetting phenomena on graphene is the first step towards quantifying its surface properties, because the interfacial energies involved directly determine the macroscopic contact angle, θ of a liquid droplet on graphene. Using the concepts and methods that we discussed in class, we can approach this interesting system in a simple and insightful manner. Here are the assumptions used in the homework:

1. Graphene is a two-dimensional sheet with zero thickness, and the mass is uniformly distributed in the sheet.
2. Graphite is a lamellar structure of graphene with the interlayer distance of $d_0 = 3.35 \text{ \AA}$.
3. van der Waals (vdW) interactions are perfectly additive and pairwise.

In this question we will derive the surface tension of graphene and its stacks using the knowledge learned from the lecture. We assume the graphene sheets in graphite are dominated by the vdW forces. The vdW potential between two carbon atoms is given by: $V_{CC} = -\beta_{CC}/r^6$, where r is the distance between the two carbon atoms.

Please answer the following questions to solve the problem step-by-step.

1. Please show that the surface tension of single layer graphene γ_{G1} is given by $\gamma_{G1} = \frac{\pi\sigma^2\beta_{CC}}{4d_0^4}$, where σ is the surface density of carbon atoms on graphene. Graphene has hexagonal unit cell with lattice constant $a = 2.49 \text{ \AA}$ (Figure 1).
2. Assume two stacks of graphene A and B, both composed of parallel graphene sheets with interlayer distance d_0 separated by a distance δ (Figure 2). Stack A contains m layers of graphene, and graphene stack B contains n layers. Please derive the expression for the work of adhesion $\Delta W_{AB}(m, n)$ between A and B separated by a distance δ as function of m and n .
3. If we have $m \rightarrow \infty$ and $n \rightarrow \infty$, $\Delta W_{AB}(\infty, \infty)$ essentially becomes the work of adhesion for **graphite**. Assuming that the distance $\delta = d_0$, please write the expression for the surface tension of graphite $\gamma_{G\infty}$ using the variables given here.

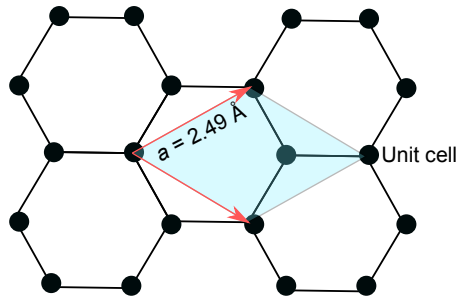


Figure 1: Structure of graphene. The unit cell and lattice constant are shown.

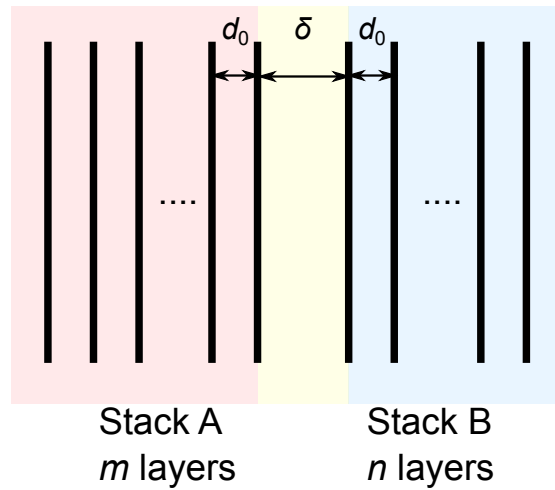


Figure 2: Scheme of graphene stacks A and B separated by a distance δ with layer numbers m and n , respectively.

4. Experimentally, the surface tension of graphite $\gamma_{G\infty}$ has been found to be $129 \text{ mJ}\cdot\text{m}^{-2}$ ¹.

Using the expression you obtained in Q1.3, calculate the value of β_{CC} .

Q2 Derivation of the Van der Waals Equation of State from the Lennard-Jones Potential

The Van der Waals (VdW) equation of state provides a foundational model for describing the behaviour of real gases. By incorporating the effects of intermolecular interactions and the finite size of molecules, it offers a simple yet instructive framework that successfully predicts phenomena such as the liquid-gas phase transition.

In this exercise, we will derive the VdW equation directly from the Lennard-Jones (LJ) potential discussed in lecture I. This approach allows us to gain a deeper understanding of how microscopic interactions influence macroscopic thermodynamic properties. This exercise will guide you through the derivation step-by-step, using concepts discussed in class.

To simplify the derivation, we adopt the following assumptions:

1. The system consists of a classical monoatomic gas.
2. The pairwise interaction potential $u(r)$ is modelled using the “hard-sphere” Lennard-Jones potential, which combines a short-range repulsive term and a long-range attractive term (LJ r^{-6}):

$$u(r) = \begin{cases} +\infty & r < r^* \\ -\beta \left(\frac{r^*}{r}\right)^6 & r \geq r^* \end{cases}$$

Here, r^* represents the distance at which the potential reaches its minimum value $u_0 = -\beta$, corresponding to the minimum energy of the interaction.

Please answer the following questions to solve the problem step-by-step.

1. Our starting point is the ideal gas. Therefore, we begin by considering a system of non-interacting molecules, where each molecule is independent, contributing only with kinetic energy. The single-molecule partition function is:

$$q = \frac{V}{\Lambda^3}$$

where

$$\Lambda = \sqrt{\frac{h}{2\pi mk_B T}}$$

is the thermal de Broglie wavelength.

For a gas of N independent and indistinguishable molecules, the total canonical partition function is:

$$Q = \frac{1}{N!} q^N = \frac{1}{N!} \left(\frac{V}{\Lambda^3}\right)^N.$$

Given that:

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

Find the equation of state and confirm that is exactly the ideal gas law.

¹Renju Zacharia, Hendrik Ulbricht, and Tobias Hertel. “Interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons”. In: *Phys. Rev. B* 69 (2004), p. 155406.

2. In the VdW model, to account for LJ attraction and repulsion, we modify Q , using the following assumptions:

- (a) Since $u(r) = +\infty$ for $r < r^*$, not all volume V is available to the gas:

$$V \rightarrow V_{\text{eff}}.$$

- (b) We can add an energy term equal to the total interaction energy felt by a single molecule due to the "mean field" of the rest (assumed distributed randomly with uniform density $\rho = N/V$). Use as template the derivation done in lecture I and show that the total interaction energy can be written as

$$\varphi = -\frac{2aN}{V}$$

where $a = \frac{2\pi\beta}{3}r^*$.

- (c) The single-molecule partition function is modified by a Boltzmann factor $e^{-\varphi/2k_B T}$, where the factor of 2 is to avoid double counting:

$$q = \frac{V_{\text{eff}}e^{-\varphi/2k_B T}}{\Lambda^3},$$

where V_{eff} is the effective volume. Remembering that each molecule excludes a volume of $b = \frac{4\pi(r^*)^3}{3} \frac{1}{2}$ due to hard-core repulsion, where $\frac{1}{2}$ accounts for the fact that the effect is also due to pair interactions. Write the effective volume.

Derive the total partition function using these new assumptions. From this, now derive the equation of state as before.

3. Critical parameters.

Now you will calculate the critical parameters. First rewrite the equation of state (EoS) found in point 2 in terms of molar quantities using $v = V/N$ and write the pressure p as function of v and T .

The critical point is then found as the inflection point of p - v curve which is equivalent to the following two equations:

$$\left(\frac{\partial p}{\partial v}\right)_T = 0$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$$

Solving the system gives the critical volume v_c and the critical temperature T_c . Substituting back into the EoS gives the critical pressure p_c .

4. To help plot the EoS we write the parameters v , P and T in dimensionless form by normalizing them by their critical values. The reduced variables are defined as:

$$p_r = \frac{p}{p_c}, \quad v_r = \frac{v}{v_c}, \quad T_r = \frac{T}{T_c}.$$

Now write the Van der Waals equation in reduced form $P_r(T_r, v_r)$. This expression demonstrates that the Van der Waals equation, in terms of reduced variables, is independent of the material-specific parameters a and b . This universality is known as the

Law of Corresponding States, which implies that all substances described by the Van der Waals equation share the same behaviour when expressed in terms of their reduced variables. Plot the VdW EoS in the reduced variables at different values of T_r . Explain what happens at $T_r = 1$ and why the critical point is an inflection point in the p-v curve.

5. Instability region and spinodal curve.

In the (T, V, N) ensemble, the appropriate thermodynamic potential is the Helmholtz free energy $F(T, V, N)$ where

$$dF = -SdT - pdV$$

The stability condition for an isotherm requires that: $\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,N} \geq 0$ so that F must be a convex function of the volume.

Show that it is equivalent to the condition that $p(v)$ must be strictly decreasing. Plot the region of the p-v plane that is unstable according to the VdW EoS. Observe that it vanishes at the critical point. What happens in this region?

6. Saturation curve.

The spinodal points delimit the region of instability in the $p - v$ plane where phase separation by spinodal decomposition occurs. However in each isotherm:

$$p_{\min}(T) \neq p_{\max}(T),$$

where $p_{\min}(T)$ and $p_{\max}(T)$ are the spinodal points at temperature T. Therefore saturation must occur at some intermediate value between $p_{\min} < p_s < p_{\max}$ and at v not within the unstable area.

This suggests that phase separation (at constant $T = T_s$) occurs when

$$v_s^{\text{gas}} > v(p_{\max}) > v(p_{\min}) > v_s^{\text{liq}}.$$

To find the saturation curve, we need to solve (for each value of T) for $(p_s, v_s^{\text{gas}}, v_s^{\text{liq}})$, and we need three equations:

- (a) EoS for the liquid phase
- (b) EoS for the gas phase
- (c) $\mu^{\text{gas}} = \mu^{\text{liq}}$

For a single component system the molar Gibbs free energy is equal to the chemical potential $g = \mu$. On an isotherm $dg = vdp = d(pv) - pdv$. Therefore, equation (c) can be obtained by integrating from v_s^{liq} to v_s^{gas} .

$$\Delta g = g_{\text{gas}} - g_{\text{liq}} = p_s(v_s^{\text{gas}} - v_s^{\text{liq}}) - \int_{v_s^{\text{liq}}}^{v_s^{\text{gas}}} pdv$$

Write down these equations and show that (c) can be written as follows

$$k_B T \left[\frac{v_s^{\text{gas}}}{v_s^{\text{gas}} - b} - \frac{v_s^{\text{liq}}}{v_s^{\text{liq}} - b} - \ln \left(\frac{v_s^{\text{gas}} - b}{v_s^{\text{liq}} - b} \right) \right] - 2a \left(\frac{1}{v_s^{\text{gas}}} - \frac{1}{v_s^{\text{liq}}} \right) = 0$$

Now write the same system in reduced variables $(\bar{p}_s, \bar{T}_s, \bar{v}_{\text{liq}}, \bar{v}_{\text{gas}})$.

7. Optional numerical solution for extra points.

Given \bar{T}_s we can numerically solve for each T_s and plot $(\bar{p}_s, \bar{v}_{liq}, \bar{v}_{gas})$.

Solve numerically for one value of T and draw the 2 points: $(\bar{p}_s, \bar{v}_{gas})$ and $(\bar{p}_s, \bar{v}_{liq})$.