CH-242(b) - Part 1
Lecture 2 - Surface Thermodynamics

Resources:

- from Butt et al., *Physics and Chemistry of Interfaces*, third (2013) edition:
  - Chapter 3 – "Thermodynamics of Interfaces"
  - Section 11.2 – "Spherical Micelles, Cylinders, and Bilayers" (for micelle content)
- for an excellent text on the fundamentals of thermodynamics:
  - Callen, Herbert B. *Thermodynamics and an Introduction to Thermostatistics.* Second ed. New York, Wiley, 1985.

Summary

- Thermodynamics review
  - The state of a macroscopic system in equilibrium is characterized by a small number of *state variables.*
  - *First law:* The system energy U is a function of the state variables, and the change $\Delta U = \Delta W + \Delta Q$ in the system energy as a result of some process is determined by the work ΔW done on the system and the heat ΔQ absorbed by the system.
  - *Second law:* The system entropy S is a state variable, and for any adiabatic process ($\Delta Q = 0$) we have $\Delta S \geq 0$. For a general process we have $T\Delta S \geq \Delta Q$.
  - A quasi-static process is defined to be one where $T\Delta S = \Delta Q$.
  - The system temperature T is equal to $\partial_S U$.
  - The unconstrained state variables of an adiabatically closed system will spontaneously evolve to maximize the system entropy S. The unconstrained state variables of a system in thermal contact with a heat reservoir will spontaneously evolve to minimize the system's Helmholtz free energy $F \equiv U - TS$.

- Thermodynamics of surfaces
  - The surface tension γ of an interface is equal to $\partial_A U$, where U is the interfacial energy and A is the interfacial area.
  - Single component interfaces:
    - The interfacial Helmoltz free energy density $f \equiv F/A$ is equal to the surface tension γ.
    - The interfacial entropy density $s \equiv S/A$ is equal to $-\partial_T \gamma$.
    - The interfacial energy density $u \equiv U/A$ is equal to $\gamma - \partial_T \gamma$.
  - In the Gibbs convention, the interface is defined to be an infinitely thin (i.e. two-dimensional) surface of constant solvent density positioned so that the surface excess Γ_1 of solvent molecules is zero.
  - The interfacial surface excess $\Gamma_2 \equiv \Gamma$ of a solute dissolved in solute can be estimated using the Gibbs adsorption isotherm $\Gamma = -\frac{1}{RT}\partial_{\ln c}\gamma$, where c is the concentration of solute in solution.
- Micelles
  - Beyond a certain surfactant concentration $\bar{c}_{CMC}$ known as the *critical micelle concentration* (or CMC), monomeric surfactant molecules in solution will begin to coalesce, forming large spherical structures known as *micelles.*
  - The CMC can be estimated by identifying a discontinuity in the slope of a graph plotting surface tension γ vs. the logarithm $\ln \bar{c}$ of the surfactant concentration.
  - The Gibbs energy ΔG^o of micellization can be estimated from the CMC.

1 Fundamentals of thermodynamics – crash course

1.1 State variables

The observable properties of a macroscopic system in equilibrium are determined by a set of variables called *state variables* that are remarkably small in number in light of the enormous ($\approx N_a \approx 10^{23}$) number of coordinates required to specify the state of all of the system's microscopic degrees of freedom. Included among the state variables for simple systems consisting of a pure substance (e.g. a gas of carbon dioxide, liquid water, solid diamond, etc.) are the familiar system volume V and the particle number N. For a magnetic system for example we would add to the list of state variables its magnetic moment, and for an interface we include as a state variable the interfacial area A. State variables should also have the property of being *extensive* in that doubling the system requires doubling the values of all its state variables.

A question poses itself: given a system, how does one identify its state variables? This question turns out to be a subtle one, and we will satisfy ourselves with the following loose definition which will be adequate for our purposes: the state variables are, with a single notable exception, all the independent extensive properties of a system that can be directly *measured* and/or *controlled*. Clearly properties like volume and particle number meet the criteria of measurability/controllability. The single exception mentioned above which completes the list of state variables is, you may have guessed, a variable called the system *entropy*, denoted S. Our task in the remainder of this crash course is to enunciate the defining properties of the system entropy and its relation to the other central notion of thermodynamics: the system *energy*.

1.2 Energy and the first law of thermodynamics

Abstractly, the system energy, which we denote with the symbol U, is a *function* of the state variables $(X_1 \equiv S, X_2, \ldots, X_N)$, i.e. $U(X_1, \ldots, X_N)$. This function is also extensive in the sense for any number $\lambda > 0$ we have

$$U(\lambda X_1, \lambda X_2, \ldots, \lambda X_N) = \lambda U(X_1, X_2, \ldots, X_N) \tag{1}$$

i.e. a doubling of all the state variables results in a doubling of the energy.

Suppose we subject our system to some transformation. This transformation could be an increase of its volume, a reduction of its particle number, or an increase in its temperature (though we haven't yet defined what we mean by temperature). No matter what transformation we consider, the resulting change ΔU in the system energy U can be decomposed into two contributions:

- the work ΔW done *on* the system *by* its surroundings, and
- the heat ΔQ *absorbed by* the system *from* its surroundings.

Mathematically this fact, termed the *first law of thermodynamics*, is written as

$$\Delta U = \Delta W + \Delta Q \tag{2}$$

1.2.1 Work

Of course this equation as it stands it not very useful since we have not defined what we mean by the work ΔW or the heat ΔQ incurred in some transformation. We attack first the work ΔW and begin by noting that in practice it is possible, by enclosing the system with thermally insulating walls, to prevent heat transfer between the system and its surroundings, i.e. to arrange it so that $\Delta Q = 0$. A transformation of a system under such conditions is called an *adiabatic* process.

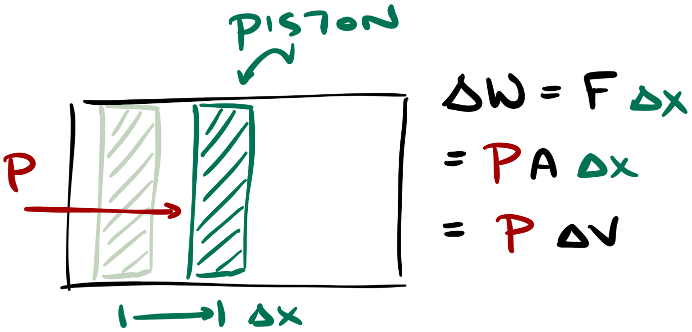
It is an empirical fact of nature that, given any two system states $A \equiv \left(X_1^A, X_2^A, \ldots, X_N^A\right)$ and $B \equiv \left(X_1^B, X_2^B, \ldots, X_N^B\right)$, at least one of the two following statements is true:

- There is an adiabatic process which brings a system beginning in state A to the state B.

- There is an adiabatic process which brings a system beginning in state B to the state A.

Now the work ΔW required to achieve such a transformation is presumed to be measurable. This fact, combined with the earlier-mentioned general existence of adiabatic (i.e. thermally insulating) walls, implies that the energy difference ΔU between any two system states A and B can be measured by noting the quantity of work ΔW done by the surroundings in the adiabatic process taking the system from $A \to B$ or $B \to A$ (whichever one is possible).

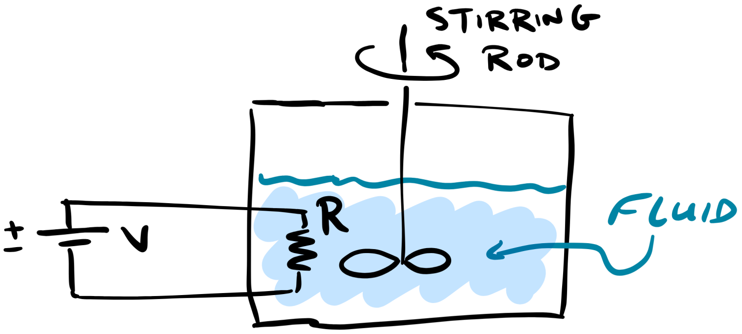
The preceding discussion is rendered more clear by looking at a couple simple examples. Consider first a volume of gas enclosed in a cylinder with a movable wall (i.e. piston) on one end:



If we displace the piston inwards by a distance Δx while applying a pressure P on the face piston of area A, then evidentally we perform a work $\Delta W = F\Delta x = PA\Delta x$ on the system. Note that this work is *positive* ($\Delta W > 0$) since the displacement of the piston is in the same direction as the applied force. It is of course entirely possible, depending on the thermodynamic state of the enclosed gas, that the pressure P' exerted *by* the gas on the cylinder might exceed the pressure P that we (i.e. the "surroundings") exert on the piston. In this case the piston will be pushed *outwards* against our opposing force $PA < P'A$. The displacement Δx would then be negative if we take the force $F = PA$ we exert on the piston to be positive. The work $\Delta W = F\Delta x$ done *by* the surroundings would then be *negative*, in which case would we say that the system does work *on* its surroundings.

No matter the direction of the displacement Δx, if the walls of the cylinder – piston included – are adiabatic, then the change in the system energy ΔU created by the displacement will be $\Delta U = \Delta W + \Delta Q = \Delta W = PA\Delta x = -P\Delta V$, where $\Delta V = -A\Delta x$ is the change in the system volume.

We now consider two transformations/processes that differ fundamentally in character from the one just presented. For convenience we illustrate both processes in the same diagram, shown below:



Shown above is a fluid comprised of a single inert pure substance. Integrated into the fluid is a stirring rod and a resistor of resistance R connected to an external battery of voltage V. If we begin spinning the stirring rod, then we will encounter a drag force due to the fluid's viscosity so that if we want to rotate the rod at an angular ω we will need to apply a torque $\tau = b\omega$ to overcome the drag force exerted by the fluid, where b is some constant. If we apply this torque for a time Δt then we rotate the rod by an angle $\Delta\phi = \omega\Delta t$ and therefore do a quantity of work $\Delta W = \tau\Delta\phi = b\omega^2\Delta t$. Similarly, to supply a current $I = V/R$ the battery must deliver a power $P = VI = V^2/R$ to the resistor, so that in a time Δt there is a work done equal to $\Delta W = \frac{V^2}{R}\Delta t$.

These processes differ in character from that performed on the piston in the sense that they involve no change in the non-entropic state variables. Indeed for a pure fluid the states variables are simply V, N, and S, so it is only the system entropy S which will have changed as a result of the stirring of the rod or the driving of electrical current through the resistor. Qualitatively we also have some intuition that both of these activities will lead to some "heating up" of the fluid. The increase in system entropy we therefore expect to be reflected in a change in the system temperature (which we still have yet to define). This is all true even if the fluid is enclosed by adiabatic walls, so that $\Delta Q = 0$ during the processes. From these examples we arrive therefore at two conclusions which might appear to you as rather suprising or unintuitive:

- The entropy of a system S can change during an adiabatic process.
- A system can heat up even during a process where the heat transfer ΔQ between the system and its surroundings is zero.

1.2.2 Heat

We are now prepared to quanitify the heat ΔQ absorbed by a system in some non-adiabatic (or "diabatic") process. In a diabatic process taking a system from a state A to a state B, the heat absorbed ΔQ is given by

$$\Delta Q = \Delta W_{\text{adiabatic}} - \Delta W \tag{3}$$

where ΔW is the work done in the diabatic process and $\Delta W_{\text{adiabatic}}$ is the work done in an adiabatic process taking the system from A to B. If no such adiabatic process exists, then an adiabatic process $B \to A$ must exist, in which case $\Delta W_{\text{adiabatic}}$ is simply the *negative* of the work required for the adiabatic process. Convince yourself that equation (3) follows straightforwardly from the first law of thermodynamics.

Suppose for example we begin with a fluid in a state $A = (V_A, N_A, S_A)$ and in this state a reading of the fluid's temperature (via e.g. a mercury thermometer) gives a temperature T_A. We then enclose the fluid in an adiabatic container and stir it for a time Δt, doing on the fluid a work $\Delta \bar{W} = b\omega^2 \Delta t > 0$ and thereby raising its temperature to $T_B > T_A$. The system is now in some different state $B = (V_B = V_A, N_B = N_A, S_B \neq S_A)$. We then place the fluid in a diabatic container and put it in thermal contact with a cold body, returning its temperature back to T_A. The fluid volume and particle number are still the same, so the cooling process has the effect of returning the system back to state A. The work ΔW done in the (diabatic) cooling process is zero, there being no identifiable sources of work employed during the cooling. Applying equation (3), the heat ΔQ "absorbed" by the system during the diabatic cooling process $B \to A$ is

$$\begin{aligned} \Delta Q &= \Delta W_{\text{adiabatic}} - \Delta W \\ &= \Delta W_{\text{adiabatic}} - 0 \\ &= \Delta W_{\text{adiabatic}} \\ &= -\Delta \bar{W} \\ &= -b\omega^2 \Delta t < 0 \ , \end{aligned} \tag{4}$$

so that we might more intuitively say that the system "gives off" a positive quantity of heat $\Delta \bar{W}$ to its surroundings.

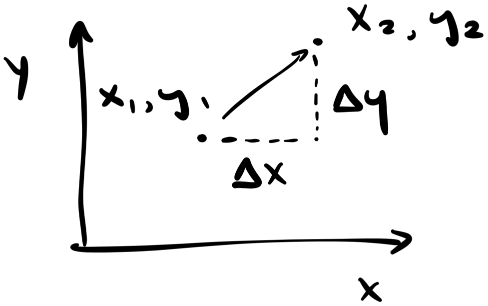
1.3 Mathematical detour - differentials

Before developing further it is helpful at this juncture to pause briefly to address the concept of differentials as they are employed in the study of thermodynamics. Perhaps in previous expositions of thermodynamics you have encoutered equations like

$$dU = TdS - PdV \tag{5}$$

which apply to simple closed ($\Delta N = 0$) single-component systems. Perhaps you are like me and have always been puzzled by these types of equations. How big is dS? How big is dV? Is dV related to dS? The aim in this subsection is to make clear what is trying to be expressed by these types of equations.

Take an arbitrary function $z(x, y)$ of two variables x and y. Take a "point", i.e. pair of values (x_1, y_1), and a nearby point $(x_2, y_2) = (x_1 + \Delta x, y_1 + \Delta y)$:



We now pose the question: what is the difference $\Delta z = z(x_2, y_2) - z(x_1, y_1)$ in the value of the function z between these two points? If the function z is sufficiently smooth and the separation $(\Delta x, \Delta y)$ between the points sufficiently small, then we might estimate the value of z at (x_2, y_2) via a first-order taylor expansion about the point (x_1, y_1):

$$z(x_2, y_2) \approx z(x_1, y_1) + \partial_x z(x_1, y_1)\Delta x + \partial_y z(x_1, y_1)\Delta y \tag{6}$$

where $\partial_x z(x_o, y_o)$ means "the partial derivative of z with respect to x (i.e. its first argument), evaluated at the point (x_o, y_o)", and likewise for $\partial_y z(x_o, y_o)$. Evidently we have then

$$\Delta z \approx \partial_x z \Delta x + \partial_y z(x_1, y_1)\Delta y \tag{7}$$

This approximation of course becomes better and better as $\Delta x, \Delta y \to 0$, so that when we write

$$dz = z_x dx + z_y dy \tag{8}$$

you should translate it in your head into the following phrase:

> The difference dz in the value of a function $z(x, y)$ between two points (x_o, y_o) and $(x', y') = (x_o + dx, y_o + dy)$ is *approximately equal* to $z_x dx + z_y dy$, where $z_x = \partial_x z(x_o, y_o)$ and $z_y = \partial_y z(x_o, y_o)$, and the accuracy of this approximation improves as dx and dy become smaller and smaller.

Note that as $dx, dy \to 0$ we also have $\partial_x z(x', y') \to \partial_x z(x_o, y_o)$ and $\partial_y z(x', y') \to \partial_y z(x_o, y_o)$, so that so long as dx and dy are sufficiently small it is not important at which point ((x_o, y_o) or (x', y')) we evaluate the partial derivatives.

Now take our function U representing the system energy, and suppose it is a simple one-component system so that its state is characterized by the usual volume V, particle number N, and entropy S. To estimate the difference dU in system energy at two states (S_o, V_o, N_o) and $(S_o + dS, V_o + dV, N_o + dN)$ we therefore must compute

$$dU = TdS - PdV + \mu dN \tag{9}$$

where, evidently:

- $T = \partial_S U$ and is, we will see, equal to the (absoslute) temperature of the system,
- $P = -\partial_V U$ and is equal to the mechanical pressure exerted *by* the system on the walls of its container, and
- $\mu = \partial_N U$ is the "chemical potential" quantifying the energy penalty/incentive involved in particle transfer to/from the system and its surroundings.

One finds thus that various physically-relevant system properties are encoded as first derivatives of the energy function U. The energy function U in fact completely characterizes a thermodynamic system[1], so that *any* property of interest is encoded by U. A system's heat capacity and compressibility are for example encoded in the second derivatives of U.

1.4 Entropy and the second law of thermodynamics

The second law of thermodynamics relates the heat, energy, and entropy. It states that for any process, the change in entropy ΔS and the heat absorbed ΔQ are related by the following inequality

$$T\Delta S \geq \Delta Q \tag{10}$$

The law written in this form implicitly assumes that the temperature $T = \partial_S U$ is constant throughout the process and so applies only to processes which result in only a very small change in the system state, e.g. processes for which equation (9) holds. Processes resulting in large changes in the system state can always be decomposed into a series of small processes so the law as stated is perfectly general.

Asserting that temperature is always a positive quantity, then applying the second law to adiabatic processes we have that

$$\Delta S \geq 0 \ , \tag{11}$$

which is perhaps the form of the second law of thermodynamics more familiar to you. This form is in fact as general as the previous version, since any non-adiabatic process can be considered as adiabatic if one enlarges the system under consideration to include the surroundings with which any heat transfer is taking place.

When we have equality, i.e. when $T\Delta S = \Delta Q$ we talk about a "quasi-static" process. For our simple (S, V, N) systems we have for quasi-static processes:

$$\begin{aligned} \Delta W &= \Delta U - \Delta Q \\ &= \Delta U - T\Delta S \\ &= (T\Delta S - P\Delta V + \mu\Delta N) - T\Delta S \\ &= -P\Delta V + \mu\Delta N \end{aligned} \tag{12}$$

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[1] For this reason U is known as the "fundamental relation"

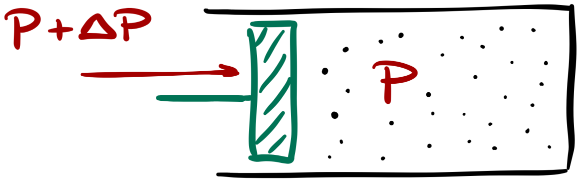
If the system is "closed" then $\Delta N = 0$ and we recover the standard formula relating work, volume, and pressure:

$$\Delta W = -P\Delta V \tag{13}$$

1.5 Quasi-static processes

The equation (13) however only applies for quasi-static processes. In physical terms a quasi-static process is one which occurs slowly enough that the system remains arbitrarily close to equilibrium at all times during the process. We return to our previous examples to clarify this distinction between quasi-static and non-quasi-static processes.

Let's look again the adiabatic compression of a volume of gas:



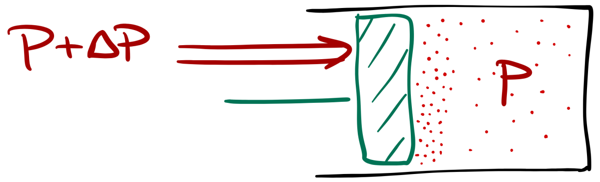
We consider two cases:

- $\Delta P \to 0$. We are then applying barely enough force to overcome the pressure P applied by the gas on the container. In this case the cylinder will move very slowly, slowly enough that the density of the gas remains uniform at all times throughout the collision. This process we therefore expect to be effectively quasi-static, and indeed when we compute the work ΔW done we obtain

  $$\Delta W = (P + \Delta P)\, A\Delta x \xrightarrow[\lim \Delta P \to 0]{} PA\Delta x = -P\Delta V$$

  thus recovering equation 13 for quasi-static work. The negative sign on the right-hand-side comes from the fact that the work done in compression is positive (so that $\Delta x > 0$) while the change in volume ΔV in compression is negative. Since the compression is also adiabatic we have from equation (11) $\Delta S = 0$

- $\Delta P \gg 0$. In this case we have a large excess force $\Delta P A$ acting to rapidly accelerate the piston. If the speed of the piston is on the order of the speed of sound of the gas, then the gas particles can not move quickly enough to redistribute themselves uniformly throughout the gas, setting up a large pressure gradient:



> In this case there is an "extra" energy from the extra work $\Delta P|\Delta V|$ that is put into the system in this form of acoustic waves created by the afore-mentioned pressure gradient. These waves eventually dissipate and when the system reaches equilibrium there will be an increase $\Delta S = \Delta P|\Delta V|/T > \Delta Q = 0$ in the system entropy that we did not have in the quasi-static case. This increased entropy will be reflected in a higher gas temperature than that observed for quasi-static ($\Delta P \to 0$) adiabatic compression for the same volume change ΔV.

The adiabatic stirring ($b\omega^2$) and joule-heating (V^2/R) of the fluid are on the other hand *necessarily* non-quasi-static. There are two ways of seeing this, one rigorous and the other hand-waving. For the rigorous explanation we note simply that for an adiabatic process we necessarily have $\Delta U = \Delta W$ and for the stirring and joule-heating processes considered we have $\Delta W > 0$. We also have for these processes $\Delta V = \Delta N = 0$. Therefore from equation (9) $\Delta U = T\Delta S$. Putting this all together we get $T\Delta S = \Delta U = \Delta W > 0$ or $T\Delta S > 0 = \Delta Q$, so that the process is non-quasi-static.

From the hand-waving persective, we think of quasi-static processes as those propelled by a very small impetus. In the case of adiabatic compression this impetus was a very small pressure difference ΔP producing a force $\Delta F = A\Delta P$ which drives the compression. For the stirring process our impetus would be the torque τ applied to the stirring rod. However, since $\Delta W \propto \omega^2$ and $\tau \propto \omega$, there is no first-order change in the system as $\tau \to 0$. It is only at finite torque that we can effectively change the system, so that the impetus driving any finite change in the system is necessarily *not* "very small". The same argument applies to joule-heating, where the impetus is the potential V which does a work $\Delta W \propto V^2$ that is quadratic in the impetus V.

1.6 Surface tension revisited

For a single-component gas-liquid interface the state variables are simply the entropy S and the surface area A.[2] The analog of equation (9) for this system is then

$$dU = TdS + \sigma dA \tag{14}$$

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[2] You may wonder why the particle number N does not appear among the state variables for a single-component gas-liquid interface. The reason, addressed in more detail later, is one of convention (the "Gibbs convention"). It is possible to consistently partition a single-component two-phase system consisting of a gas phase, liquid phase, and their interface in such a way that the number of molecules precisely "at" the interface is exactly zero.

where

$$\sigma = \partial_A U \tag{15}$$

For some process producing a change ΔA in the area of the interface we then have from equation (14) and the first law of thermodynamics

$$\Delta W = \Delta U - \Delta Q = T\Delta S + \sigma\Delta A - \Delta Q \tag{16}$$

from which via the second law of thermodynamics (equation (10)) we obtain

$$\Delta W \geq \sigma\Delta A \ , \tag{17}$$

so that σ is the coefficient relating the minimum work required to achieve a change ΔA in interfacial area. This is however precisely the same (energy-based) definition that we gave to the interfacial surface tension γ, i.e. $\sigma = \gamma$. In other words, we can alternatively (or rather more precisely) define the surface tension γ via

$$\gamma = \left(\frac{\partial U}{\partial A}\right)\bigg|_S \tag{18}$$

where the subscript S indicates that the entropy be held fixed. In other words, the surface tension is equal to the rate of change of the interfacial energy U with respect changes in interfacial area ΔA for processes occurring at constant interfacial entropy S.

1.7 Temperature

In this subsection we justify our identification of the system's temperature T with the partial derivative $\partial_S U$. We do this by demonstrating that when two systems are put into thermal contact, heat will spotaneously transfer from the system with the larger $\partial_S U$ to the system with the smaller $\partial_S U$, i.e. heat spotaneously flows from hot to cold.

Take two closed rigid systems A and B that were previously seperated and bring them into thermal contact. We assume the pair of systems to be isolated from the surrounding environment, and that no external work is done on either system. We can say then that for the total energy $U = U_A + U_B$ of the combined system we have

$$\Delta U = \Delta W + \Delta Q = 0 + 0 = 0 \tag{19}$$

We do not however rule out the possibility of energy transfer *between* the two systems, so that ΔU_A and ΔU_B are not necessarily zero. In light of the previous equation however we do require

$$\Delta U_B = -\Delta U_A \tag{20}$$

so that overall $\Delta U = 0$. We now assume only small changes in system state, so that equation (9) applies separately to both systems. Since both systems are closed and rigid we have

$$\Delta V_A = \Delta V_B = 0 \tag{21}$$

$$\Delta N_A = \Delta N_B = 0 \tag{22}$$

so that

$$\Delta U_A = T_A \Delta S_A \tag{23}$$

$$\Delta U_B = T_B \Delta S_B \tag{24}$$

where we remind the reader that T_A and T_B represent respectively $\partial_{S_A} U_A$ and $\partial_{S_B} U_B$. Given equation (20), the above relations imply

$$\Delta S_B = -\frac{T_A}{T_B} \Delta S_A \tag{25}$$

now from the second law of thermodynamics applied to adiabatic process (equation (11)) we have

$$\Delta S = \Delta S_A + \Delta S_B \geq 0 \tag{26}$$

which, combining with equation (25), yields

$$\begin{aligned} 0 \leq & \Delta S_A + \Delta S_B \\ = & \Delta S_A - \frac{T_A}{T_B} \Delta S_A \\ = & \Delta S_A \left(1 - \frac{T_A}{T_B}\right) \\ = & T_A \Delta S_A \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \\ = & \Delta U_A \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \\ = & \Delta U_A \frac{T_B - T_A}{T_A T_B} \end{aligned} \tag{27}$$

so that the energy or "heat" transfer $\Delta U_A = -\Delta U_B$ to system A from system B is positive if $\partial_{S_B} U_B = T_B > T_A = \partial_{S_A} U_A$. Therefore our identification of a system's temperature with the partial derivative $\partial_S U$ is shown to reproduce the well-known fact that heat flows spontaneously from higher temperature bodies to lower temperature bodies.

1.8 The second law and spontaneous evolution

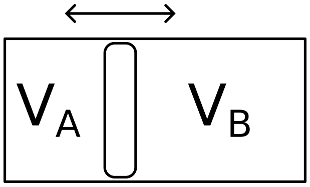
We close our crash course on thermodynamics with a short elaboration on the content of the second law of thermodynamics. Take the adiabatic version of the second law (equation (11), which states that any physically realizable process for an isolated system is subject to the constraint $\Delta S \geq 0$. We would like in fact to strengthen this statement by adding to it the principle "anything that can happen *will* happen". The second law becomes

> Any adiabatically isolated system will *spontaneously* evolve over its unconstrained state variables in order to maximize its entropy. When the entropy is maximized we say the system has reached equilibrium. (28)

The unconstrained state variables for the example of two systems A and B in thermal contact discussed in subsection 1.7 are the subsystem energies U_A and U_B, or more precisely just their difference $U_A - U_B$, since their sum $U_A + U_B = U$ being fixed by the first law of thermodynamics. We argued that in this example a transfer of energy from the hotter system to the colder system would result in an increase in the total system entropy. Our augmented second law (equation 28) asserts such a transfer *must* occur, and will continue to occur so long as it produces an increase in entropy. In other words the energy difference $U_A - U_B$ will *spontaneously* evolve until the change in entropy ΔS accompanying an energy transfer ΔU between the two subsystems is zero, which in light of equation (25) occurs when $T_A = T_B$, in line with our intuition.

How long this "equilibration" will take is incidentally a question outside of the scope of thermodynamics. Evidently this will be determined by many factors, including the thermal conductivity of the material composing the two systems as well as the conductivity of the diabatic walls putting them in thermal contact.

Similarly, we can imagine two systems placed in thermal contact via a *movable* diabatic wall:



In this case the unconstrained variables are expanded to include the volume difference $V_A - V_B$ between the two subsystems. A similar analysis to that carried out in subsection 1.7 reveals that the combined system can increase its entropy by an "transfer" of volume from the system with the lower "pressure" $P = -\partial_V U$ to the higher pressure system, with equilibrium (i.e. $\Delta S = 0$) reached once both the temperatures and pressures of the systems equalize. This justifies our identification of the partial derivative $-\partial_V U$ with the mechanical pressure P of the system.

Analogously, if exchange of particles between two subsystems is permitted, then the particle number difference $N_A - N_B$ is unconstrained. Particle transfer then spontaneously occurs from the system of higher chemical potential $\mu = \partial_N U$ to lower chemical potential until the chemical potentials equalize. The chemical potential plays a central role in several of the interfacial chemistry topics covered this semester, including micelle formation (discussed later in this lecture) as well as electrocapillarity and electric double-layer formation (lecture 3).

Concept quiz:

In section 1 we covered the process of adiabatic compression of a gas where from some initial state A the system is brought to a state B doing some work

ΔW, resulting in a reduction in the system volume by some amount ΔV and an increase in the system temperature by some amount ΔT. Now consider a process where the system beginning again in some state A is brought to a *different* state B' by *diabatic* compression where some heat $\delta Q > 0$ is *given off* by the system in the process. We might imagine for example that cylinder walls are replaced with a material that is more thermally conducting. The process requires a work $\Delta W' = \Delta W$ equal to that of the adiabatic process $A \to B$ and results in the same compression $\Delta V' = \Delta V$ but a lower final temperature $\Delta T' < \Delta T$. What experiment/measurement could you subsequently perform to determine the heat δQ given off during the diabatic compression?

Answer:

By the first law of thermodynamics, the energy difference $U_{B'} - U_A$ between states A and B is $\Delta W' + \Delta Q'$, where $\Delta Q'$ is the heat *absorbed* by the system during the diabatic compression. Similarly the energy difference $U_B - U_A$ between states A and B is ΔW. If we knew the energy difference $U_B - U_{B'}$ between states B and B' then we could determine the heat $\delta Q = -\Delta Q'$ given off by the gas during the diabatic compression by

$$\begin{aligned}
\delta Q &= -\Delta Q' \\
&= \Delta W' - (U_{B'} - U_A) \\
&= \Delta W' - (U_B - U_A) + (U_B - U_{B'}) \\
&= \Delta W' - \Delta W + (U_B - U_{B'}) \\
&= U_B - U_{B'}
\end{aligned} \tag{29}$$

since by assumption $\Delta W = \Delta W'$. Now in subsection 1.2.1 it was asserted that between any two states C and C' there is an adiabatic process bringing either state C to C' or an adiabatic process bringing state C' to C. Between states B' and B it is state B' that has the lower temperature, so it should therefore be possible to adiabatically transform the system from B' to B by, for example, the mechanical stirring or electrical joule-heating processes described in the same section.

Practically this would require fixing the piston so it was not allowed to move, thereby fixing the volume, and insulating the gas (i.e. reducing the thermal conductivity of the cylinder walls) to prevent heat exchange with its surroundings. One monitors the gas temperature during the process and stops the heating once the temperature reaches that attained during the adiabatic process $A \to B$. The system – characterized by state variables S, V, and N – is now in a state B'' where its volume V, particle number N, and temperature T of the system are equal to that of the gas in the state B. The system entropy S must therefore also be equal to that of state B (otherwise their temperatures would necessarily differ), and we conclude that $B'' = B$. By the first law of thermodynamics, the work $\Delta W''$ required to achieve this temperature rise is equal to $U_B - U_{B'}$ and thus by equation (29) equal to the heat δQ transferred from the gas to its surroundings during the diabatic compression $A \to B'$.

2 Thermodynamics of Interfaces

2.1 Helmholtz free energy and the Young-Laplace law revisited

Consider a thermodynamic system of fixed volume in thermal contact with a "heat reservoir", i.e. a system so large that its temperature T_R remains effectively constant even after finite (and possibly large) heat transfers ΔQ to the system. We presume as well that the thermal contact is sufficiently strong that the system temperature is constrained to be at all times equal to the temperature T_R of the reservoir. Let's inspect the change in the system quantity $U - TS$ during some small process:

$$\begin{aligned} \Delta\left(U - TS\right) &= \Delta U - \Delta\left(TS\right) \\ (1) &= \Delta U - \Delta T S - T\Delta S \\ (2) &= \Delta U - (0)S - T_R\Delta S \\ (3) &= -\Delta U_R - T_R\Delta S \\ (4) &= -T_R\Delta S_R - T_R\Delta S \\ &= -T_R\left(\Delta S_R + \Delta S\right) \\ (5) &= -T'\Delta S' \\ (6) &\leq 0 \ \ . \end{aligned} \tag{30}$$

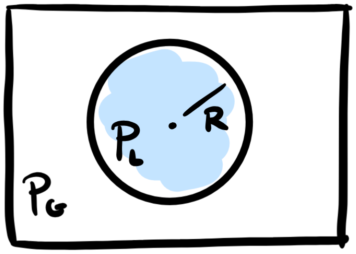
We give below an explanation for the various steps:

- (1) Product rule for derivatives
- (2) The system temperature T is at all times equal to the reservoir temperature T_R and so the change ΔT during any process is constrained to be zero.
- (3) We assume the system and reservoir are collectively isolated from their surroundings so the total change $\Delta U' = \Delta U + \Delta U_R = \Delta W' + \Delta Q' = 0 + 0$ in their collective energy is zero.
- (4) We assume the non-entropic (volume, particle number, etc.) state variables of the reservoir are fixed so that $\Delta U_R = T_R \Delta S_R$.
- (5) The system and reservoir can be considered collectively as a larger thermodynamic system with entropy $S' = S + S_R$ and temperature $T' = T_R$.
- (6) Application of the second law of thermodynamics to the combined system.

What does equation (30) tell us? It asserts that, for any process undergone by a system in contact with a heat reservoir, the change in the function $U - TS$ is necessarily negative. Contrast this with an isolated system, for which any process will necessarily ocassion an increase in system entropy S. By analogy we can say that:

> The unconstrained state variables of any system in contact with a heat reservoir will spontaneously evolve in order to *minimize* the system's "Helmholtz free energy" $F \equiv U - TS$. (31)

We now apply this principle to derive from thermodynamic principles the Young-Laplace equation (discussed at length in the previous lecture) relating the radius of curvature R of a gas-liquid interface to the pressure difference ΔP across the interface. Suppose for simplicity that we have a single-component two-phase gas-liquid system, e.g. liquid water in contact with its own vapor:



As a thermodynamic system it can be considered a composite of three subsystems – the gaseous vapor, the liquid phase, and their interface. We suppose that the composite system is closed and has a fixed total volume and that it is in contact with a heat reservoir of temperature T. We consider first the change in the Helmholtz potential F_G of the gaseous phase for some small process:

$$\begin{aligned} dF_G &= d\left(U_G - TS_G\right) \\ &= dU_G - TdS_G \\ &= \left(TdS_G - P_G dV_G + \mu_G dN_G\right) - TdS_G \\ &= -P_G dV_G + \mu_G dN_G \quad . \end{aligned} \tag{32}$$

Likewise for the liquid phase we have

$$dF_L = -P_L dV_L + \mu_L dN_L \quad , \tag{33}$$

while for the interface we have, from equation (14):

$$dF_S = \gamma dA \tag{34}$$

where A is again the interfacial surface area and γ the interfacial surface tension.

Now since the total volume of the system is fixed we have $dV_L = -dV_G \equiv dV$, and since the system is closed we have $dN_L = -dN_G \equiv dN$. If we assume a spherical shape of radius R for the interface then we have

$$dV = d\left(\frac{4}{3}\pi R^3\right) = 4\pi R^2 dR \tag{35}$$

$$dA = d\left(4\pi R^2\right) = 8\pi R dR \tag{36}$$

the minimization principle for the Helmholtz free energy (equation (31)) asserts that equilibrium is achieved when

$$dF = d\left(F_G + F_L + F_S\right) = 0 \tag{37}$$

Plugging in equations (32)–(34) we obtain:

$$dF = -\left(P_L - P_G\right) dV + \gamma dA + \left(\mu_L - \mu_G\right) dN \tag{38}$$

which after plugging in equations (35) and (36) becomes:

$$dF = \left(\gamma 8\pi R - \left(P_L - P_G\right) 4\pi R^2\right) dR + \left(\mu_L - \mu_G\right) dN \tag{39}$$

Since the interfacial radius R is an unconstrained variable, the system we be out of equilibrium unless

$$\gamma 8\pi R - \left(P_L - P_G\right) 4\pi R^2 = 0 \tag{40}$$

or

$$\Delta P = \frac{\gamma}{2R} \tag{41}$$

where $\Delta P \equiv P_L - P_G$, thereby recovering the Young-Laplace equation.

Incidentally, while the Young-Laplace equation places an equilibrium constraint on the pressure *difference* ΔP between the gaseous and liquid phases, it imposes no constraint on the vapor pressure P_G of the gas phase. However, returning back to equation (39) we find that the lack of constraints on particle transfer between the liquid and gaseous phases imposes the additional equilibrium condition:

$$\mu_L = \mu_G \quad . \tag{42}$$

This condition, in combination with the Laplace equation, turns out to be equivalent to the Kelvin equation (also discussed at length in the previous lecture) relating vapor pressure above an interface to interface curvature.

2.2 Surface energy and surface entropy

In this subsection we derive formulas relating the central thermodynamical interfacial properties of surface energy and surface entropy to measurable quantities. We start by stating without proof a mathematical theorem called "Euler's theorem" that asserts that any extensive function $f(x, y, \ldots, z)$, i.e. any function for which for any number λ it holds that $f(\lambda x, \lambda y, \ldots, \lambda z) = \lambda f(x, y, \ldots, z)$, can be written in the following form

$$f = x\partial_x f + y\partial_y f + \ldots + z\partial_z f \tag{43}$$

applying Euler's theorem to the surface energy U we obtain via equation (14)

$$U = TS + \gamma A \tag{44}$$

The surface Helmholtz free energy F can then be written

$$F = U - TS = (TS + \gamma A) - TS = \gamma A \tag{45}$$

so that for the surface Helmholtz free energy *density* $f \equiv F/A$ we have simply

$$f = \gamma \tag{46}$$

In addition, we have

$$\begin{aligned} dF &= d\,(U - TS) \\ &= dU - d\,(TS) \\ &= dU - TdS - SdT \\ &= (TdS + \gamma dA) - TdS - SdT \\ &= -SdT + \gamma dA \end{aligned} \tag{47}$$

so that

$$S = -\partial_T F \tag{48}$$

$$\gamma = \partial_A F \tag{49}$$

This implies the following relation for the surface entropy density $s \equiv S/A$:

$$\begin{aligned} s &= \frac{S}{A} \\ &= -\frac{\partial_T F}{A} \\ (!)^{3} &= -\partial_T \left(\frac{F}{A}\right) \\ &= -\partial_T f \\ &= -\partial_T \gamma \end{aligned} \tag{50}$$

We therefore find that surface entropy can be determined experimentally by measuring the temperature dependence of the surface tension γ.

The surface energy density $u \equiv U/A$ also permits a convenient formulation in terms of the surface tension and temperature:

$$\begin{aligned} u &= \frac{U}{A} \\ &= \frac{F + TS}{A} \\ &= \frac{F}{A} + T\frac{S}{A} \\ &= f + Ts \\ &= \gamma - T\partial_T \gamma \end{aligned} \tag{51}$$

---

[3] In the step marked (!) we were able to bring the A inside the partial derivative because there is an implicit understanding that the temperature derivative in equation (48) is performed at constant interfacial area A.

Below we find a table of surface tension, and surface entropy and energy densities of various pure substances measured at room temperature[4]:

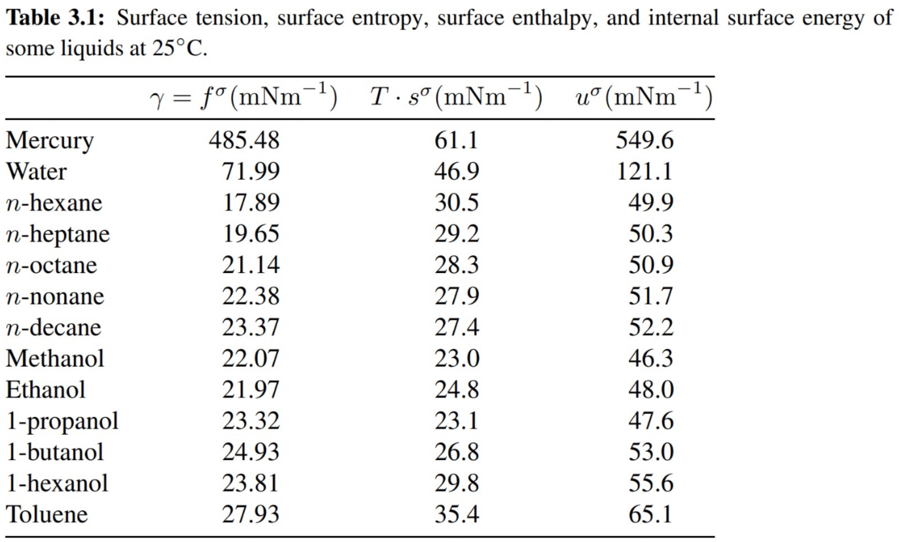


Table 3.1: Surface tension, surface entropy, surface enthalpy, and internal surface energy of some liquids at 25°C.

	$\gamma = f^\sigma(\mathrm{mNm}^{-1})$	$T \cdot s^\sigma(\mathrm{mNm}^{-1})$	$u^\sigma(\mathrm{mNm}^{-1})$
Mercury	485.48	61.1	549.6
Water	71.99	46.9	121.1
n-hexane	17.89	30.5	49.9
n-heptane	19.65	29.2	50.3
n-octane	21.14	28.3	50.9
n-nonane	22.38	27.9	51.7
n-decane	23.37	27.4	52.2
Methanol	22.07	23.0	46.3
Ethanol	21.97	24.8	48.0
1-propanol	23.32	23.1	47.6
1-butanol	24.93	26.8	53.0
1-hexanol	23.81	29.8	55.6
Toluene	27.93	35.4	65.1

2.2.1 Gibbs dividing surface and surface excesses

In this section we address the question: where precisely *is* the interface between two phases? This is of course a matter of definition, and we adhere in this course to the definition proposed by American scientist J.W. Gibbs (1839-1903). Gibbs defined the interface as an infinitesimally thin surface S (not to be confused with entropy) dividing the two phases A and B in such a way that the solvent density is constant everywhere on S and

$$N_1^A + N_1^B = N_1 \tag{52}$$

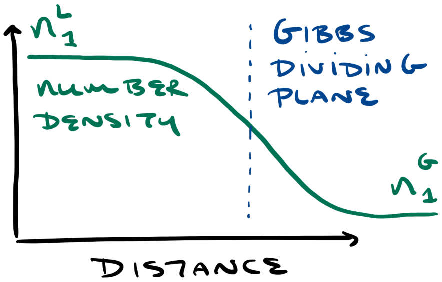
where:

- N_1 is total quantity of solvent shared among the two phases, and
- $N_1^A \equiv n_1^A V^A$ is the mole number of solvent in phase A, where:
    - V^A is the volume of the region on the phase A side of the dividing surface S, and
    - n_1^A is the molar density of solvent measured at a point inside of the bulk of phase A far from the interface.

---

[4] From chapter 3 of *Physics and Chemistry of Interfaces* (2013 edition).

The quantities N_1^B, V^B and n_1^B are defined similarly. The following diagram showing a very zoomed-in view of a gas-liquid (i.e. $A \sim G$, $B \sim L$) interface may be helpful:



The Gibbs dividing plane S is positioned so that equation (52) holds. Moving away from the dividing plane, the molar density of the solvent in the liquid phase asymptotically approaches its bulk value n_1^L and, moving in the other direction, the molar density of the solvent in the gaseous phase asymptotically approaches its bulk value $n_1^G < n_1^L$. If the Gibbs plane is moved to the right or left then we will have (in light of the definitions of N_1^G and N_1^L) $N_1^G + N_1^L > N_1$ or $N_1^G + N_1^L < N_1$, respectively.

Now if our system contains $m - 1$ other molecular species of total mole numbers $N_2, N_3, \ldots, N_m$ in addition to the solvent species (of mole number N_1), then for these species $i = 2, \ldots, m$ we will have in general

$$N_i^A + N_i^B \neq N_i, \ , \tag{53}$$

i.e. for the non-solvent species equation (52) will in general not hold. The difference $N_i^S \equiv N_i - \left(N_i^A + N_i^B\right)$, normalized to the interfacial area A is termed the "surface excess" Γ_i, i.e.

$$\Gamma_i = N_i^S / A \tag{54}$$

The surface excess gives, in the context of the Gibbs convention, a measure of the concentration of the molecules at the interface.

2.3 Gibbs adsorption isotherm

In this section we derive an important formula relating interfacial surface tension γ and the surface excess $\Gamma_2 \equiv \Gamma$ of a single solute species dissolved in solvent. For such a system we must add to the list of the surface state variables S and A the interfacial mole number $N_2^S \equiv N^S$. The analog of equation (14) becomes

$$dU = TdS + \gamma dA + \mu^S dN^S \tag{55}$$

where we now have $\mu^S \equiv \partial_{N^S} U$. Applying Euler's theorem we have

$$U = TS + \gamma A + \mu^S N^S \tag{56}$$

Subtracting the former equation from the differential of the latter we obtain

$$SdT + Ad\gamma + N^S d\mu^S = 0 \ , \tag{57}$$

and restricting attention to isothermal ($dT = 0$) processes we get

$$Ad\gamma = -N^S d\mu^S \tag{58}$$

which after rearrangement becomes:

$$d\gamma = -\Gamma d\mu^S \tag{59}$$

The above relation demonstrates that the surface excess of the solute can be estimated by determining the dependence of the surface tension on the surface chemical potential μ^S of the solute species. To do this we exploit the fact that there is no constraint to the transfer of solute molecules between the interface and the liquid solution. In equilibrium therefore the chemical potentials are equal: $\mu^S = \mu^L$. The chemical potential of the solute in solution at fixed temperature T obeys the relation

$$\mu^L = \mu_o^L + RT \ln \frac{a}{a_o} \tag{60}$$

where a is the activity of the solute. At low solute concentrations the a becomes approximately equal to the solute concentration c, so that in this limit we have:

$$\mu^L = \mu_o^L + RT \ln \frac{c}{c_o} \tag{61}$$

where μ_o^L is the chemical potential of the solute at an arbitrary reference concentration c_o, often taken to be 1 molar. So the chemical potential μ^S can be varied by varying μ^L via the solute concentration c.

Taking the differential of the above equation yields

$$d\mu^L = \frac{RT}{c} dc \tag{62}$$

Since $\mu^S = \mu^L$ of course implies $d\mu^S = d\mu^L$, then, plugging the above equation back into equation (59), we obtain finally the "Gibbs adsorption isotherm":

$$\Gamma = -\frac{c}{RT} \partial_c \gamma = -\frac{1}{RT} \partial_{\ln c} \gamma \tag{63}$$

3 Micelles

3.1 Gibbs equation and lysophospholipid surface excess

As an application of the Gibbs isotherm, we take a look at the following plot showing the measured interfacial surface tension versus concentration $\bar{c}$ different lysophospholipids[5] in aqueous solution:

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[5] Lysophospholipids are a product of the enzyme-catalysed decomposition of phospholipids.

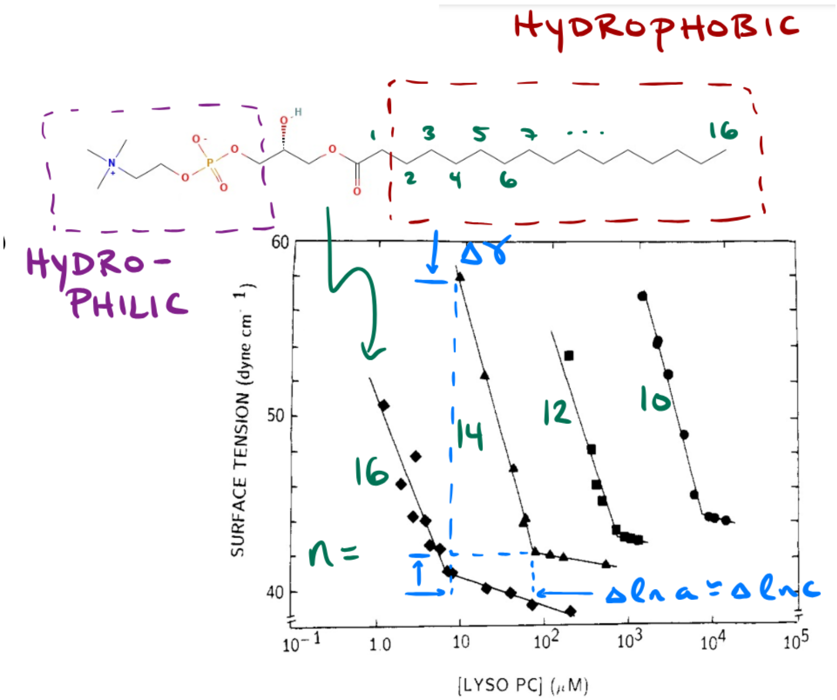

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Figure 1: Experimental measurements of interfacial surface tension as a function of lysophospholipid concentration in aqueous solution. The structure of a lysophospholipid molecules with alkyl chain length $n = 16$ is shown for reference.

The different markers indicate the number of carbon atoms composing the lysophospholipid alkyl tail. From the diagram one can see that lysophospholipids have a surfactant-like hydrophilic-hydrophobic head-tail structure, so it is not surprising that the surface tension should exhibit a strong decrease with increasing lysophospholipid concentration.

Ignoring for the moment the discontinuity in the slope at higher concentrations, we can try to estimate the lysophospholipid surface excess using the Gibbs adsorption isotherm. Let's take the $n = 14$ data, we estimate a change

$$\Delta\gamma \approx 42\,\mathrm{mN\,m^{-1}} - 58\,\mathrm{mN\,m^{-1}} = -16\,\mathrm{mN\,m^{-1}}$$

in the measured surface tension for a change

$$\Delta \ln \bar{c} \approx \ln 10^{1.8}\mu\mathrm{M} - \ln 10^{1.0}\mu\mathrm{M} = \ln 10^{0.8} = 0.8 \ln 10 \approx 1.8$$

in the log solute concentration. Taking the room temperature value of $RT \approx 2.5\,\mathrm{kJ\,mol^{-1}}$, we can apply the Gibbs adsorption isotherm (equation (59)), obtaining

$$\Gamma \approx -\frac{1}{2.5\,\mathrm{kJ\,mol^{-1}}} \times \frac{-16\,\mathrm{mN\,m^{-1}}}{1.8} \approx 3.6 \times 10^{-6}\,\mathrm{mol\,m^{-2}}$$

or

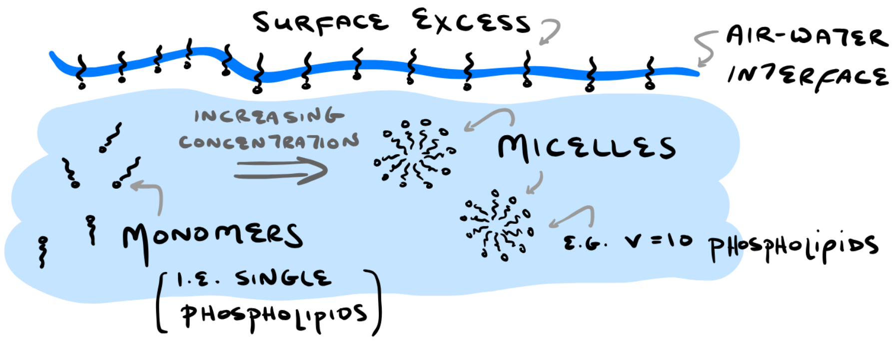
$$\Gamma \approx \left(\frac{50\,\text{Å}^2}{\text{molecule}}\right)^{-1}$$

Considering the somewhat bulky structure of the hydrophilic head, this concentration corresponds to a more-or-less "shoulder-to-shoulder" packing of surfactant molecules at the interface.

3.2 Micellization

How do we make sense of the observed discontinuity in the slope of the γ vs. $\ln \bar{c}$ data (figure 1) presented in the previous subsection? A naive application of the Gibbs adsorption isotherm might lead one to conclude that at lower surfactant concentrations the surfactant surface Γ excess is essentially constant (as reflected in the roughly linear depedence of γ on $\ln \bar{c}$ at low concentrations), but that beyond a certain concentration there is a sudden drastic reduction in the surface excess, reflected in the abrupt flattening of the γ vs. $\ln \bar{c}$ curves at higher concentrations.

In fact the breaks in the curves of figure 1 do not reflect a change in the surface excess but rather reflect a change in the structure of the solute in the bulk of the solution. The slope discontinuity marks the onset of stable *micelle formation* in the bulk:



Micelles are formed by the coalescence of a large number $\nu \gg 1$ of individual surfactant molecules (or *monomers*, for short). At low bulk surfactant concentration $\bar{c}$, micelle formation is unstable in that, in the rare occurence that a micelle might form, it is quickly broken back up into monomers by thermal agitation. It is only at sufficiently high surfactant concentrations where micelle formation, which requires the many monomers to "find one another", is sufficiently frequent to compensate their short lifetime and produce an appreciable bulk concentration relative to that of the monomer concentration. In fact one often observes with increasing surfactant concentration a transition of the appearance of the fluid from clear to cloudy/milky. This transition coincides with the discontinuity in the γ vs. $\ln c$ slope, and is explained by the size of the micelles, whose dimensions are comparable to that of the wavelength of visible light, making them much more efficient in scattering light.

In what follows we attempt a more rigorous analysis of the qualitative description of micelle formation given in the previous paragraph. We start by formalizing micelle formation as the following chemical reaction

$$\nu m \longleftrightarrow M \tag{64}$$

i.e. a transformation between ν monomers m and a single micelle M. From the law of mass action[6] we have the following equation relating the monomer concentration c and the micelle concentration c':

$$\frac{c^\nu}{c'} = \exp\left(\frac{\Delta G^o}{RT}\right) \tag{65}$$

where ΔG^o is the change in the solution's "Gibbs free energy" $G \equiv U - TS + PV$ in forming one mole of micelles when the monomer and micelle concentrations are both 1 molar.

From the mass action equation we can immediately make a couple observations. First, at very low monomer concentrations there will be essentailly no

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[6] The mass action equation can be derived from the second law of thermodynamics applied to dilute solutions. See, e.g., chapter 7 §27 of Enrico Fermi's text *Thermodynamics* (ISBN-13 978-0-486-60361-2).

micelles:

$$\frac{c'}{c} = \frac{\exp\left(-\frac{\Delta G^o}{RT}\right) c^\nu}{c} = \exp\left(-\frac{\Delta G^o}{RT}\right) c^{\nu-1} \xrightarrow[c\to 0]{} 0 \tag{66}$$

since we assume $\nu \gg 1$. By similar reasoning, at high concentrations the micelles will dominate over the monomers. In fact, one can show that in the limit $\bar{c} = c + \nu c' \to \infty$ where the total surfactant concentration $\bar{c}$ becomes very large, the effect of doubling $\bar{c}$ is to only increase the monomer concentration by a factor $1/2^{\nu+1}$, i.e. $\Delta \ln c / \Delta \ln \bar{c} \approx 1/\nu$.

We can now explain the flattening of the γ vs. $\ln \bar{c}$ curve. What is being represented in figure 1 is a measurement of the surface tension as the total surfactant concentation $\bar{c} = c + \nu c'$ is being increased. However, since we assume that it is the monomer species that is populating the interface, for application of the Gibbs isotherm we are only interested in the monomer concentration c. Now at low concentrations this is no issue since in this limit we have $\bar{c} \approx c$, and so

$$\left(\frac{\Delta\gamma}{\Delta \ln \bar{c}}\right)\Bigg|_{\bar{c}\to 0} \approx \frac{\Delta\gamma}{\Delta \ln c} = -RT\Gamma \tag{67}$$

At high concentrations however we have $\frac{\Delta \ln c}{\Delta \ln \bar{c}} \approx \nu^{-1}$ so that, if we assume the surface excess Γ is the same at high monomer concentrations as it is at low monomer concentrations, on applying the Gibbs adsorption isotherm we have

$$\left(\frac{\Delta\gamma}{\Delta \ln \bar{c}}\right)\Bigg|_{\bar{c}\to\infty} \approx \frac{1}{\nu}\frac{\Delta\gamma}{\Delta \ln c} = -RT\Gamma/\nu \approx \frac{1}{\nu}\left(\frac{\Delta\gamma}{\Delta \ln \bar{c}}\right)\Bigg|_{\bar{c}\to 0} \tag{68}$$

or in other words we expect a factor $\nu \gg 1$ reduction in the slope of the experimental γ vs. $\ln \bar{c}$ data in going from low concentrations to high concentrations, as is observed.

3.3 Critical micelle concentration

Now we still have two lingering questions to answer:

- At what concentration $\bar{c}_{CMC}$, called the *critical micelle concentration* or CMC, do we expect to observe the onset of micellization?
- Why is the change in the γ vs. $\ln \bar{c}$ slope *discontinuous*, i.e. we is the transition from a monomer-dominated solution to a micelle-dominated solution so abrubt?

We attack the first question first. Let's define the onset of micellization to be the point at which a single surfactant molecule added into solution is just as likely to become part of a micelle as it is to exist as a monomer. That is, we want to know at what surfactant concentration $\bar{c}$ does the "micelle occupation probability" (let's call it x) becomes 50%, i.e. when does an increase in the total surfacant concentration by some small amount ϵ, i.e. $\bar{c} \to \bar{c} + \epsilon$ result in the following change in the monomer and micelle concentrations c and c':

$$\begin{aligned} c &\to c + \epsilon(1-x) \\ c' &\to c' + \frac{1}{\nu}\epsilon x \end{aligned} \tag{69}$$

where the micelle occupation probability x is equal to $1/2$. From the mass action equation we have

$$\frac{(c + \epsilon(1-x))^{\nu}}{c' + \frac{1}{\nu}\epsilon x} = \exp \Delta G^o/RT = \frac{c^{\nu}}{c'} \tag{70}$$

We leave it as an exercise to the reader to show that, in the limit $\epsilon \to 0$, this equation is satisfied when

$$x = \left(1 + \frac{1}{\nu^2}\frac{c}{c'}\right)^{-1} \tag{71}$$

so that when $x = 1/2$ we have

$$c = \nu^2 c' \tag{72}$$

In other words the onset of micellization occurs when one out of every ν surfactant molecules is part of a micelle[7]. At these concentrations we have

$$\exp\left(\Delta G^o/RT\right) = \frac{c^{\nu}}{c'} = \frac{c^{\nu}}{c/\nu^2} = \nu^2 c^{\nu-1} \approx \nu^2 c^{\nu} \tag{73}$$

We have for the critical micelle concentration

$$\ln \bar{c}_{CMC} \approx \ln c = -2\ln\nu + \frac{1}{\nu}\Delta G^o/RT \approx \frac{1}{\nu}\Delta G^o/RT \tag{74}$$

where in the first step is justified by noting that since $c' = c/\nu^2$ at the onset of micellization and $\nu \gg 1$ we therefore have $\bar{c}_{CMC} \approx c$, and in the final step we assume $\Delta G^o \gg \nu RT$. The above equation demonstrates that the information about the energetics of micellization, namely the reaction energy ΔG^o, which occurs in the bulk of a solution, can be determined via measurements of the properties associated to the interface between the solution and the gas phase, namely the surface tension γ. See section 11.2.3 of *PCI* (2013 edition) for an interesting discussion of solvent-surfactant interactions and their influence on the energetic and entropic effects affecting micellization.

3.4 Micellization phase transition

It remains thus to explain the abruptness of the onset of micellization, i.e. the discontinuity of the measured γ vs. $\bar{c}$ slope. Now at low concentrations, any surfactant molecule added to the solution will exist in solution as a monomer,

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[7] We assume throughout that the interfacial surface area A is small enough that only a negligible quantity of surfactant molecules populate the interface.

and at high concentrations any molecule added will become part of one of the many micelles. At the CMC, an added molecule is just as likely to exist as a monomer or become part of a micelle. Apparently this "micelle occupation probability" x, defined in equation (69), transitions abruptly from 0% to 100% as the surfactant concentration goes from below the CMC to above the CMC.

Let's look at how x changes with a small increase $c \to (1+\epsilon)\,c$ in the monomer near the CMC. Since $c' = c/\nu^2$ and $x = 1/2$ at the CMC, then when $c \to (1+\epsilon)\,c$ we have

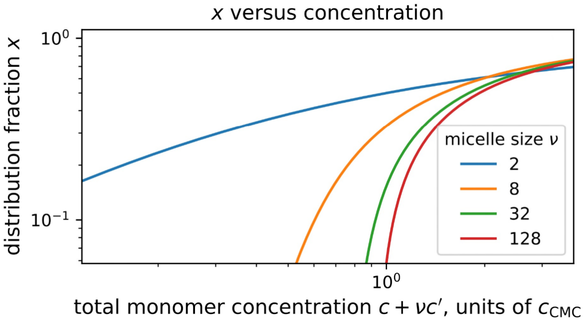
$$c' \to c' + \Delta c' = c/\nu^2 + \Delta c' = c/\nu^2 + \Delta c/\nu = c/\nu^2 + \epsilon c/\nu \tag{75}$$

Plugging these values into equation (71) and solving for $x = 1/2 + \Delta x$ in the limit $\epsilon \to 0$ we find (after some algebra):

$$\frac{\Delta x}{\Delta \epsilon} = \frac{1}{4}\,(\nu - 1) \approx \nu/4 \tag{76}$$

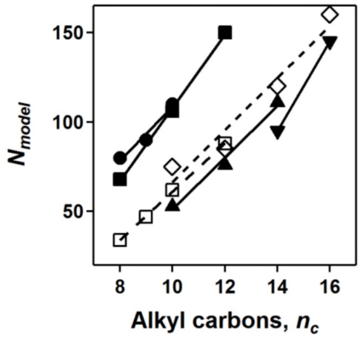
Which is precisely what we sought to demonstrate, i.e. that the micelle occupation probability x changes abruptly with changes in surfactant concentration to the extent that the micelles are large, i.e. to the extent that $\nu \gg 1$.

Using numerical techniques one can compute x for an arbitrary concentration. In the following plot we do so for micelles of varying size ν:



The simulation results are consistent with the hypothesis that the abruptness of the onset of micellization is a result of the large micelle size. If one assumes a small micelle (e.g. $\nu = 2$), one gets a very gradual transition in x, while for large micelles (e.g. $\nu = 128$) x transitions from $x < 5\%$ to $x \approx 50\%$ from just a factor two increase in the total surfactant concentration.

Just how large are micelles in reality? Below we show the estimated monomer size $\nu \sim N_{model}$ vs. alkyl chain length for different surfactant molecules:



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The monomer sizes are estimated from x-ray scattering measurements (see article for details). Is the roughly linear increase in micelle size ν with alkyl chain length in keeping with your intuitive expectations?