Lipid-Protein Interactions Alter Line Tensions and Domain Size Distributions in Lung Surfactant Monolayers

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Supporting Material
Figure S1: Schematic of a two-dimensional liquid plane containing two phases separated by a line EE′

Derivation of Gibbs equation at a line interface:

Consider a 2-d liquid plane (analogous to a 3-d liquid column) with I number of components in two phases l₁ (α) and l₂ (β) separated from each other by a line. The (surface) composition of the i\textsuperscript{th} component in the l₁ and l₂ phases are c\textsubscript{io} and c\textsubscript{id}. If n\textsubscript{i,o} and n\textsubscript{i,d} stand for the total moles of the i\textsuperscript{th} component in the two phases, then we can define a line excess (analogous to Gibbs surface excess) where the line excess n\textsubscript{i,x} of the i\textsuperscript{th} component should be

\[ n_{i,x} = n_{i,t} - n_{i,o} - n_{i,d} \]  

where n\textsubscript{i,t} is the total moles of the i\textsuperscript{th} component for a given composition of the 2-d system.

The line excess internal energy:  

\[ E_{x} = E_{t} - E_{o} - E_{d} \]  

where E\textsubscript{o} is the internal energy in the a phase, E\textsubscript{d} is the internal energy in the b phase, and E\textsubscript{t} is the total internal energy.

Similarly, the entropy may be given by

\[ S_{x} = S_{t} - S_{o} - S_{d} \]  

For an open system:

\[ dE_{t} = TdS_{t} - dW + \sum_{i}^{I} \mu_{i} dn_{i} \]  

where \[ dW = \pi_{So} dA_{o} + \pi_{Sd} dA_{d} - \lambda dl \]

A\textsubscript{o} and A\textsubscript{d} stand for the actual area in the two phases, π\textsubscript{o} and π\textsubscript{d} are the surface pressures in the two phases, \λ is the interfacial (line) tension, and \µ\textsubscript{i} is the chemical potential of the i\textsuperscript{th} component. Substituting for dW (Eq. 5) in Eq. 4, we get an expression for the change in the total internal energy in terms of the surface pressures:

\[ dE_{t} = TdS_{t} - \pi_{So} dA_{o} - \pi_{Sd} dA_{d} + \lambda dl + \sum_{i}^{I} \mu_{i} dn_{i} \]  

The changes in the internal energy in the idealized phases l₁ and l₂ may be expressed as:

\[ dE_{o} = TdS_{o} - \pi_{So} dA_{o} + \sum_{i}^{I} \mu_{i} dn_{i} \]  

\[ dE_{d} = TdS_{d} - \pi_{Sd} dA_{d} + \sum_{i}^{I} \mu_{i} dn_{i} \]  

Note that the idealized systems have two two-dimensional phases without any physical interface.
The line excess internal energy difference may then be written as (Eq (6) –((7)+(8))):

\[dE^x = TdS^x + \lambda dl + \Sigma_i \mu_i dn_i^x\]  
(9)

Integrating equation 9, with T, \( \lambda \), and \( \mu_i \) constant gives:

\[E^x = TS^x + \lambda l + \Sigma_i \mu_i n_i^x\]  
(10)

In general, if we differentiate equation 10, we get

\[dE^x = TdS^x + S^x dT + \lambda dl + l d\lambda + \Sigma_i \mu_i d n_i^x + \Sigma_i n_i^x d \mu_i\]  
(11)

Since (9) = (11) we get:

\[-l d\lambda = S^x dT + \Sigma_i n_i^x d \mu_i\]  
(12)

Dividing throughout by \( l \) we get

\[-d\lambda = \frac{S^x}{l} dT + \Sigma_i \frac{n_i^x}{l} d \mu_i\]  
(13)

In equation 13, \( \frac{S^x}{l} = S^x_\sigma \) is the line excess entropy per unit length and \( \frac{n_i^x}{l} = \Gamma_i^x \) is the number of moles of the \( i \)th component per unit length. Then equation 13 may be rewritten as

\[-d\lambda = S^x_\sigma dT + \Sigma_i \Gamma_i^x d \mu_i\]  
(14)

Since the magnitudes of \( S^x_\sigma \) and \( \Gamma_i^x \) are dependent on the position x of the line EE’, we can fix the position of the line such that \( n_i^x = n_{i0} + n_{id} \) and \( n_i^x = 0 \). Further, if the two phases are at the same temperature then, equation 14 can be converted to the form

\[-d\lambda = \Sigma_i \Gamma_i^1 d \mu_i\]  
(15)

and \( \Gamma_i^1 = \Gamma_i^x - \Gamma_i^x \frac{c_{i0} - c_{id}}{c_{i10} - c_{i1d}} \) is defined as the relative line excess of a species in solvent 1. Since \( \mu_i = \mu_i^0 + RT \ln a_i \), substituting this in equation 15 gives

\[-d\lambda = RT \Sigma_i \Gamma_i^1 d \ln a_i = RT \Sigma_i \Gamma_i^1 f d \ln c_i\]

This is analogous to Gibbs Adsorption Equation\(^1\) to a surface.