Supplementary Material: The Interactions between Thermodynamic Anomalies.

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I. THE GRADIENT OF THE SPINODAL LINE IN DIFFERENT PROJECTIONS.

In order to explore the behaviour of the spinodal line in the PT projection we have to derive an expression that describes the gradient. Consider the pressure differential as a function of volume and temperature:

$$\mathrm{d}P = \left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial P}{\partial V}\right)_T \mathrm{d}V. \tag{SI-1}$$

Differentiating this with respect to temperature along the spinodal line gives:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\mathrm{spinodal}} = \left(\frac{\partial P}{\partial T}\right)_V. \tag{SI-2}$$

The second term in equation SI-1 goes to zero at a spinodal.

In order to determine the gradient of the spinodal line in the VT projection we consider the differential of the condition for a spinodal point and expand it in T and V:

$$\mathrm{d}\left(\frac{\partial P}{\partial V}\right)_T = \frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T \mathrm{d}T + \frac{\partial}{\partial V}\left(\frac{\partial P}{\partial V}\right)_T \mathrm{d}V. \tag{SI-3}$$

We divide the expression by $\mathrm{d}T$ and require that we are on a spinodal line which gives zero for the left side since the derivative is always zero and is invariant,

$$-\frac{\partial^2 P}{\partial V \partial T} = \left(\frac{\partial^2 P}{\partial V^2}\right)_T \left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\mathrm{spinodal}}, \tag{SI-4}$$

where we adopted the short-hand notation for mixed second derivatives. As a result, the gradient of the spinodal line in the VT projection is:

$$\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\mathrm{spinodal}} = -\frac{\dfrac{\partial^2 P}{\partial V\,\partial T}}{\left(\dfrac{\partial^2 P}{\partial V^2}\right)_T}. \tag{SI-5}$$

In the VT projection the gradient of the spinodal line depends on the spinodal branch we choose (denominator) which will be of constant sign depending on which branch we choose (the maximum or minimum in the PV projection).

II. THE DENSITY ANOMALY.

A. The Equivalence of the Density Anomaly conditions.

Consider the definition of the density anomaly:

$$\left(\frac{\partial \rho}{\partial T}\right)_P = 0. \tag{SI-6}$$

For a fixed number of particles we can rewrite the above as:

$$\left(\frac{\partial \rho}{\partial T}\right)_P = N\left(\frac{\partial \frac{1}{V}}{\partial T}\right)_P = 0, \tag{SI-7}$$

and so:

$$\left(\frac{\partial \rho}{\partial T}\right)_P = N\left(\frac{\frac{\partial V^{-1}}{\partial V}\partial V}{\partial T}\right)_P = -\frac{\rho}{V}\left(\frac{\partial V}{\partial T}\right)_P, \tag{SI-8}$$

which is equivalent to finding an opposite extremum (ie. minimum for TMD and maximum for TminD) in:

$$\left(\frac{\partial V}{\partial T}\right)_P = 0. \tag{SI-9}$$

Using a cyclic relation we can write:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T, \tag{SI-10}$$

where part of the right-hand side of the equation is the isothermal compressibility $VK_T = -\left(\frac{\partial V}{\partial P}\right)_T$ which is strictly positive. As a result,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{VK_T}\left(\frac{\partial V}{\partial T}\right)_P, \tag{SI-11}$$

and so we can rewrite the condition for finding the density maximum as finding a minimum or the density minimum as finding a maximum in:

$$\left(\frac{\partial P}{\partial T}\right)_V = 0. \tag{SI-12}$$

This enables us to establish the location of TMD lines from simulations performed in the NVT ensemble by calculating isochores and identifying minima in the pressure as a function of temperature. Note that this equivalence is only valid in the limit as we approach the density anomaly or spinodal line. This is because all cyclic relations are based on the implicit function theorem and underlying condition that all partial derivatives and their reciprocals involved have a non-zero value. As a result, cyclic relations are invalid at the density anomaly and spinodal lines, but they are valid in the limit as we approach them from any side. Such an argument is in the spirit of the Taylor expansion approach[1]. As a result, great care needs to be taken when using the cyclic relations in the derivation of thermodynamic equations. Formally the implicit function theorem is only valid on a domain on which all thermodynamic variables are differentiable functions of other thermodynamic variables. This is obviously violated at the points when a derivative is infinity. However in certain projections these problematic points are still valid functions and can often be used without any special considerations. The Taylor expansion approach is in those cases a rigorous way of considering the problem.

B. The Density Anomaly loci in the PT projection.

Next we derive the gradient of the density anomaly in the PT projection. We follow the derivation discussed for the singularity-free interpretation[2]. Consider the definition for the density anomaly $\left(\frac{\partial V}{\partial T}\right)_P = 0$ and expand the differential in T and P:

$$\mathrm{d}\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\right)_P \mathrm{d}T + \left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T \mathrm{d}P. \tag{SI-13}$$

The derivative of this quantity with respect to T along the density anomaly path in pressure and temperature space is:

$$\begin{aligned}\left(\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\partial V}{\partial T}\right)_P\right)_{\rho_{\mathrm{extr}}} &= \\ &= \left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P\right)_P + \left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}} \\ &= \left(\frac{\partial^2 V}{\partial T^2}\right)_P + \left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}}.\end{aligned} \tag{SI-14}$$

Note that, at the density anomaly, the condition $\left(\frac{\partial V}{\partial T}\right)_P = 0$ is satisfied and so the left side of equation SI-14 is zero. As a result, it becomes:

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right)_T = -\frac{\left(\frac{\partial^2 V}{\partial T^2}\right)_P}{\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}}}, \tag{SI-15}$$

which we can rewrite to obtain an expression for the gradient of the TMD (or TminD) line:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}} = -\frac{\left(\dfrac{\partial^2 V}{\partial T^2}\right)_P}{\dfrac{\partial^2 V}{\partial P\,\partial T}}. \tag{SI-16}$$

C. The Density Anomaly loci in the VT projection.

We now follow the analogous procedure starting from the alternative definition for the density anomaly to find the gradient in the VT projection:

$$\mathrm{d}\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V\right)_V \mathrm{d}T + \left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T \mathrm{d}V. \tag{SI-17}$$

We evaluate along the density anomaly path and divide by $\mathrm{d}T$:

$$0 = \left(\frac{\partial^2 P}{\partial T^2}\right)_V + \left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T \left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}}, \tag{SI-18}$$

giving

$$\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}} = -\frac{\left(\dfrac{\partial^2 P}{\partial T^2}\right)_V}{\dfrac{\partial^2 P}{\partial V\,\partial T}}. \tag{SI-19}$$

Finally we want to find the link between the gradients in the PT and VT projections as this will be crucial for our efforts in identifying scenarios for collision between these two lines. We start by expanding the differential of P:

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}T. \tag{SI-20}$$

Dividing both sides by $\mathrm{d}T$ and evaluating along the density anomaly path gives:

$$\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}} = \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}} \left(\frac{\partial V}{\partial P}\right)_T = -VK_T \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}}. \tag{SI-21}$$

This indicates that the sign of the gradient of the density anomaly locus and the general trends in the VT and PT projections are equivalent but with inverted signs (as K_T and V are always positive).

D. The second derivative of the density anomaly locus.

We want to derive an expression for the second derivative of the density anomaly locus. Consider the second order differential of P:

$$\mathrm{d}^2 P = \left(\frac{\partial^2 P}{\partial T^2}\right)_V \mathrm{d}T^2 + 2\frac{\partial^2 P}{\partial T \partial V}\mathrm{d}T\mathrm{d}V + \left(\frac{\partial^2 P}{\partial V^2}\right)_T \mathrm{d}V^2, \tag{SI-22}$$

dividing by $\mathrm{d}T^2$ to obtain:

$$\begin{aligned}\left(\frac{\mathrm{d}^2 P}{\mathrm{d}T^2}\right)_{\rho_{\mathrm{extr}}} &= \left(\frac{\partial^2 P}{\partial T^2}\right)_V + 2\frac{\partial^2 P}{\partial T \partial V}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\rho_{\mathrm{extr}}} \\ &+ \left(\frac{\partial^2 P}{\partial V^2}\right)_T \left(\frac{\mathrm{d}^2 V}{\mathrm{d}T^2}\right)_{\rho_{\mathrm{extr}}}.\end{aligned} \tag{SI-23}$$

Using equation SI-19 gives

$$\left(\frac{\mathrm{d}^2 P}{\mathrm{d}T^2}\right)_{\rho_{\mathrm{extr}}} = -\left(\frac{\partial^2 P}{\partial T^2}\right)_V + \left(\frac{\partial^2 P}{\partial V^2}\right)_T \left(\frac{\mathrm{d}^2 V}{\mathrm{d}T^2}\right)_{\rho_{\mathrm{extr}}} . \tag{SI-24}$$

We can finally rearrange to obtain:

$$\left(\frac{\mathrm{d}^2 P}{\mathrm{d}T^2}\right)_{\rho_{\mathrm{extr}}} + \left(\frac{\partial^2 P}{\partial T^2}\right)_V = \left(\frac{\partial^2 P}{\partial V^2}\right)_T \left(\frac{\mathrm{d}^2 V}{\mathrm{d}T^2}\right)_{\rho_{\mathrm{extr}}} . \tag{SI-25}$$

III. COMPRESSIBILITY ANOMALIES.

In order to explore the behaviour of compressibility anomalies we start by differentiating the definition of the compressibility with respect to temperature at constant pressure:

$$\begin{aligned}
\left(\frac{\partial K_T}{\partial T}\right)_P &= -\left(\frac{\partial}{\partial T}\left(\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\right)\right)_P \\
&= -\left(\frac{\partial \frac{1}{V}}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V}\left(\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right)_P \\
&= -\left(\frac{\partial \frac{1}{V}}{\partial V}\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V}\frac{\partial^2 V}{\partial P_T \partial T_P} \\
&= \frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V}\frac{\partial^2 V}{\partial P \partial T} \\
&= -K_T \alpha_P - \frac{1}{V}\frac{\partial^2 V}{\partial P \partial T},
\end{aligned} \tag{SI-26}$$

where $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ is the thermal expansion coefficient which is zero at density anomaly.

A. The nature of the Compressibility Anomaly.

Another key expression to monitor is the second derivative of the compressibility with respect to T. We can evaluate it by differentiating the end result of equation SI-26 with respect to T:

$$\begin{aligned}
\left(\frac{\partial^2 K_T}{\partial T^2}\right)_P &= \frac{\alpha_P}{V}\frac{\partial^2 V}{\partial T \partial P} - \frac{1}{V}\frac{\partial^3 V}{\partial T^2 \partial P} \\
&\quad - \alpha_P \left(\frac{\partial K_T}{\partial T}\right)_P - K_T \left(\frac{\partial \alpha_P}{\partial T}\right)_P .
\end{aligned} \tag{SI-27}$$

Evaluating this expression at the compressibility anomaly is useful for monitoring the conditions at which the compressibility minimum changes to a maximum (and vice versa):

$$\left(\frac{\partial^2 K_T}{\partial T^2}\right)_P = -\alpha_P^2 K_T - \frac{1}{V}\frac{\partial^3 V}{\partial T^2 \partial P} - K_T \left(\frac{\partial \alpha_P}{\partial T}\right)_P . \tag{SI-28}$$

If we expand the final term by differentiating the definition of the thermal expansion coefficient we see that:

$$\begin{aligned}
\left(\frac{\partial^2 K_T}{\partial T^2}\right)_P &= -\alpha_P^2 K_T - \frac{1}{V}\frac{\partial^3 V}{\partial T^2\, \partial P} \\
&\quad + K_T \alpha_P^2 - \frac{K_T}{V}\left(\frac{\partial^2 V}{\partial T^2}\right)_P \\
&= -\frac{1}{V}\frac{\partial^3 V}{\partial T^2\, \partial P} - \frac{K_T}{V}\left(\frac{\partial^2 V}{\partial T^2}\right)_P .
\end{aligned} \tag{SI-29}$$

B. The gradient of Compressibility anomalies.

Next we investigate the gradient of the compressibility anomalies. We start by writing the differential of the condition for the compressibility anomaly:

$$\mathrm{d}\left(\frac{\partial K_T}{\partial T}\right)_P = \left(\frac{\partial^2 K_T}{\partial T^2}\right)_P \mathrm{d}T + \frac{\partial^2 K_T}{\partial T \partial P}\mathrm{d}P = 0. \tag{SI-30}$$

We divide both sides by $\mathrm{d}T$ to obtain:

$$0 = \left(\frac{\partial^2 K_T}{\partial T^2}\right)_P + \frac{\partial^2 K_T}{\partial T\,\partial P}\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{K_T^{\mathrm{extr}}}, \tag{SI-31}$$

and so

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{K_T^{\mathrm{extr}}} = -\frac{\left(\frac{\partial^2 K_T}{\partial T^2}\right)_P}{\frac{\partial^2 K_T}{\partial T\,\partial P}}. \tag{SI-32}$$

In order to evaluate the gradient of the compressibility anomaly locus we can expand equation SI-32. We expand the $\frac{\partial^2 K_T}{\partial T\,\partial P}$ term by starting from equation SI-26:

$$\begin{aligned}\frac{\partial}{\partial P}\left(\frac{\partial K_T}{\partial T}\right)_P = \frac{\partial^2 K_T}{\partial T \partial P} = -\frac{K_T}{V}\frac{\partial^2 V}{\partial T \partial P} - \frac{1}{V}\frac{\partial^3 V}{\partial T \partial P^2}\\ - \alpha_P\left(\frac{\partial K_T}{\partial P}\right)_T - K_T\left(\frac{\partial \alpha_P}{\partial P}\right)_T.\end{aligned} \tag{SI-33}$$

At the compressibility anomaly,

$$-\frac{1}{V}\frac{\partial^2 V}{\partial T \partial P} = K_T \alpha_P, \tag{SI-34}$$

from equation SI-26 and $\left(\frac{\partial \alpha_P}{\partial P}\right)_T = -\left(\frac{\partial K_T}{\partial T}\right)_P$. This is easily provable by comparing equation SI-26 with that obtained by differentiating α_P. As a result, we obtain:

$$\frac{\partial^2 K_T}{\partial T\,\partial P} = -\frac{1}{V}\frac{\partial^3 V}{\partial T \partial P^2} - \alpha_P\left(\frac{\partial K_T}{\partial P}\right)_T + K_T^2 \alpha_P. \tag{SI-35}$$

Lastly we can expand the compressibility derivative ($\alpha_P\left(\frac{\partial K_T}{\partial P}\right)_T = \alpha_P K_T^2 - \frac{\alpha_P}{V}\left(\frac{\partial^2 V}{\partial P^2}\right)_T$) to obtain a more compact form:

$$\frac{\partial^2 K_T}{\partial T\,\partial P} = -\frac{1}{V}\frac{\partial^3 V}{\partial T\,\partial P^2} + \frac{\alpha_P}{V}\left(\frac{\partial^2 V}{\partial P^2}\right)_T. \tag{SI-36}$$

We now insert this expression into equation SI-32:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{K_T^{\mathrm{extr}}} = -\frac{\left(\frac{\partial^2 K_T}{\partial T^2}\right)_P}{-\frac{1}{V}\frac{\partial^3 V}{\partial T\,\partial P^2} + \frac{\alpha_P}{V}\left(\frac{\partial^2 V}{\partial P^2}\right)_T}. \tag{SI-37}$$

We can also insert the second derivative of K_T expression (equation SI-29) into the above expression to obtain:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{K_T^{\mathrm{extr}}} = \frac{\frac{\partial^3 V}{\partial T^2\,\partial P} + K_T\left(\frac{\partial^2 V}{\partial T^2}\right)_P}{\frac{\partial^3 V}{\partial T\,\partial P^2} - \alpha_P\left(\frac{\partial^2 V}{\partial P^2}\right)_T}. \tag{SI-38}$$

IV. HEAT CAPACITY ANOMALIES.

A. An Alternative Heat Capacity anomaly condition.

We start from the definition of the heat capacity anomaly:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = T\frac{\partial^2 S}{\partial P \partial T} = 0. \tag{SI-39}$$

Consider now the differential of the Gibbs free energy $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$. Following the approach of Rebelo *et al*[3] we can partially differentiate the Gibbs free energy with respect to T twice and P once to obtain:

$$\frac{\partial^3 G}{\partial T^2 \partial P} = -\frac{\partial^2 S}{\partial P \partial T} = -\frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T. \tag{SI-40}$$

If we now change the order of partial differentiation (which we are allowed to do according to Schwartz's theorem) we can obtain:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = T\frac{\partial^2 S}{\partial P \partial T} = -T\frac{\partial^3 G}{\partial P \partial T^2} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P. \tag{SI-41}$$

To obtain the second derivative of the heat capacity we differentiate the definition of the heat capacity anomaly with respect to pressure to obtain:

$$\left(\frac{\partial^2 C_P}{\partial P^2}\right)_T = \left(\frac{\partial T}{\partial P}\right)_T \frac{\partial^2 S}{\partial P\,\partial T} + T\frac{\partial^3 S}{\partial P^2\,\partial T} = T\frac{\partial^3 S}{\partial P^2\,\partial T} \tag{SI-42}$$

or if we use the alternative definition we obtain:

$$\left(\frac{\partial^2 C_P}{\partial P^2}\right)_T = -\left(\frac{\partial T}{\partial P}\right)_T \left(\frac{\partial^2 V}{\partial T^2}\right)_P - T\frac{\partial^3 V}{\partial P\,\partial T^2} = -T\frac{\partial^3 V}{\partial P\,\partial T^2}. \tag{SI-43}$$

B. The gradient of the Heat Capacity anomaly.

We start by expressing the differential of the condition for the heat capacity anomaly:

$$\mathrm{d}\left(\frac{\partial C_P}{\partial P}\right)_T = \left(\frac{\partial^2 C_P}{\partial P^2}\right)_T \mathrm{d}P + \frac{\partial^2 C_P}{\partial P\,\partial T}\mathrm{d}T \tag{SI-44}$$

Next, we divide the whole expression by $\mathrm{d}T$ and take the path of the compressibility anomaly to eliminate the left hand side:

$$0 = \left(\frac{\partial^2 C_P}{\partial P^2}\right)_T \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{C_P^{\mathrm{extr}}} + \frac{\partial^2 C_P}{\partial P\,\partial T}. \tag{SI-45}$$

Rearranging we obtain the expression for the gradient of the heat capacity anomaly in the PT projection:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{C_P^{\mathrm{extr}}} = -\frac{\dfrac{\partial^2 C_P}{\partial P\,\partial T}}{\left(\dfrac{\partial^2 C_P}{\partial P^2}\right)_T} \tag{SI-46}$$

To obtain the full expression for the gradient of the heat capacity anomaly we expand the mixed derivative:

$$\frac{\partial^2 C_P}{\partial T \partial P} = \frac{\partial^2 S}{\partial P \partial T} + T\frac{\partial^3 S}{\partial P \partial T^2} = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P - T\left(\frac{\partial^3 V}{\partial T^3}\right)_P. \tag{SI-47}$$

At the heat capacity anomaly $\left(\dfrac{\partial^2 V}{\partial T^2}\right)_P = \dfrac{\partial^2 S}{\partial P\,\partial T} = 0$ (as evident from equation SI-41). If we insert this condition into the previous equation (SI-47) we obtain:

$$\frac{\partial^2 C_P}{\partial T\,\partial P} = -T\left(\frac{\partial^3 V}{\partial T^3}\right)_P. \tag{SI-48}$$

Inserting this into equation SI-46 gives:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{C_P^{\mathrm{extr}}} = -T\frac{\dfrac{\partial^3 S}{\partial P\,\partial T^2}}{\left(\dfrac{\partial^2 C_P}{\partial P^2}\right)_T} = T\frac{\left(\dfrac{\partial^3 V}{\partial T^3}\right)_P}{\left(\dfrac{\partial^2 C_P}{\partial P^2}\right)_T}. \tag{SI-49}$$

We have obtained the link between the gradient of the heat capacity anomaly locus and the nature of the anomaly (in terms of it being a minima or maxima). Using equation SI-43 and equation SI-42 we obtain:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{C_P^{\mathrm{extr}}} = -\frac{\dfrac{\partial^3 S}{\partial P\,\partial T^2}}{\dfrac{\partial^3 S}{\partial P^2\,\partial T}} = -\frac{\left(\dfrac{\partial^3 V}{\partial T^3}\right)_P}{\dfrac{\partial^3 V}{\partial T^2\,\partial P}}. \tag{SI-50}$$

[1] P. G. Debenedetti and M. C. D'Antonio, The Journal of Chemical Physics **84**, 3339 (1986).
[2] S. Sastry, P. G. Debenedetti, F. Sciortino, and H. E. Stanley, Phys. Rev. E **53**, 6144 (1996).
[3] L. P. N. Rebelo, P. G. Debenedetti, and S. Sastry, Journal of Chemical Physics **109**, 626 (1998).