Assignment 4

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November 9, 2010

1 Harden Problem 1

A Langmuir trough is a device to study molecules confined to fluid-vapor interfaces, by varying the surface pressure Π of the interface and measuring its area A. Consider a collection of N surfactant molecules of mass m at the air-water interface in a Langmuir trough. Assuming that these surfactants are neither volatile nor are soluble in the water subphase, we can treat them are being confined to the air-water interface for all values of the applied surface pressure Π.

1.1 Problem 1.a

Assuming that the surfactant molecules act as a classical two-dimensional (2D) ideal gas of indistinguishable particles, calculate the Gibbs partition function $\mathcal{Z} = (T, \Pi, N)$:

$$
\begin{aligned}
\mathcal{Z} &= \sum_{\mu_s} \exp\left(\beta \vec{J} \cdot \vec{x} - \beta \mathcal{H}\right) \\
&= \int \exp\left(-\beta \Pi A - \beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right) \\
&= \int_0^\infty \exp\left(-\beta \Pi A\right) dA \underbrace{\frac{1}{N!} \int \frac{1}{h^{2N}} \prod_{i=1}^{N} d^2\vec{q}_i d^2\vec{p}_i \exp\left(-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right)}_{=(A/\lambda^2)^N}.
\end{aligned}
$$

Notice, we just swiped the normal solution to the gaseous phase space integral of

$$\lambda = h\left(\frac{1}{2\pi m k_B T}\right)^{1/2} = h\left(\frac{\beta}{2\pi m}\right)^{1/2} \tag{1}$$

but since it's in 2D rather than 3D we made it to the power 2 rather than 3 and $V \to A$. So then

$$\begin{aligned}
\mathcal{Z} &= \int_0^\infty \exp\left(-\beta \Pi A\right) dA \frac{1}{N!}\left(\frac{A}{\lambda^2}\right)^N \\
&= \frac{\lambda^{-2N}}{N!}\int_0^\infty A^N \exp\left(-\beta \Pi A\right) dA \\
&= \frac{\lambda^{-2N}}{N!}\left(-\frac{1}{\beta}\right)^N \frac{\partial^N}{\partial \Pi^N}\int_0^\infty \exp\left(-\beta \Pi A\right) dA \\
&= \frac{\lambda^{-2N}}{N!}\left(-\frac{1}{\beta}\right)^N \frac{\partial^N}{\partial \Pi^N}\left(\frac{1}{\beta \Pi}\right) \\
&= \frac{\lambda^{-2N}}{N!}\left(-\frac{1}{\beta}\right)^N \left(\frac{1}{\beta}(-1)^N N! \Pi^{-(N+1)}\right) \\
&= \lambda^{-2N}\left(\frac{1}{\beta \Pi}\right)^{N+1}
\end{aligned}$$

$$\boxed{\mathcal{Z} = \left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^N \left(\frac{k_\mathrm{B} T}{\Pi}\right)^{N+1}}. \tag{2}$$

1.2 Problem 1.b

Use $\mathcal{Z}$ to calculate the isothermal compressibility of the 2D surfactant system.

We know the average area is given by

$$A = -k_\mathrm{B} T \frac{\partial}{\partial \Pi}\ln \mathcal{Z} \tag{3}$$

$$\begin{aligned}
&= -k_\mathrm{B} T \frac{\partial}{\partial \Pi}\ln\left[\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^N \left(\frac{k_\mathrm{B} T}{\Pi}\right)^{N+1}\right] \\
&= -k_\mathrm{B} T \frac{\partial}{\partial \Pi}\left[N \ln\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right) + (N+1)\ln\left(\frac{k_\mathrm{B} T}{\Pi}\right)\right] \\
&= -k_\mathrm{B} T \frac{\partial}{\partial \Pi}\left[0 + (N+1)\ln\left(\frac{k_\mathrm{B} T}{\Pi}\right)\right] \\
&= -k_\mathrm{B} T\left(N+1\right)\frac{\partial}{\partial \Pi}\ln\left(\frac{k_\mathrm{B} T}{\Pi}\right) \\
&= k_\mathrm{B} T\left(N+1\right)\frac{\partial}{\partial \Pi}\ln\left(\Pi\right) \\
&= \frac{k_\mathrm{B} T\left(N+1\right)}{\Pi}.
\end{aligned} \tag{4}$$

So then the isothermal compressibility is just

$$\begin{aligned}\kappa_T &= -\frac{1}{A}\left.\frac{\partial A}{\partial \Pi}\right|_T \\ &= -\frac{1}{A}\left[\frac{\partial}{\partial \Pi}\frac{k_\mathrm{B}T\,(N+1)}{\Pi}\right]_T \\ &= \frac{1}{A}\frac{k_\mathrm{B}T\,(N+1)}{\Pi^2} \\ &= \frac{1}{A}\frac{A}{\Pi}\end{aligned} \tag{5}$$

$$\boxed{\kappa_T = \Pi^{-1}}. \tag{6}$$

1.3 Problem 1.c

Use $\mathcal{Z}$ to calculate the constant Π heat capacity of the 2D surfactant system.

The heat capacity is given as the derivative of the enthalpy

$$C_\Pi = \left.\frac{\partial H}{\partial T}\right|_\Pi \tag{7}$$

and we know the enthalpy from the Gibbs partition function to be

$$\begin{aligned}H &= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta}\ln\left[\left(\frac{2\pi m}{\beta h^2}\right)^N\left(\frac{k_\mathrm{B}T}{\beta\Pi}\right)^{N+1}\right] \\ &= -\frac{\partial}{\partial \beta}\left[\ln\left(\frac{2\pi m}{h^2}\right)^N - N\ln\beta + \ln\left(\frac{k_\mathrm{B}T}{\Pi}\right)^{N+1} - (N+1)\ln\beta\right] \\ &= 0 + \frac{N}{\beta} + 0 + \frac{N+1}{\beta} \\ &= \frac{2N+1}{\beta} \\ &\approx \frac{2N}{\beta}\end{aligned} \tag{8, 9}$$

in the $N \gg 1$ limit. Therefore, the heat capacity is

$$\begin{aligned}C_\Pi &= \left.\frac{\partial H}{\partial T}\right|_\Pi \\ &= \frac{\partial}{\partial T}2Nk_\mathrm{B}T\end{aligned}$$

$$\boxed{C_\Pi = 2Nk_\mathrm{B}}. \tag{10}$$

2 Harden Problem 2

Consider the epitaxial growth of a thin film by adsorption of atoms size a from the gas phase onto a solid substrate made up of a lattice of the same atoms. The adsorption takes place at fixed chemical potential, as set by conditions in the gas phase. Suppose that substrate has $N \gg 1$ independent sites per unit area, and that atoms from the gas phase can pile up on each site in a sequential adsorption process in which subsequent adsorption events lower the energy of the adsorbing atom by $-\epsilon$, resulting in a forest of pilars.

2.1 Problem 2.a

Calculate the grand canonical partition function $\mathcal{Q}$ in terms of T, ϵ, μ, N.

We let $\mathcal{Q}_1$ be the Gibbs partition function for a single site such that for the N sites the total partition function is $\mathcal{Q} = \mathcal{Q}_1^N$ since the sites are independent. Let the site of interest have n particles residing at it such that the grand partition function for that site is

$$\begin{aligned}
\mathcal{Q}_1 &= \sum_{n=0}^{\infty} \exp\left(\beta n\mu - \beta\mathcal{H}\right) \qquad (11)\\
&= \sum_{n=0}^{\infty} \exp\left(\beta n\mu - \beta\sum_{i=0}^{n}(-\epsilon)\right)\\
&= \sum_{n=0}^{\infty} \exp\left(\beta n\mu + \beta n\epsilon\right)\\
&= \sum_{n=0}^{\infty} \left[\exp\beta\left(\mu+\epsilon\right)\right]^n \qquad (12)
\end{aligned}$$

We summed to infinity because any given site can assumulate an arbitrary number of atoms from the gas. Now we assume $\mu < -\epsilon$ (which is sort of implied since we handled it as a chemical potential and not an explicit energy term) then

$$x = \exp\beta\left(\mu+\epsilon\right) < 1$$

and we remember the convergent sum

$$\begin{aligned}
\mathcal{Q}_1 &= \sum_{n=0}^{\infty} x^n\\
&= \frac{1}{1-x}\\
&= \frac{1}{1-\exp\beta\left(\mu+\epsilon\right)}
\end{aligned}$$

$$\boxed{\mathcal{Q} = \mathcal{Q}_1^N = \left[1-\exp\beta\left(\mu+\epsilon\right)\right]^{-N}}. \qquad (13)$$

2.2 Problem 2.b

Use $\mathcal{Q}$ to calculate the average film thickness $< h >$ as a function of T, ϵ, μ.

The average height is the average number of adsorbed particles times the height of each particle

$$< h > = a < n > .$$

Notice we have to be a touch careful here: We can find the cumulant $< n >_c$ from the grand potential $\mathcal{G}_1 = -k_{\mathrm{B}}T \ln \mathcal{Q}_1$ since we want the average number at a site. We know $< n >_c = < n >$ and that n goes along with μ therefore:

$$\begin{aligned}
< h > = a < n > = a < n >_c = -a \left.\frac{\partial \mathcal{G}_1}{\partial \mu}\right|_\beta \\
&= a k_{\mathrm{B}} T \frac{\partial \ln \mathcal{Q}_1}{\partial \mu} \\
&= a k_{\mathrm{B}} T \frac{\partial}{\partial \mu} \ln \left[1 - \exp \beta \left(\mu + \epsilon\right)\right]^{-1} \\
&= -a k_{\mathrm{B}} T \frac{\partial}{\partial \mu} \ln \left[1 - \exp \beta \left(\mu + \epsilon\right)\right] \\
&= -a k_{\mathrm{B}} T \frac{1}{1 - \exp \beta \left(\mu + \epsilon\right)} \frac{\partial}{\partial \mu} \left[1 - \exp \beta \left(\mu + \epsilon\right)\right] \\
&= a k_{\mathrm{B}} T \frac{\beta \exp \beta \left(\mu + \epsilon\right)}{1 - \exp \beta \left(\mu + \epsilon\right)}
\end{aligned}$$

$$\boxed{< h > = \frac{a}{\exp\left[-\beta\left(\mu + \epsilon\right)\right] - 1}} \tag{14}$$

2.3 Problem 2.c

Calculate the root mean square deviation in height, $\Delta h = \sqrt{< h^2 > - < h >^2}$ as a function of T, ϵ, μ and use the result to discuss roughness of the film.

We can find $< n^2 >_c$ in exactly the same way as we found $< n >_c$ above but one order higher:

$$\begin{aligned}
< n^2 >_c = \left(-k_{\mathrm{B}} T\right)^2 \left.\frac{\partial^2 \ln \mathcal{Q}_1}{\partial \mu^2}\right|_\beta \\
&= \left(k_{\mathrm{B}} T\right)^2 \frac{\partial^2}{\partial \mu^2} \ln \left[1 - \exp \beta \left(\mu + \epsilon\right)\right]^{-1}
\end{aligned}$$

and we already know the first derivative from the last part of this question:

$$\begin{aligned}
< n^2 >_c = -k_{\mathrm{B}} T \frac{\partial}{\partial \mu} < n >_c \\
&= -k_{\mathrm{B}} T \frac{\partial}{\partial \mu} \left(\frac{1}{\exp\left[-\beta\left(\mu + \epsilon\right)\right] - 1}\right) \\
&= -k_{\mathrm{B}} T \left(\frac{1}{\exp\left[-\beta\left(\mu + \epsilon\right)\right] - 1}\right)^2 \left(-\beta \exp\left[-\beta\left(\mu + \epsilon\right)\right]\right) \\
&= \frac{\exp\left[-\beta\left(\mu + \epsilon\right)\right]}{\left(\exp\left[-\beta\left(\mu + \epsilon\right)\right] - 1\right)^2}
\end{aligned}$$

and since

$$< n^2 >_c = < n^2 > - < n >^2$$

we know

$$\begin{aligned}\Delta h &= \sqrt{< h^2 > - < h >^2} = \sqrt{a^2 < n^2 > - a^2 < n >^2} \\ &= a\sqrt{< n^2 > - < n >^2} = a\sqrt{< n^2 >_c}\end{aligned}$$

$$\boxed{\Delta h = a\frac{\exp\left[-\beta\left(\mu+\epsilon\right)/2\right]}{\exp\left[-\beta\left(\mu+\epsilon\right)\right]-1}} \tag{15}$$