$dF = -S \cdot dT - P \cdot dV + \mu \cdot dN$
$U = F + T \cdot S$
$0.45 < T/T_c < 1.13$
$T_c$
$n = \frac{N}{V}$
$\eta = packingFraction$
$\Lambda =$

$$\frac{F}{N \cdot k \cdot T} = a^{IDEAL} + a^{HS} + \beta \cdot a_1^{SW} + \beta^2 \cdot a_2^{SW} \tag{1}$$

$$a^{IDEAL} = ln\left(n \cdot \Lambda^3\right) - 1 \tag{2}$$

$$a^{HS} = -ln(1 - 4 \cdot \eta) \tag{3}$$

$$a_1^{SW} = a_1^{VDW} \cdot g^{HS}(1; \eta_{eff}) \tag{4}$$

$$a_1^{VDW} = -4 \cdot \eta \cdot \epsilon \cdot (\lambda^3 - 1) \tag{5}$$

$$g^{HS}(1; \eta_{eff}) = \frac{1 - \eta_{eff}/2}{(1 - \eta_{eff})^3} \tag{6}$$

$$n_{eff} = c1 \cdot \eta + c_2 \cdot \eta^2 + c_3 \cdot \eta^3 \tag{7}$$

$$\left(c\right)_1{}^{c_2 c_3 = \left(2\right).25855-1.503490.249434-0.6692701.40049-0.82773910.1576-15.04275.30827\times\left(1\right)\lambda\lambda^2} \tag{8}$$

$$a_2^{SW} = \frac{1}{2} \cdot \epsilon K^{HS} \eta \cdot \frac{\partial a_1^{SW}}{\partial \eta} \tag{9}$$

$$K^{HS} = \frac{(1-\eta)^4}{1 + 4 \cdot \eta + 4 \cdot \eta^2} \tag{10}$$

$$Z = Z_{ideal} \cdot Z_{HS} \cdot Z_{disp} \tag{11}$$

$$Z_{ideal} = Z_{ideal}^{SAFT} \tag{12}$$

$$Z_{HS} = e^{-S_{HS}/k} \tag{13}$$

$$Z_{disp} = \frac{Z_{interaction}}{Z_{HS}} = \frac{\sum_i \alpha \cdot D(E_i) \cdot e^{-\beta \cdot E_i}}{\lim_{T\to\infty} \sum_i \alpha \cdot D(E_i) \cdot e^{-\beta \cdot E_i}} = \frac{\sum_i D(E_i) \cdot e^{-\beta \cdot E_i}}{\sum_i D(E_i)} \tag{14}$$

$S_{HS}$
$T = \infty$
$P_{success}$
$\Delta S_{HS} = k \cdot ln(P_{success})$
$S_{HS}$

$$\frac{}{N! \sum e^{-\beta \cdot E_i} 15 = \frac{1}{N!} \int \cdots \int e^{-\beta \cdot [\{P_1^2/2m + P_2^2/2m + \dots\} + V(\vec{R_1}, \vec{R_2}, \dots)]} d\vec{P_1} \cdot d\vec{P_2} \cdots d\vec{P_N} \cdot d\vec{R_1} \cdot d\vec{R_2} \cdots d\vec{R_N}}$$

$$where Z_{interaction} = \frac{1}{V^N} \cdot \int \cdots \int e^{-\beta \cdot V(\vec{R_1}, \vec{R_2}, \ldots)} d\vec{R_1} \cdot d\vec{R_2} \cdots d\vec{R_N} \tag{22}$$

$$and Z_{disp} = \frac{Z_{interaction}}{Z_{HS}} \tag{23}$$

$T_0$
$T_0$
$T_0$
$F_{ideal} =$
$U_{ideal} -$
$T \cdot$
$S_{ideal}$

$$U_{ideal} = 3/2 \cdot N \cdot k \cdot T \tag{24}$$

$$S_{ideal^*} \approx k \cdot N \left( ln \left[ \frac{V}{N} \left( \frac{4 \cdot \pi \cdot m}{3 \cdot h^2} \cdot \frac{U}{N} \right)^{3/2} \right] + \frac{5}{2} \right) \tag{25}$$

**??**

$$S_{ideal} = k \cdot N \left( ln \left[ V \cdot N!^{-1/N} \left( \frac{4 \cdot \pi \cdot m}{3 \cdot h^2} \cdot \frac{U}{N} \right)^{3/2} \right] + \frac{3}{2} \right) \tag{26}$$

$T \to \infty$

$$Z_{exc} = Z_{HS} \cdot Z_{disp} \Rightarrow \tag{27}$$

$$F_{exc} = -k \cdot T \cdot ln(Z_{exc}) = -k \cdot T \cdot ln(Z_{HS}) - k \cdot T \cdot ln(Z_{disp}) \Rightarrow \tag{28}$$

$$S_{exc.\infty} = \lim_{T \to \infty} - \left( \frac{\partial F_{exc}}{\partial T} \right)_{V,N} but \lim_{T \to \infty} Z_{exc} = constant \Rightarrow \tag{29}$$

$$S_{exc.\infty} = -k \cdot ln(Z_{HS.\infty}) - k \cdot ln(Z_{disp.\infty}) \tag{30}$$

$$but Z_{HS} is also constant and Z_{disp.\infty} = \frac{Z_{interaction.\infty}}{Z_{HS}} = Z_{HS}/Z_{HS} = 1 \Rightarrow \tag{31}$$

$$S_{exc.\infty} = -k \cdot ln(Z_{HS}) - k \cdot ln(1) = -k \cdot ln(Z_{HS}) \Rightarrow \tag{32}$$

$$Z_{HS} = e^{-S_{exc.\infty}/k} \tag{33}$$

$T \to \infty$

$$F = U - T \cdot S \Rightarrow S = (U - F)/T \approx -F/T = k \cdot ln(Z) \tag{34}$$

$$let Z_{small} = partition function of the smaller box \tag{35}$$

$$let Z_{big} = partition function of the bigger box \tag{36}$$

$$\Delta S = S_{small} - S_{big} = k \cdot ln(Z_{small}) - k \cdot ln(Z_{big}) = k \cdot ln(Z_{small}/Z_{big}) \tag{37}$$

$Z_{big}$
$\Delta S$
$Z_{small}$
$Z_{valid}$

$$let Z_{big} = Z_{valid} + Z_{invalid} \tag{38}$$

$\mu_{liquid} =$
$\mu_{gas}$
$P_{liquid} =$
$P_{gas}$

$$\mu = \left(\frac{\partial F(T,V1,N)}{\partial N}\right)_{T,V1}\Bigg|_{N1} = \left(\frac{\partial F(T,V1,N)}{\partial N}\right)_{T,V1}\Bigg|_{N2}$$
(61)

$$P = \left(\frac{\partial F(T,V,N1)}{\partial V}\right)_{T,N1}\Big|_{V1} = \left(\frac{\partial F(T,V,N2)}{\partial V}\right)_{T,N2}\Big|_{V2}$$
(62)

$F/V =$
$f$
$F(T,N,V)/V =$
$f(T,N/v) =$
$f(T,n)$
**??**

$$\mu = \left(\frac{\partial F(T,V,N)}{\partial N}\right)_{T,V} \cdot \frac{V}{V} = \left(\frac{\partial (F(T,V,N)/V)}{\partial (N/V)}\right)_{T,V} = \left(\frac{\partial f(T,n)}{\partial n}\right)_{T,V}$$
(63)

$\mu_1 =$
$\mu_2$
**??**
**??**

$$P = \left(\frac{\partial F(T,V,N)\cdot V/V}{\partial V}\right)_{T,N} = \left(\frac{\partial f(T,n)\cdot V}{\partial V}\right)_{T,N} = f + V \cdot \left(\frac{\partial f(T,n)}{\partial V}\right)_{T,N}$$
(64)

$(f,N,V)$

$$\left(\frac{\partial X}{\partial Y}\right)_Z \cdot \left(\frac{\partial Y}{\partial Z}\right)_X \cdot \left(\frac{\partial Z}{\partial X}\right)_Y = -1 \rightarrow$$

$$\left(\frac{\partial f(T,n)}{\partial V}\right)_{N,T} \cdot \left(\frac{\partial V}{\partial N}\right)_{f(T,n),T} \cdot \left(\frac{\partial N}{\partial f(T,n)}\right)_{V,T} = -1$$
(65)

**??**
$\left(\frac{\partial N}{\partial f(T,n)}\right)_{V,T} =$
$\frac{V}{\mu}$
$f(T,n) =$
$constant \Rightarrow$
$f(T,N/V) =$
$constant \Rightarrow$
$N/V =$
$n =$
$constant \Rightarrow$
$\left(\frac{\partial V}{\partial N}\right)_{f(T,n),T} =$
$1/n$
**??**

$$\left(\frac{\partial f(T,n)}{\partial V}\right)_{N,T} \cdot \frac{1}{n} \cdot \frac{V}{\mu} = -1$$
(66)

**??**
**??**

$$P = f + V \cdot \left(\frac{n \cdot \mu}{V}\right) = f - n \cdot \mu$$
(67)

$P_1 =$
$P_2 \Rightarrow$
$f1+$
$n1\cdot$
$\mu =$
$f2+$
$n2\cdot$
$\mu$
**??**
$\mu$

$$\mu = \frac{f2 - f1}{n2 - n1}$$
(68)

$$from eq. \textbf{??} : \mu = \left(\frac{\partial f(T,n)}{\partial n}\right)_{T,V1}\Bigg|_{n1} = \left(\frac{\partial f(T,n)}{\partial n}\right)_{T,V}\Bigg|_{n2}$$

**Here resolution reduction of the data is demonstrated. The data must be generated from a range of box sizes, and for each box size it is possible to run simulations From 2 atoms in a box all the way up to the desired filling fraction of 0.5; depending on the box size, a filling fraction of 0.5 can correspond to only 40 atoms or it could be as much as 100 atoms. Running simulations with every possible filling fraction will indeed**