Motivation

The surface tension plays a major role in interfacial phenomena. It is the fundamental quantity that determines the pressure change across a surface due to curvature. This in turn is the basis for the stability analysis of both thin films and liquid jets. While experimental data exists for many pure fluids, it is the goal of this project to develop an approximation that describes most pure fluids. This would allow the determination of the surface tension even when experimental data is not readily available.

Density-Gradient Theory

The surface tension of an interface can be thought of as an excess energy due to the presence of the interface. In the density gradient theory, the interface is not thought of as a perfect dividing plane between the two phases. Instead there is a region in which the density changes from that of the high-density phase to that of the low-density phase. The energy in the interface region is a function of the density at each point in the interface. So, the surface tension represents the excess energy present in the interface region due to the "gradient" in density.

So to derive a relationship between the energy in the interface and the surface tension, we start with the energy balance for the interface region:

$$\sigma *S = A + PV - N\mu$$

Where A is the Helmholtz energy of the system, S is the interfacial area, P is the pressure, V is the volume, N is the number of molecules and μ is the chemical potential.

Dividing the energy equation by the area gives (derived in Appendix A, part 1):

 $\sigma = (A + P - \rho \mu) dx$

Where the limits of integration are from infinity to minus infinity.

This must be integrated over the interface. The density gradient model assumes a planar interface in the sense that the density is only changing in the direction perpendicular to the interface. For this derivation, we will call this the x-direction. Using

the expansion for the Helmholtz energy derived in Appendix A, part 2, the expression for the surface tension becomes:

 $\sigma = (\Delta a + \frac{1}{2} k(\rho) \rho_x^2) dx$

Where Δa is given by $a_0(\rho) + P - \rho \mu$

The quantity Δa represents the excess Helmholtz energy per volume in the interface. The $\rho\mu$ term in this expression is evaluated at the bulk compositions, as is the pressure. The $a_o(\rho)$ term represents the Helmholtz energy in the interface, which is a function of density, which changes in the interface. Therefore, this expression represents the excess energy, the energy in the interface minus the energy in the bulk.

This integral represents the total excess energy in the system due to the presence of the interface. At equilibrium, thermodynamics requires that the system energy will be at a minimum. So, the integral must be minimized in order to minimize the excess energy. Minimization of this integral using the calculus of variation is shown in Appendix B.

The result is:

$$\sigma = (2 k(\rho) \Delta a)^{1/2} d\rho$$

Where the limits of integration are from ρ_l to ρ_g . Note that the variable of integration has been changed from x to ρ . This allows the calculation of the surface tension without ever having to determine the actual dimensions of the interface region. This is the result of the density gradient theory that will be used to calculate the surface tension.

Lattice Fluid Model.

An expression for σ can be found by using an expression for Δa that is explicit in ρ . The lattice fluid model provides the necessary equations. However, the integration of these equations usually requires a numerical integration technique. In order to obtain an analytical solution, a Taylor series expansion of Δa will be used. First, the Sanchez-

Lacombe EOS expressions for a and μ are made dimensionless, as are k and σ . The expressions are:

$$\mu = -\rho + P/\rho + T((1/\rho - 1) \ln(1-\rho) + 1/r \ln \rho)$$

and

$$\Delta a = \rho \mu(\rho, P)$$
- P - a_e

Here a_e represents the Helmholtz that the system would have if it were homogeneous. The italics represent dimensionless numbers. The dimensionless relationships are:

 $T=T/T* T*=\epsilon*/k$ $P=P/P* P*=\epsilon*/v*$ $\rho=\rho/\rho*$ $\sigma=\sigma/\sigma* \sigma*=(P*)^{2/3}(kT*)^{1/3}$ $\mu=\mu/Nr\epsilon* a=a/P*$

Here, the quantities P*, T*, ρ * and r which describes the molecular size, are tabulated for a large number of pure compounds.

In order to apply the dimensionless form of the Helmholtz energy, the equation for the surface tension must be determined in terms of the dimensionless Helmholtz energy. It is given by:

$$\sigma = 2 \qquad (k(\rho) \,\Delta a)^{1/2} \,\mathrm{d}\rho$$

Now Δa is expanded in a double Taylor series, first around ρ_l and then around ρ_g . The result is derived in appendix C. It should be noted that *k* is taken as a constant in this expansion. Sanchez reports that for the SL EOS, the value of *k* is 1/6. This is the value that will be used in this derivation. The result is :

$$\sigma = 2 k^{1/2} \Delta \rho^{3/2} \left[\rho_{\rm g} + P/\rho_{\rm l} + T \left[\frac{1}{2}(1 - \frac{1}{r})(1 + \rho_{\rm g}/\rho_{\rm l}) + \frac{1}{\rho_{\rm l}} \left(\ln(1 - \rho_{\rm l}) + \frac{1}{2}((\rho_{\rm l} - \rho_{\rm g})/(1 - \rho_{\rm l})) \right) \right]^{1/2}$$

In this equation, the values for ρ_{l} , ρ_{g} , *P*, and *T* are such that they must satisfy the EOS, which is

$$\rho^2 + P + T \left[\ln (1 - \rho) + (1 - 1/r)\rho \right] = 0$$

and the chemical potential in each phase must be the same. This gives three equations for three unknowns for a one-component two-phase system with one degree of freedom.

As a side note, in order to get good agreement with experimental data, a factor of 1/3 was applied to the equation. So, the final equation is:

$$\sigma = 2/3 k^{1/2} \Delta \rho^{3/2} \left[\rho_{\rm g} + P/\rho_{\rm l} + T \left[\frac{1}{2}(1 - \frac{1}{r})(1 + \rho_{\rm g}/\rho_{\rm l}) + \frac{1}{\rho_{\rm l}} \left(\ln(1 - \rho_{\rm l}) + \frac{1}{2}((\rho_{\rm l} - \rho_{\rm g})/(1 - \rho_{\rm l})) \right) \right]^{1/2}$$

this can be simplified to:

$$\sigma = 2/3 k^{1/2} \Delta \rho^{3/2} T^{1/2} \left[\frac{1}{2} (1 - 1/r) + \frac{1}{\rho_l} \left(\frac{\ln(1 - \rho_l)}{1 - \rho_l} \right)^{1/2} \right]^{1/2}$$

Here the reduced density of the gas and the reduced pressure have been assumed to be negligible. The reduced gas density is of the order 10^{-3} and the reduced pressure is of the order 10^{-4} to 10^{-8} . Neglecting these quantities makes less than 0.1% difference in the results.

Calculations

The calculation procedure that was used is quite simple. Given the temperature of the system, the reduced temperature can be calculated. Then a reduced pressure must be guessed. With these two quantities, the equation of state can be solved for the two density roots, the gas density and the liquid density. Then the chemical potential is set equal in each phase. This allows for a new reduced pressure to be calculated. With this new reduced pressure, the reduced densities are recalculated and then used to calculate a new reduced pressure. This usually only requires two or three iterations and can be done on a calculator with a root finding function. This was the method used to find all the numerical results for this problem.

Results

<u>Substance</u>	Temperature	$\sigma_{\underline{experimental}}$	$\sigma_{\underline{predicted}}$	<u>%diff</u>
Benzene	20C	28.88	29.67	2.73
	30C	27.49	27.76	0.98
	80C	21.2	19.66	7.26
ethylene	-120C	19.5	19.55	0.26
	-110C	17.65	17.04	3.46
	-100C	15.71	14.82	5.66
propane	230K	15.94	15.91	0.19
n-butane	230K	20.64	20.93	1.40
iso-butane	230K	18.30	18.50	1.09
diethylether	20C	16.96	16.22	4.36
oxygen	-193C	15.7	15.02	4.33
Carbon Tetrachloride	20C	26.8	27.70	3.36

Some of the results calculated using the above equation are presented below.

It can be seen that the agreement is reasonable as an estimate for these compounds. In order to determine the accuracy of this equation over a large temperature range, the equation was used to predict surface tension values for propane, butane, and benzene. The predicted values are plotted along with the experimental surface tensions on the following page. It can be seen that good agreement with experimental data is obtained over a large temperature range, almost 200K for butane. So, this equation gives good estimates of the surface tension not only at ambient conditions, but also at points far away from ambient. This equation surprisingly does a good job near the critical points of the fluids even though the reduced pressure was neglected. So, overall this equation fulfills the goal of giving a reasonable estimate for the surface tension of pure fluids. References:

-Poser, C, I.; Sanchez, I. C. J. Colloid Interface Sci. 1979, 69, 539.

-Vargaftik, N. B., "Tables in the Thermophysical Properties of Liquids and Gases," 2nd

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Determination of Pure Fluid Surface Tensions

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