Landau theory of first order phase transitions

Examples on Water and P(VDF:TrFE)

This text deals with finding parameters for Landau's theory of phase transitions like it is explained on:
http://lamp.tu-graz.ac.at/~hadley/ss2/landau/first_order.php.

Starting from the expanded free energy,

$$f(T) = f_0(T) + \alpha_0(T - T_c)m^2 + \frac{1}{2}\beta m^4 + \frac{1}{3}\gamma m^6$$

three parameters have to be calculated:

$$\alpha_0 > 0 \qquad \beta < 0 \qquad \gamma > 0$$

The idea is to do this out of the „jumps" in the different thermodynamic properties.

Water - Vapor

Order parameter for this phase transition is the density.
To calculate the three Landau-parameters, at least 3 thermodynamic properties at the critical temperature have to be known. I chose density, latent heat and specific heat.
In the following, the formulas used:

$$\Delta m = \sqrt{\frac{-\beta}{\gamma}} \qquad L = T\Delta s = \frac{\alpha_0 \beta T_c}{\gamma} \qquad \Delta c_v = \frac{\alpha_0^2 T_c}{\beta}$$

Water is well known, so data can be found easily online. I used these webpages as sources;

- http://en.wikipedia.org/wiki/Water_(data_page)
- http://en.wikipedia.org/wiki/Latent_heat#Table_of_latent_heats
- http://physchem.kfunigraz.ac.at/sm/Service/Water/H2Ocv.htm

and derived for the jump in density $\Delta m = 957.7526 \frac{kg}{m^3}$, for the latent heat $L = 2260 \frac{kJ}{kg}$ and for the jump in specific heat $\Delta c_v = 2288 \frac{J}{kgK}$.

Used in the above formulas, one gets for the Landau-parameters:

$$\alpha_0 = \frac{L}{T_c \Delta m^2} = 0.0066$$

$$\beta = \frac{\alpha_0^2 T_c}{\Delta c_v} = -7.1128 * 10^{-6}$$

$$\gamma = \frac{-\beta}{\Delta m^2} = 7.7541 * 10^{-12}$$

And for T_1

$$T_1 = \frac{\beta^2}{4\alpha_0 \gamma} + T_c = 620.3\ K$$

a value which is very close to the critical point at 647 K.

Also the temperature dependence of the high temperature free energy term can be fitted. This was also done with data from http://en.wikipedia.org/wiki/Water_(data_page)#Standard_conditions (see Figure 1) and resulted in an 2nd degree polynomial fit:

$$f_0(T) = -1.4 * T^2 - 7056 * T + 2.6 * 10^6$$

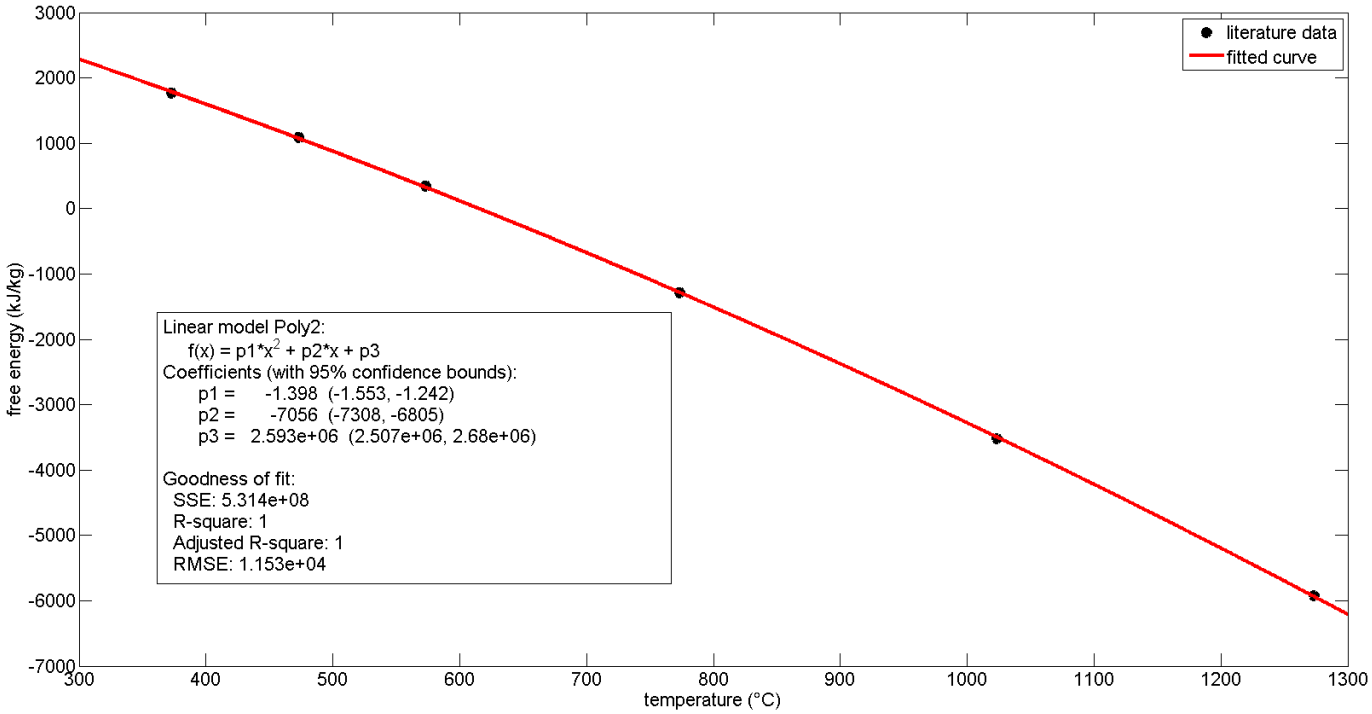
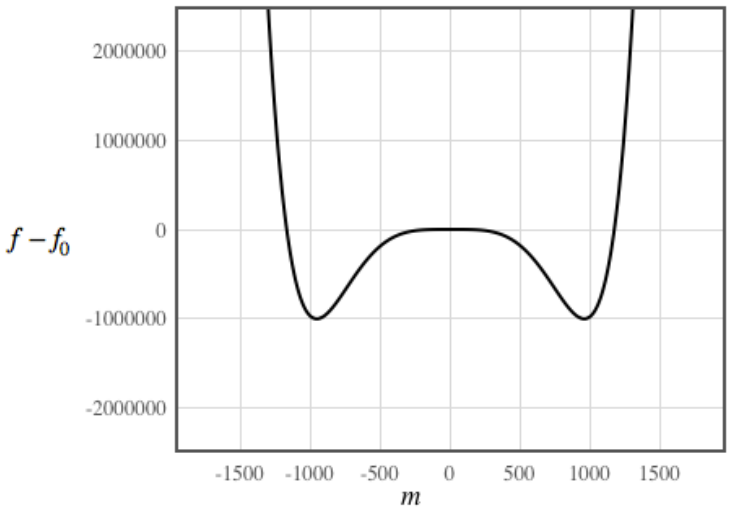


Figure 1: Fitting of the free energy F of vapor.

Now everything is available to fill in the form on http://lamp.tu-graz.ac.at/~hadley/ss2/landau/first_order.php



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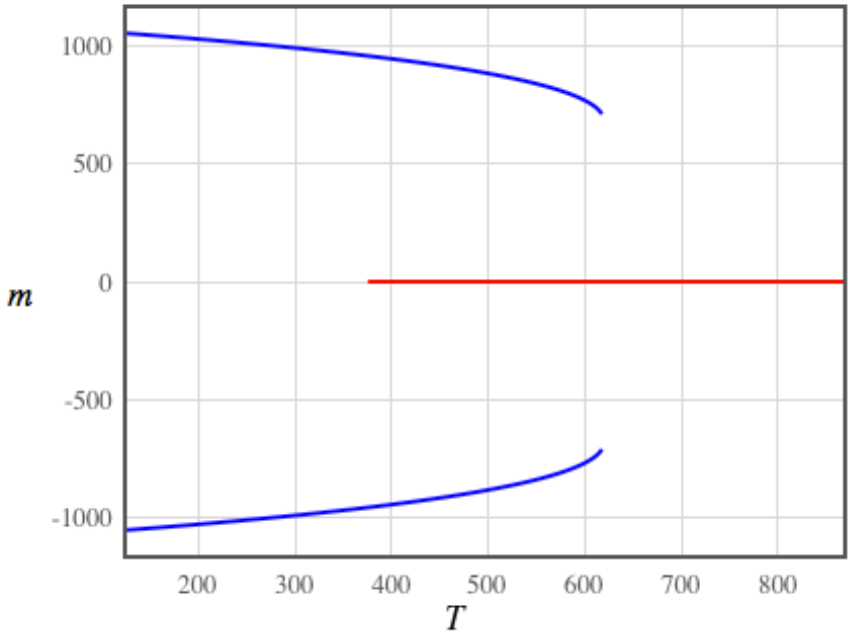

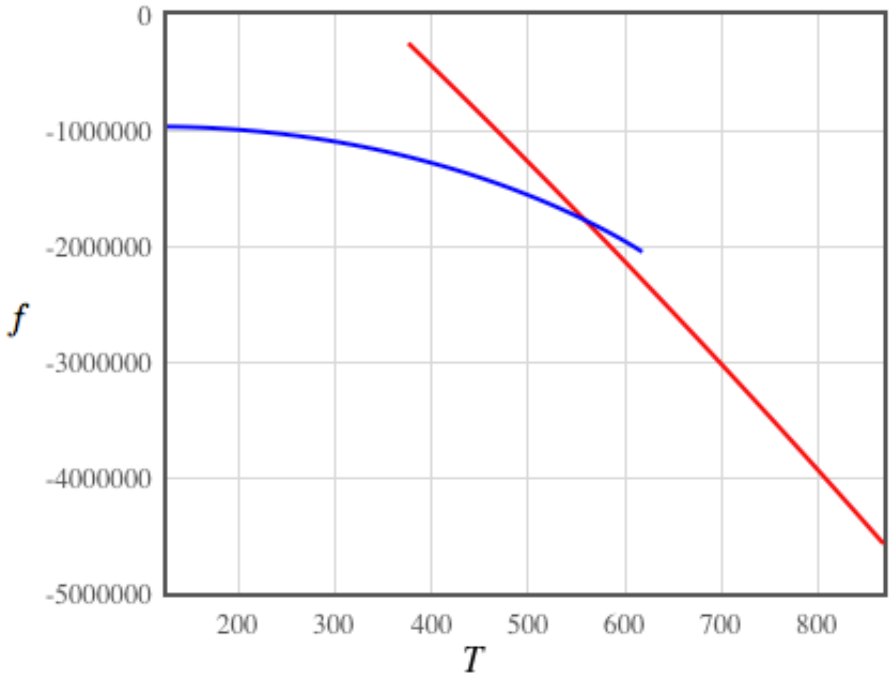

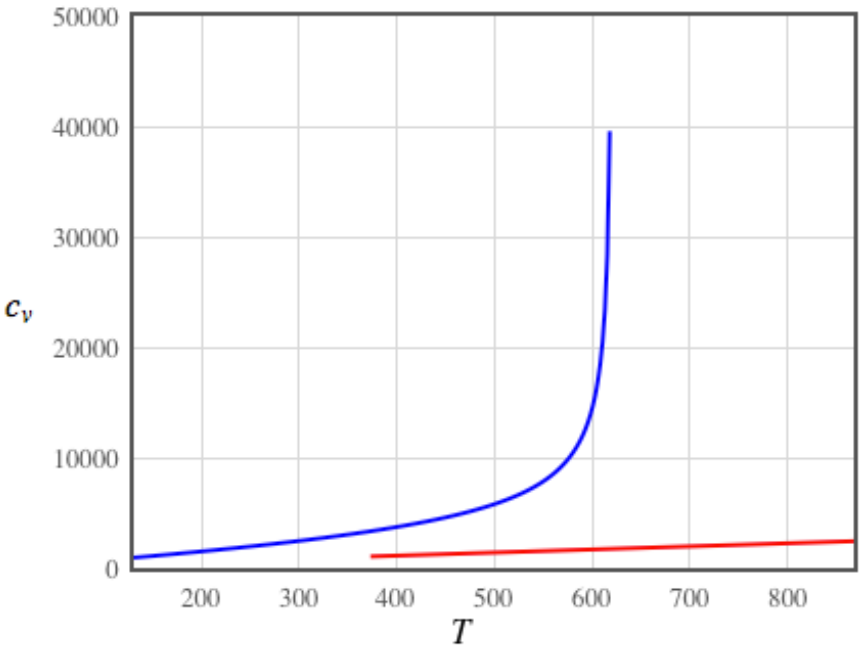
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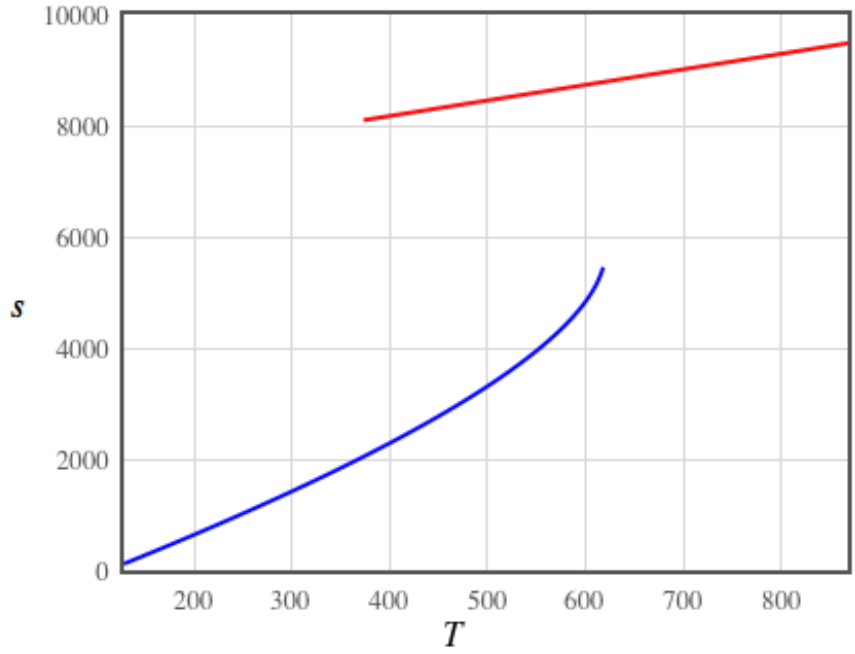
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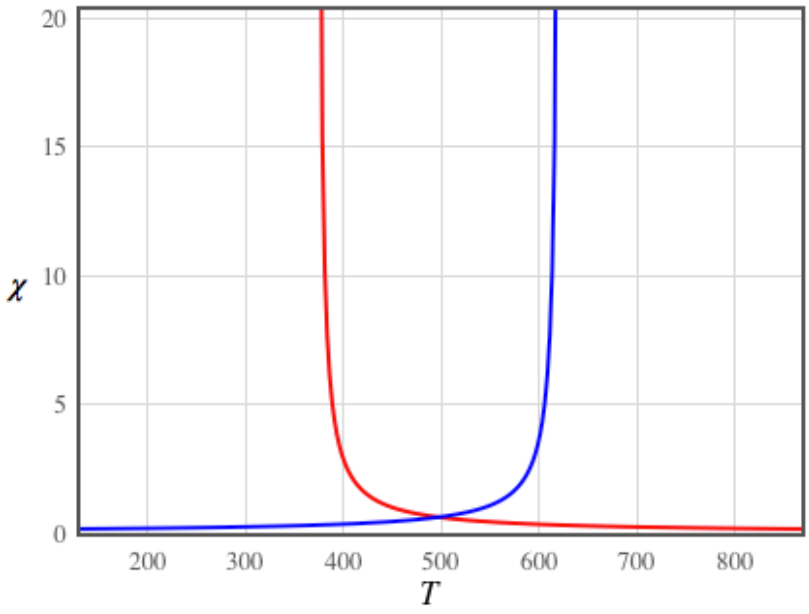
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P(VDF:TrFE) - ferroelectric to paraelectric phase transition

P(VDF:TrFE) is a widely used ferroelectric material and shows a transition to a paraelectric phase at around 60 °C.
This phase transition was calculated for a commercial 60/40 wt% P(VDF:TrFE) film. The data used is taken from: **A Navid, C S Lynch, L Pilon;** *Purified and porous poly(vinylidene fluoride-trifluorethylene) thin films for pyroelectric infrared sensing and energy harvesting*, Smart Mater. Struct. 19 (2010)
The calculations done here differ in such way, that instead of a latent heat, the two transition temperatures T_c = 333 K and T_1 = 339 K where used.

Order parameter is the polarization P, which is not measured directly in the paper, but can be derived through the pyroelectric coefficient p;

$$p = \left(\frac{\partial D}{\partial T} \right)_{\sigma, E} \qquad D = \epsilon_0 E + P$$

$$p_{T_c} = 11.76 * 10^{-5} \frac{C}{m^2 K} \rightarrow \Delta D = 0.0392 \frac{C}{m^2}$$

Biggest source of error is definitely the specific heat, which i had to read out of Figure 3 in the paper, because the summarized data in Table 1 is only given in steps of 5 °C and doesn't hit the peak at its maximum. So the jump in specific heat is approximately

$$\Delta c_v = 2400 \frac{J}{kgK}$$

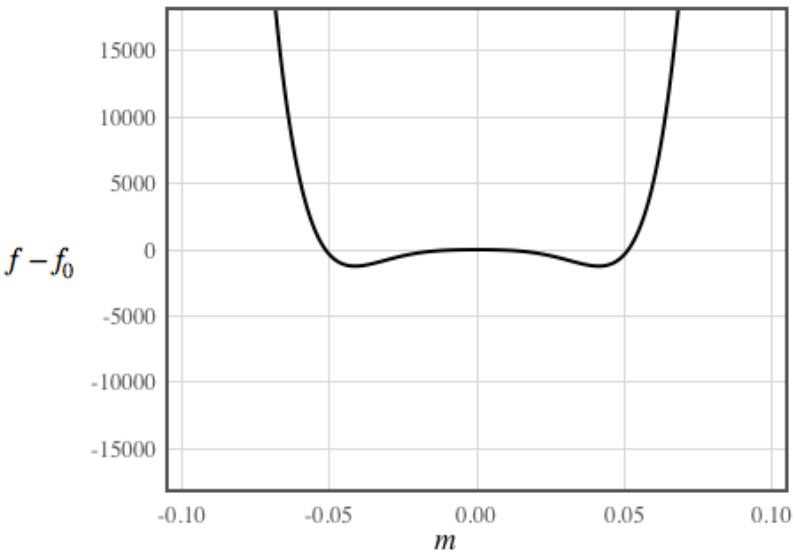
The calculations of the Landau-coefficients yield then:

$$\alpha_0 = \frac{4 * \Delta c_v * (T_1 - T_c)}{T_c * \Delta D^2} = 1.1257 * 10^5$$

$$\beta = \frac{\alpha_0^2 * T_c}{\Delta c_v} = -1.7582 * 10^9$$

$$\gamma = \frac{-\beta}{\Delta D^2} = 1.1442 * 10^{12}$$

As P(VDF:TrFE) is also in its paraelectric phase an insulator, the free energy goes with $-T^4$. The value used as input on http://lamp.tu-graz.ac.at/~hadley/ss2/landau/first_order.php is only a guess.



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$\beta =$ -1.7582e9
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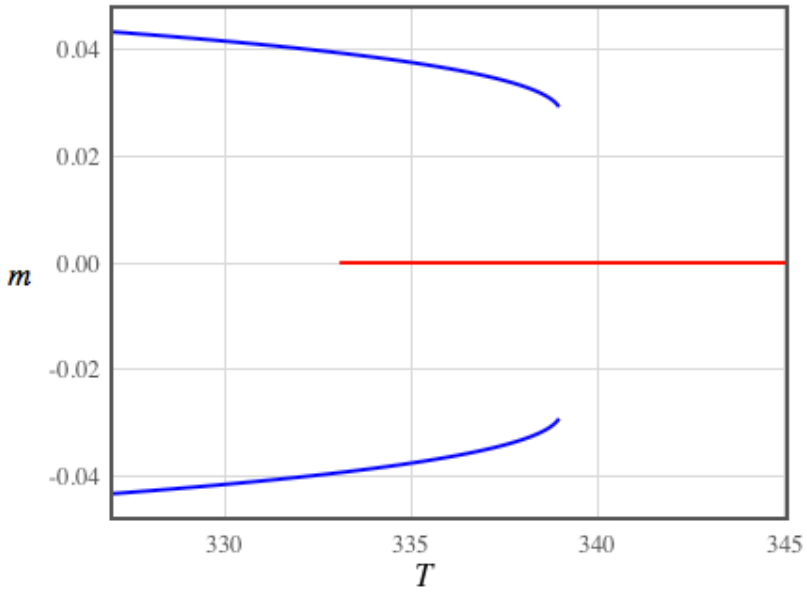
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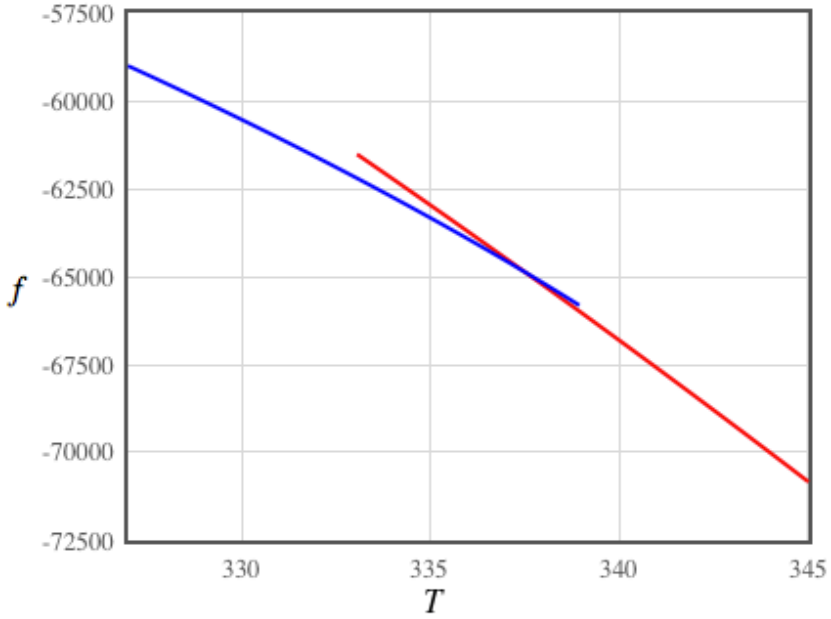
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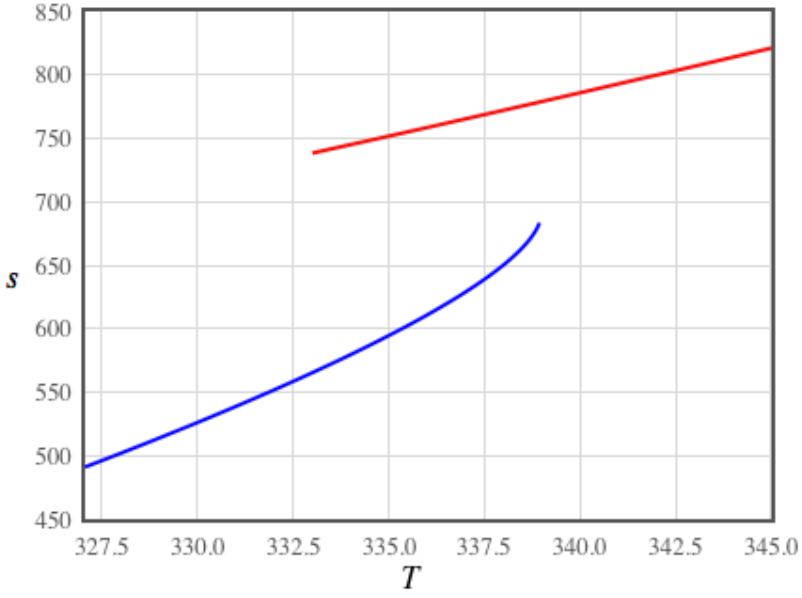
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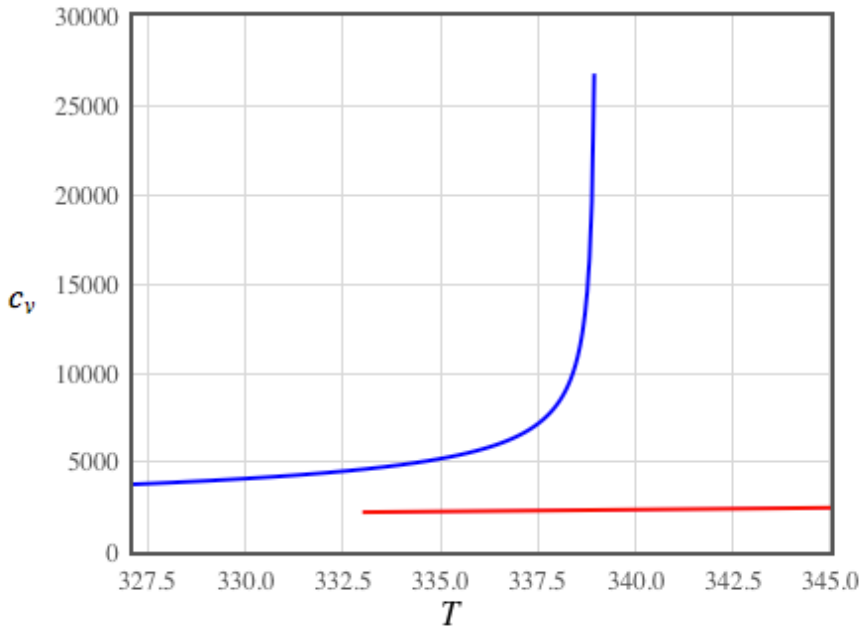
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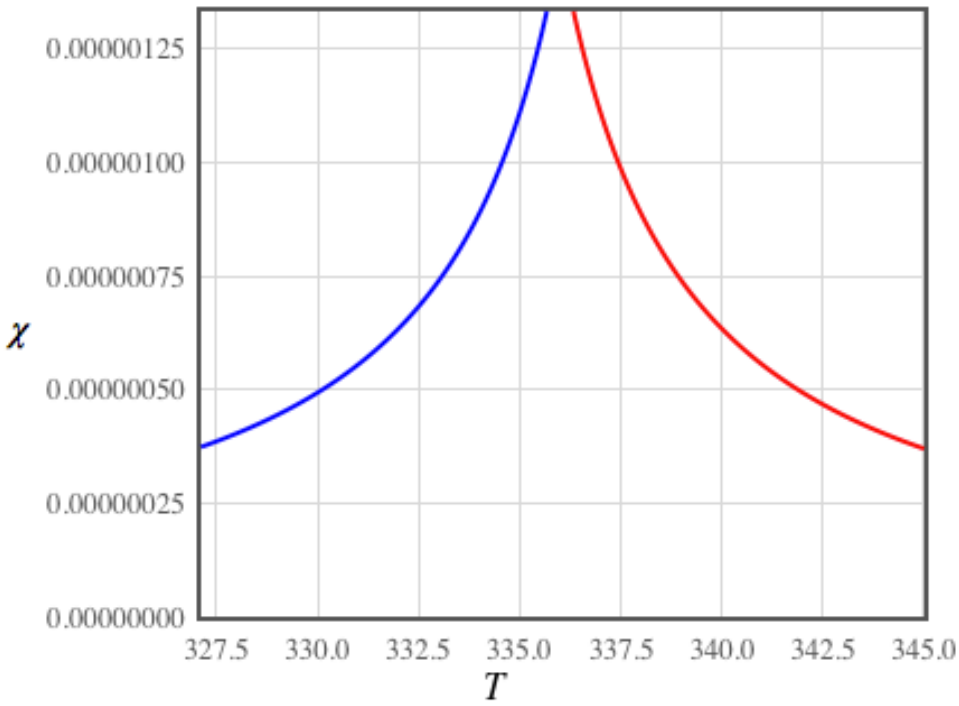
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