

A Property Derivations

A.1 Pure Solvent Properties

A.1.1 Density

Starting with the equation used to calculate the density experimentally,

$$\rho = \frac{M}{\langle V \rangle} \quad (1)$$

Recall from the derivative form for the Gibbs free energy $dG = Vdp - SdT + \sum_i \mu_i dN_i$ that V can be found from the Gibbs free energy with

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,N} \quad (2)$$

The density can therefore be found from the Gibbs free energy.

$$\rho = \frac{M}{\left(\frac{\partial G}{\partial p} \right)_{T,N}} \quad (3)$$

The derivative can be estimated using a central difference numerical method utilizing Gibbs free energies reweighted to different pressures.

$$\left(\frac{\partial G}{\partial p} \right)_{T,N} \approx \frac{G_{p+\Delta p} - G_{p-\Delta p}}{2\Delta p} \quad (4)$$

The density can be estimated.

$$\rho \approx \frac{M}{\frac{G_{p+\Delta p} - G_{p-\Delta p}}{2\Delta p}} \quad (5)$$

A.1.2 Dielectric Constant

This equation was provided by a literature reference authored by CJ Fennell ("Simple Liquid Models with Corrected Dielectric Constants"). Below, $\epsilon(0)$ is the zero frequency dielectric constant, V is the system volume and M is the total system dipole moment. Note that the $\langle \rangle$ operator denotes an ensemble average for the system.

$$\epsilon(0) = 1 + \frac{4\pi}{3k_B T \langle V \rangle} (\langle M^2 \rangle - \langle M \rangle^2) \quad (6)$$

A.1.3 Isothermal Compressibility

The definition of isothermal compressibility is:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (7)$$

$$\kappa_T = -\frac{\left(\frac{\partial^2 G}{\partial P^2} \right)_{T,N}}{\left(\frac{\partial G}{\partial P} \right)_{T,N}} \quad (8)$$

κ_T can also be estimated from the ensemble average and fluctuation of volume or particle number, thusly:

$$\kappa_T = \beta \frac{\langle \Delta V^2 \rangle_{NTP}}{\langle V \rangle_{NTP}} = V \beta \frac{\langle \Delta N^2 \rangle_{VT}}{\langle N \rangle_{VT}} \quad (9)$$

Dadarlat et al. "Insights into Protein Compressibility from MD Simulations" used as reference

A.1.4 Molar Enthalpy

Section on relation of enthalpy to Gibbs free energy (should we need it). The enthalpy, H , can be found from the Gibbs free energy, G , by the Gibbs-Helmholtz relation:

$$H = -T^2 \left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right)_{P,N} \quad (10)$$

Transforming the derivative in the Gibbs-Helmholtz relation to be in terms of β instead of T yields:

$$H = -T^2 \frac{\beta^2}{\beta^2} \left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \frac{\partial T}{\partial \beta} \frac{\partial \beta}{\partial T} \right)_{P,N} \quad (11)$$

Recall that $\beta = \frac{1}{k_B T}$, therefore $\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$. Substituting these values into the enthalpy equation gives:

$$H = \frac{1}{k_B^3 T^2 \beta^2} \left(\frac{\partial \left(\frac{G}{T} \right)}{\partial \beta} \right)_{P,N} = \frac{1}{k_B} \left(\frac{\partial \left(\frac{G}{T} \right)}{\beta} \right)_{P,N} \quad (12)$$

Applying the quotient rule to the partial derivative yields

$$H = \frac{T}{k_B} \left(\frac{\partial G}{\partial \beta} \right)_{P,N} - \frac{G}{k_B} \left(\frac{\partial T}{\partial \beta} \right)_{P,N} = \frac{1}{T k_B} \left(\frac{\partial G}{\partial \beta} \right) - \frac{G}{T^2 k_B} \left(\frac{\partial T}{\partial \beta} \right) \quad (13)$$

Recall that $\left(\frac{\partial T}{\partial \beta} \right)_{P,N} = -k_B T^2$, which allows the enthalpy to be simplified to:

$$H = \beta \left(\frac{\partial G}{\partial \beta} \right)_{P,N} + G \quad (14)$$

The derivative can be estimated using a central difference numerical method utilizing Gibbs free energies reweighted to different temperatures.

$$\left(\frac{\partial G}{\partial \beta} \right)_{P,N} \approx \frac{G_{\beta+\Delta\beta} - G_{\beta-\Delta\beta}}{2\Delta\beta} \quad (15)$$

A.1.5 Heat Capacity

The definition of the isobaric heat capacity is:

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P,N} \quad (16)$$

$$C_P = -k_B \beta^3 \left(\frac{\partial^2 G}{\partial \beta^2} \right)_{P,N} \quad (17)$$

Finite difference approach? See section on Molar Enthalpy

The form is equivalent for isochoric heat capacity, but with derivatives at constant volume rather than pressure.

A.1.6 Speed of Sound

The definition of the speed of sound is:

$$c^2 = \sqrt{\left(\frac{\partial P}{\partial \rho} \right)_S} = -\frac{V^2}{M} \left(\frac{\partial P}{\partial V} \right)_S \quad (18)$$

$$c^2 = \frac{V^2}{\beta M} \left[\frac{\left(\frac{\gamma_V}{k_B} \right)^2}{\frac{C_V}{k_B}} + \frac{\beta}{V \kappa_T} \right] \quad (19)$$

Where:

$$\gamma_V = \left(\frac{\partial P}{\partial T} \right)_V = \frac{C_V}{T \left(\frac{\partial S}{\partial P} \right)_V} \quad (20)$$

γ_V is known as the isochoric pressure coefficient. κ_T is the same isothermal compressibility from section A.1.3

Lustig et al. "Direct molecular NVT simulation of isobaric heat capacity, speed of sound and Joule-Thomson Coefficient" used as reference

A.1.7 Enthalpy of Vaporization

The definition of the enthalpy of vaporization is:

$$\Delta H_{vap} = H_{gas} - H_{liq} = E_{gas} - E_{liq} + P(V_{gas} - V_{liq}) \quad (21)$$

If we assume that $V_{gas} \gg V_{liq}$ and that the gas is ideal (and can therefore neglect kinetic energy terms):

$$\Delta H_{vap} = E_{gas,potential} - E_{liq,potential} + RT \quad (22)$$

Can make this a single simulation calculation if we assume the intramolecular energies between the phase changes are the same...

A.2 Binary Mixture Properties

A.2.1 Mass Density, Speed of Sound and Dielectric Constant

The methods for these calculations are the same for a multicomponent system.

A.2.2 Activity Coefficient

Then the definition of the chemical potential is:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (23)$$

Where μ_i is the chemical potential of component i , n_i refers to a molecule of component i and $n_{j \neq i}$ refers to all molecules other than component i .

$$\mu_i = \mu_i^0 + k_B T \ln(x_i \gamma_i) \quad (24)$$

Where x_i is the mole fraction of component i and γ_i is the activity coefficient of component i . Rearrangement of the previous equation yields:

$$\gamma_i = \frac{\exp\left(\frac{\mu_i - \mu_i^0}{k_B T}\right)}{x_i} \quad (25)$$

A.2.3 Excess Molar Properties

The general definition of an excess molar property can be stated as follows:

$$y^E = y^M - \sum_i x_i y_i \quad (26)$$

Where y^E is the excess molar quantity, y^M is the mixture quantity, x_i is the mole fraction of component i in the mixture and y_i is the pure solvent quantity. In general, the simplest methods for calculating excess molar properties for binary mixtures will require three simulations. One simulation is run for each pure component and a third will be run for the specific mixture of interest.

A.2.4 Excess Molar Heat Capacity and Volume

Excess molar heat capacities and volume will be calculated using the methods for the pure quantities in section A.1 in combination with the general method for excess property calculation above.

A.2.5 Excess Molar Enthalpy

Excess molar enthalpy can be calculated using the general relation of molar enthalpy as it relates to Gibbs Free Energy from section A.1 and the generalized method of excess molar property calculation above or by the following:

$$H^E = \langle E^M \rangle + PV^E - \sum_i x_i \langle E_i \rangle \quad (27)$$

Where $\langle \rangle$ denotes an ensemble average and V^E is calculated using the general method of excess molar properties.