Classical Density Functional Theory for Thermopack - Entropy

Morten Hammer

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1 Introduction

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

$$\tilde{S} = -\frac{\mathrm{d}\tilde{F}}{\mathrm{d}T}\bigg|_{V,n}.$$ (1)

The Helmholtz functional in DFT is given as

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

The mol specific Helmholtz functional is then given as

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

The mol specific entropy then becomes

$$s = -\frac{\mathrm{d}f}{\mathrm{d}T}\bigg|_{\rho} = -\frac{1}{\rho}\frac{\mathrm{d}F}{\mathrm{d}T}\bigg|_{\rho}.$$ (4)

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

$$s = -\frac{1}{\bar{\rho}}\frac{\mathrm{d}F}{\mathrm{d}T}\bigg|_{\rho},$$ (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,

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

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

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

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The temperature differential of F then becomes,

$$\frac{\mathrm{d}F}{\mathrm{d}T} = \sum_\alpha \frac{\partial F}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial T} + \frac{\partial F}{\partial T} \tag{8}$$

Differentiating the equation for n_α, eq. (6), give,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\frac{\partial \left[\xi^2 (j_0(\xi) + j_2(\xi))\right]}{\partial \xi} = \frac{\partial}{\partial \xi}\left(\frac{3\sin(\xi)}{\xi} - 3\cos(\xi)\right)$$

$$= -\frac{3\sin(\xi)}{\xi^2} + \frac{3\cos(\xi)}{\xi} + 3\sin(\xi)$$

$$= -3j_1(\xi) + 3\xi j_0(\xi) \tag{21}$$

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

$$\frac{\partial (j_0(\xi) + j_2(\xi))}{\partial \xi} = 3\frac{\partial}{\partial \xi}\left(\frac{\sin(\xi)}{\xi^3} - \frac{\cos(\xi)}{\xi^2}\right)$$

$$= 3\left(3\frac{\cos(\xi)}{\xi^3} - 3\frac{\sin(\xi)}{\xi^4} + \frac{\sin(\xi)}{\xi^2}\right)$$

$$= -\frac{3}{\xi} j_2(\xi) \tag{23}$$

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

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

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

$$\frac{\partial \hat{w}_2(\mathbf{k})}{\partial R} = 8\pi R j_0(2\pi R|\mathbf{k}|) - 8\pi^2 R^2|\mathbf{k}|j_1(2\pi R|\mathbf{k}|) \tag{26}$$

$$\frac{\partial \hat{w}_3(\mathbf{k})}{\partial R} = \frac{1}{6\pi^2|\mathbf{k}|^3}\frac{\partial}{\partial R}\left((2\pi R|\mathbf{k}|)^3(j_0(2\pi R|\mathbf{k}|) + j_2(2\pi R|\mathbf{k}|))\right)$$

$$= \frac{1}{6\pi^2|\mathbf{k}|^3}3(2\pi R|\mathbf{k}|)^2 j_0(2\pi R|\mathbf{k}|)2\pi|\mathbf{k}|$$

$$= 4\pi R^2 j_0(2\pi R|\mathbf{k}|) \tag{27}$$

$$\frac{\partial \hat{w}_{V1}(\mathbf{k})}{\partial R} = -\frac{2\pi i\mathbf{k}}{3(2\pi|\mathbf{k}|)^2}\frac{\partial}{\partial R}\left((2\pi R|\mathbf{k}|)^2(j_0(2\pi R|\mathbf{k}|) + j_2(2\pi R|\mathbf{k}|))\right)$$

$$= -\frac{2\pi i\mathbf{k}}{3(2\pi|\mathbf{k}|)^2}\left(6\pi R|\mathbf{k}|j_0(2\pi R|\mathbf{k}|) - 3j_1(2\pi R|\mathbf{k}|)\right)2\pi|\mathbf{k}|$$

$$= -i\left(2\pi R\mathbf{k}j_0(2\pi R|\mathbf{k}|) - \frac{\mathbf{k}}{|\mathbf{k}|}j_1(2\pi R|\mathbf{k}|)\right) \tag{28}$$

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

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

$$= -\frac{3j_2(4\pi\psi R|\mathbf{k}|)}{R} \tag{30}$$

Finally,

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

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,

$$n^{\text{s}}_\alpha = \rho^{\text{s}}(\mathbf{r}) \otimes w_\alpha(\mathbf{r}) = \rho^{\text{s}}w^{\text{s}}_\alpha \tag{32}$$

$$\frac{\partial n^{\text{s}}_\alpha}{\partial T} = \rho^{\text{s}}\frac{\partial w^{\text{s}}_\alpha}{\partial T}. \tag{33}$$

Where,

$$w_0^s = 1 \tag{34}$$
$$w_1^s = R \tag{35}$$
$$w_2^s = 4\pi R^2 \tag{36}$$
$$w_3^s = \frac{4}{3}\pi R^3 \tag{37}$$
$$w_{V1}^s = 0 \tag{38}$$
$$w_{V2}^s = 0 \tag{39}$$
$$w_{\text{disp}}^s = 1. \tag{40}$$

Differentiating we get,

$$\frac{\partial w_0^s}{\partial R} = 0 \tag{41}$$

$$\frac{\partial w_1^s}{\partial R} = 1 \tag{42}$$

$$\frac{\partial w_2^s}{\partial R} = 8\pi R \tag{43}$$

$$\frac{\partial w_3^s}{\partial R} = 4\pi R^2 \tag{44}$$

$$\frac{\partial w_{V1}^s}{\partial R} = 0 \tag{45}$$

$$\frac{\partial w_{V2}^s}{\partial R} = 0 \tag{46}$$

$$\frac{\partial w_{disp}^s}{\partial R} = 0 \tag{47}$$

1.2 Generic weight functions

Generic weight functions of Dirac delta and heaviside functions are,

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

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

$$\tag{50}$$

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

$$\lambda_\delta(R) = \beta(R)4\pi(R\Psi)^2 \tag{51}$$

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

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

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

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

$$= \frac{\beta(R)}{6\pi^2|\mathbf{k}|^3}3\left(2\pi R\Psi|\mathbf{k}|\right)^2 j_0\left(2\pi R\Psi|\mathbf{k}|\right)2\pi\Psi|\mathbf{k}| + \beta_R\tilde{w}_\Theta$$

$$= \beta(R)4\pi R^2\Psi^2 j_0\left(2\pi R\Psi|\mathbf{k}|\right) + \beta_R\tilde{w}_\Theta \tag{54}$$

1.2.1 Generic density shift contributions

Where,

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

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

Differentiating we get,

$$\frac{\partial w_\delta^s}{\partial R} = \lambda_{\delta,R} \tag{57}$$

$$\frac{\partial w_\Theta^s}{\partial R} = \lambda_{\Theta,R} \tag{58}$$

2 Other excess quantities

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

$$u^{\text{ex}} = f^{\text{ex}} + Ts^{\text{ex}}. \tag{59}$$

Further, the enthalpy is known from,

$$h^{\text{ex}} = T s^{\text{ex}} + \sum_i \rho_i \mu_i^{\text{ex}}, \tag{60}$$

where the excess chemical potential can be calculated from

$$\mu_i^{\text{ex}} = \mu_i - k_{\text{B}} T \ln(\rho_i) - \text{Const.} \tag{61}$$

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,

$$p_\parallel = -f + \sum_i \rho_i \mu_i. \tag{62}$$

4   Results

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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.