

Classical Density Functional Theory for Thermopack - Entropy

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1 Introduction

The entropy (\tilde{S} (JK^{-1})) is generally given from the Helmholtz energy (\tilde{F} (J)) differential with respect to temperature,

$$\tilde{S} = - \left. \frac{d\tilde{F}}{dT} \right|_{V,n}. \quad (1)$$

The Helmholtz functional in DFT is given as

$$F[\rho] = \frac{\tilde{F}}{V}. \quad (2)$$

The mol specific Helmholtz functional is then given as

$$f[\rho] = \frac{F}{\rho}. \quad (3)$$

The mol specific entropy then becomes

$$s = - \left. \frac{df}{dT} \right|_{\rho} = - \left. \frac{1}{\rho} \frac{dF}{dT} \right|_{\rho}. \quad (4)$$

This is different from the definition of Stierle and Gross [1], where mol specific entropy is defined as

$$s = - \left. \frac{1}{\bar{\rho}} \frac{dF}{dT} \right|_{\rho}, \quad (5)$$

where $\bar{\rho}$ is a weighted density. $\bar{\rho}$ is not constant upon differentiating with temperature.

The functional depends on the density through the weighted densities,

$$n_{\alpha} = \int d\mathbf{r}' \rho(\mathbf{r}') w_{\alpha}(\mathbf{r} - \mathbf{r}') = \rho(\mathbf{r}) \otimes w_{\alpha}(\mathbf{r}), \quad (6)$$

where w_{α} is the a weight function. In effect the the functional becomes,

$$F = F(\mathbf{n}(T), T) \quad (7)$$

The temperature differential of F then becomes,

$$\frac{dF}{dT} = \sum_{\alpha} \frac{\partial F}{\partial n_{\alpha}} \frac{\partial n_{\alpha}}{\partial T} + \frac{\partial F}{\partial T} \quad (8)$$

Differentiating the equation for n_{α} , eq. (6), give,

$$\begin{aligned} \frac{\partial n_{\alpha}}{\partial T} &= \frac{\partial}{\partial T} \rho(\mathbf{r}) \otimes w_{\alpha}(\mathbf{r}) \\ &= \frac{\partial}{\partial T} \mathcal{F}^{-1} [\mathcal{F} [\rho(\mathbf{r})] \mathcal{F} [w_{\alpha}(\mathbf{r})]] \\ &= \frac{\partial}{\partial T} \mathcal{F}^{-1} [\hat{\rho}(\mathbf{k}) \hat{w}_{\alpha}(\mathbf{k})] \\ &= \mathcal{F}^{-1} \left[\hat{\rho}(\mathbf{k}) \frac{\partial \hat{w}_{\alpha}(\mathbf{k})}{\partial T} \right] \end{aligned} \quad (9)$$

The weight functions in Fourier space is given in the supplementary information by Stierle et al. [2].

$$\hat{w}_0(\mathbf{k}) = j_0(2\pi R|\mathbf{k}|) \quad (10)$$

$$\hat{w}_1(\mathbf{k}) = R j_0(2\pi R|\mathbf{k}|) \quad (11)$$

$$\hat{w}_2(\mathbf{k}) = 4\pi R^2 j_0(2\pi R|\mathbf{k}|) \quad (12)$$

$$\hat{w}_3(\mathbf{k}) = \frac{4}{3} \pi R^3 (j_0(2\pi R|\mathbf{k}|) + j_2(2\pi R|\mathbf{k}|)) \quad (13)$$

$$\hat{w}_{V1}(\mathbf{k}) = -\frac{i\mathbf{k}}{2R} \hat{w}_3(\mathbf{k}) \quad (14)$$

$$\hat{w}_{V2}(\mathbf{k}) = -2\pi i \mathbf{k} \hat{w}_3(\mathbf{k}) \quad (15)$$

$$\hat{w}_{\text{disp}}(\mathbf{k}) = j_0(4\pi \psi R|\mathbf{k}|) + j_2(4\pi \psi R|\mathbf{k}|) \quad (16)$$

Here j is the spherical Bessel functions of the first kind of order zero and two. The Bessel functions of order 0-2 is given as

$$j_0(\xi) = \frac{\sin(\xi)}{\xi} \quad (17)$$

$$j_1(\xi) = \frac{\sin(\xi)}{\xi^2} - \frac{\cos(\xi)}{\xi} \quad (18)$$

$$j_2(\xi) = \left(\frac{3}{\xi^2} - 1 \right) \frac{\sin(\xi)}{\xi} - \frac{3\cos(\xi)}{\xi^2}. \quad (19)$$

Differentiating the Bessel functions of order 0 and three other useful relations,

$$\frac{\partial j_0(\xi)}{\partial \xi} = -\frac{\sin(\xi)}{\xi^2} + \frac{\cos(\xi)}{\xi} = -j_1(\xi) \quad (20)$$

$$\begin{aligned} \frac{\partial [\xi^2 (j_0(\xi) + j_2(\xi))]}{\partial \xi} &= \frac{\partial}{\partial \xi} \left(\frac{3 \sin(\xi)}{\xi} - 3 \cos(\xi) \right) \\ &= -\frac{3 \sin(\xi)}{\xi^2} + \frac{3 \cos(\xi)}{\xi} + 3 \sin(\xi) \\ &= -3j_1(\xi) + 3\xi j_0(\xi) \end{aligned} \quad (21)$$

$$\frac{\partial [\xi^3 (j_0(\xi) + j_2(\xi))]}{\partial \xi} = 3\xi^2 j_0(\xi) \quad (22)$$

$$\begin{aligned} \frac{\partial (j_0(\xi) + j_2(\xi))}{\partial \xi} &= 3 \frac{\partial}{\partial \xi} \left(\frac{\sin(\xi)}{\xi^3} - \frac{\cos(\xi)}{\xi^2} \right) \\ &= 3 \left(3 \frac{\cos(\xi)}{\xi^3} - 3 \frac{\sin(\xi)}{\xi^4} + \frac{\sin(\xi)}{\xi^2} \right) \\ &= -\frac{3}{\xi} j_2(\xi) \end{aligned} \quad (23)$$

The differentials of the weight functions in Fourier space then becomes,

$$\frac{\partial \hat{w}_0(\mathbf{k})}{\partial R} = -2\pi|\mathbf{k}|j_1(2\pi R|\mathbf{k}|) \quad (24)$$

$$\frac{\partial \hat{w}_1(\mathbf{k})}{\partial R} = j_0(2\pi R|\mathbf{k}|) - 2\pi R|\mathbf{k}|j_1(2\pi R|\mathbf{k}|) \quad (25)$$

$$\frac{\partial \hat{w}_2(\mathbf{k})}{\partial R} = 8\pi Rj_0(2\pi R|\mathbf{k}|) - 8\pi^2 R^2|\mathbf{k}|j_1(2\pi R|\mathbf{k}|) \quad (26)$$

$$\begin{aligned} \frac{\partial \hat{w}_3(\mathbf{k})}{\partial R} &= \frac{1}{6\pi^2|\mathbf{k}|^3} \frac{\partial}{\partial R} \left((2\pi R|\mathbf{k}|)^3 (j_0(2\pi R|\mathbf{k}|) + j_2(2\pi R|\mathbf{k}|)) \right) \\ &= \frac{1}{6\pi^2|\mathbf{k}|^3} 3(2\pi R|\mathbf{k}|)^2 j_0(2\pi R|\mathbf{k}|) 2\pi|\mathbf{k}| \\ &= 4\pi R^2 j_0(2\pi R|\mathbf{k}|) \end{aligned} \quad (27)$$

$$\begin{aligned} \frac{\partial \hat{w}_{V1}(\mathbf{k})}{\partial R} &= -\frac{2\pi i\mathbf{k}}{3(2\pi|\mathbf{k}|)^2} \frac{\partial}{\partial R} \left((2\pi R|\mathbf{k}|)^2 (j_0(2\pi R|\mathbf{k}|) + j_2(2\pi R|\mathbf{k}|)) \right) \\ &= -\frac{2\pi i\mathbf{k}}{3(2\pi|\mathbf{k}|)^2} \left(6\pi R|\mathbf{k}|j_0(2\pi R|\mathbf{k}|) - 3j_1(2\pi R|\mathbf{k}|) \right) 2\pi|\mathbf{k}| \\ &= -i \left(2\pi R\mathbf{k}j_0(2\pi R|\mathbf{k}|) - \frac{\mathbf{k}}{|\mathbf{k}|} j_1(2\pi R|\mathbf{k}|) \right) \end{aligned} \quad (28)$$

$$\frac{\partial \hat{w}_{V2}(\mathbf{k})}{\partial R} = -8\pi^2 i\mathbf{k}R^2 j_0(2\pi R|\mathbf{k}|) \quad (29)$$

$$\begin{aligned} \frac{\partial \hat{w}_{\text{disp}}(\mathbf{k})}{\partial R} &= -\frac{3j_2(4\pi\psi R|\mathbf{k}|)}{4\pi\psi R|\mathbf{k}|} 4\pi\psi|\mathbf{k}| \\ &= -\frac{3j_2(4\pi\psi R|\mathbf{k}|)}{R} \end{aligned} \quad (30)$$

Finally,

$$\frac{\partial \hat{w}_\alpha(\mathbf{k})}{\partial T} = \frac{\partial \hat{w}_\alpha(\mathbf{k})}{\partial R} \frac{\partial R}{\partial T} \quad (31)$$

1.1 Density shift contributions

When shifting the density profiles we get contributions from convolution of constant densities (ρ^s). These contributions are given as,

$$n_\alpha^s = \rho^s(\mathbf{r}) \otimes w_\alpha(\mathbf{r}) = \rho^s w_\alpha^s \quad (32)$$

$$\frac{\partial n_\alpha^s}{\partial T} = \rho^s \frac{\partial w_\alpha^s}{\partial T}. \quad (33)$$

Where,

$$w_0^s = 1 \quad (34)$$

$$w_1^s = R \quad (35)$$

$$w_2^s = 4\pi R^2 \quad (36)$$

$$w_3^s = \frac{4}{3}\pi R^3 \quad (37)$$

$$w_{V1}^s = 0 \quad (38)$$

$$w_{V2}^s = 0 \quad (39)$$

$$w_{\text{disp}}^s = 1. \quad (40)$$

Differentiating we get,

$$\frac{\partial w_0^s}{\partial R} = 0 \quad (41)$$

$$\frac{\partial w_1^s}{\partial R} = 1 \quad (42)$$

$$\frac{\partial w_2^s}{\partial R} = 8\pi R \quad (43)$$

$$\frac{\partial w_3^s}{\partial R} = 4\pi R^2 \quad (44)$$

$$\frac{\partial w_{V1}^s}{\partial R} = 0 \quad (45)$$

$$\frac{\partial w_{V2}^s}{\partial R} = 0 \quad (46)$$

$$\frac{\partial w_{\text{disp}}^s}{\partial R} = 0 \quad (47)$$

1.2 Generic weight functions

Generic weight functions of Dirac delta and heaviside functions are,

$$\hat{w}_\delta(\mathbf{k}) = \beta(R)\tilde{w}_\delta = \beta(R)4\pi(R\Psi)^2 j_0(2\pi R\Psi|\mathbf{k}|) \quad (48)$$

$$\hat{w}_\Theta(\mathbf{k}) = \beta(R)\tilde{w}_\Theta = \beta(R)\frac{4}{3}\pi(R\Psi)^3 (j_0(2\pi R\Psi|\mathbf{k}|) + j_2(2\pi R\Psi|\mathbf{k}|)) \quad (49)$$

$$(50)$$

Here, Ψ simply scale the width of the weight, $\beta(R)$ is a prefactor depending on R . We also introduce the utility variable $\lambda(R)$,

$$\lambda_\delta(R) = \beta(R)4\pi(R\Psi)^2 \quad (51)$$

$$\lambda_\Theta(R) = \beta(R)\tilde{w}_\Theta = \beta(R)\frac{4}{3}\pi(R\Psi)^3. \quad (52)$$

The differentials of the generic weight functions in Fourier space then becomes,

$$\frac{\partial \hat{w}_\delta(\mathbf{k})}{\partial R} = \lambda_{\delta,R} j_0(2\pi R\Psi|\mathbf{k}|) - \lambda(R)2\pi R\Psi|\mathbf{k}| j_1(2\pi R\Psi|\mathbf{k}|) \quad (53)$$

$$\begin{aligned} \frac{\partial \hat{w}_\Theta(\mathbf{k})}{\partial R} &= \frac{\beta(R)}{6\pi^2|\mathbf{k}|^3} \frac{\partial}{\partial R} \left((2\pi R\Psi|\mathbf{k}|)^3 (j_0(2\pi R\Psi|\mathbf{k}|) + j_2(2\pi R\Psi|\mathbf{k}|)) \right) + \beta_R \tilde{w}_\Theta \\ &= \frac{\beta(R)}{6\pi^2|\mathbf{k}|^3} 3(2\pi R\Psi|\mathbf{k}|)^2 j_0(2\pi R\Psi|\mathbf{k}|) 2\pi\Psi|\mathbf{k}| + \beta_R \tilde{w}_\Theta \\ &= \beta(R)4\pi R^2\Psi^2 j_0(2\pi R\Psi|\mathbf{k}|) + \beta_R \tilde{w}_\Theta \end{aligned} \quad (54)$$

1.2.1 Generic density shift contributions

Where,

$$w_\delta^s = \beta(R)4\pi(R\Psi)^2 = \lambda_\delta(R) \quad (55)$$

$$w_\Theta^s = \beta(R)\frac{4}{3}\pi(R\Psi)^3 = \lambda_\Theta(R). \quad (56)$$

Differentiating we get,

$$\frac{\partial w_\delta^s}{\partial R} = \lambda_{\delta,R} \quad (57)$$

$$\frac{\partial w_\Theta^s}{\partial R} = \lambda_{\Theta,R} \quad (58)$$

2 Other excess quantities

Knowing the entropy all the other excess energy densities can be calculated. The internal energy density is known from

$$u^{\text{ex}} = f^{\text{ex}} + Ts^{\text{ex}}. \quad (59)$$

Further, the enthalpy is known from,

$$h^{\text{ex}} = Ts^{\text{ex}} + \sum_i \rho_i \mu_i^{\text{ex}}, \quad (60)$$

where the excess chemical potential can be calculated from

$$\mu_i^{\text{ex}} = \mu_i - k_B T \ln(\rho_i) - \text{Const.} \quad (61)$$

as the chemical potential, μ_i , is always specified for the simulations.

Effect of external potential?

3 Pressures

For the planar geometry the parallel component of the pressure tensor is given from the grand potential density,

$$p_{\parallel} = -f + \sum_i \rho_i \mu_i. \quad (62)$$

4 Results

References

- [1] Rolf Stierle and Joachim Gross. Hydrodynamic density functional theory for mixtures from a variational principle and its application to droplet coalescence. *J. Chem. Phys.*, 155(13):134101, October 2021. ISSN 0021-9606, 1089-7690. doi:10/gpdnrw.
- [2] Rolf Stierle, Elmar Sauer, Johannes Eller, Marc Theiss, Philipp Rehner, Philipp Ackermann, and Joachim Gross. Guide to efficient solution of PC-SAFT classical Density Functional Theory in various Coordinate Systems using fast Fourier and similar Transforms. *Fluid Phase Equilibr.*, 504:112306, January 2020. ISSN 03783812. doi:10/ggcq4v.