Limit of Superheat of Polystyrene-Cyclohexane Solutions: Theory

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Abstract

A theory for the surface tension of polymer solutions is used along with classical nucleation theory to predict the temperature rise above the solvent limit of superheat due to addition of polymer. Polystyrene, of 2000, 4000, 50,000 and 100,000 molecular weight, was added to cyclohexane and it produced a linear rise in the superheat near weight fraction = 0 to an extent that depends upon both molecular weight and concentration. So far, there has been limited progress in understanding homogeneous nucleation in polymer solutions from a theoretical standpoint. The theory presented here is used in the athermal case (dT = 0) to give the temperature rise with respect to weight fraction, which is inversely proportional to the molecular weight of the polymer, and the agreement with the data is rather good.

Keywords: Polymer solutions; nucleation; surface thermodynamics; limit of superheat.

1. Aims and scope

When a liquid is heated in its pure condition, it is possible to raise the temperature to about 0.89 of its critical point in degrees Kelvin, well above its boiling point for one atmosphere, and then it explosively vaporizes. Classical nucleation theory (Frenkel, 1955) predicts this, and there are many liquids (Blander and Katz, 1975) that show this effect. Early work on the surface tension for polymer solutions was by Prigogine and Marechal (1952).

There are a number of groups that have gathered data concerning bubble nucleation in polymer solutions. Han and Han I (1990) used laser light scattering for polystyrene in toluene, and then did a theoretical study to analyze the results, Han and Han II (1990). Also, Kim, et al (2004) solve a molecular cluster model to predict bubble nucleation in polymer solutions among other things. Guo, et al (2012) have looked at CO2 bubble nucleation in polystyrene and modeled it using an extension of diffuse interface theory, but they remark that classical nucleation theory is most successful for quantifying the process of nucleation and that limited progress has been made on this topic. Devolatilization of different kinds of polymer melts was studied by Yarin, et al (1999) for homogeneous nucleation and they said that the bubble growth is controlled by momentum transfer and diffusion.

These treatments are complicated and I opt here to have a simple model, which looks at the bulk quantities and appears to predict homogeneous nucleation for polymer solutions in general. It would seem that companies processing polymer solutions and those studying nucleation theory would show interest, because this theory predicts the temperature rise fairly accurately and gives the proper trend for high molecular weight polymer.

2. Measurements

Jennings and Middleman (1985) collected data on this phenomenon for polystyrene-cyclohexane solutions of molecular weight 2000 to 100,000 for the polymer. There are various figures in their paper (see Appendix for polymer solution data). In Figure 1, there appears the linear rise in superheat for Pentane with addition of cyclohexane, by mass fraction. Figure 2 shows the same linear effect with addition of styrene monomer, MW=2000 polystyrene and MW=4000 polystyrene. Figure 3 shows the same effect for MW=50,000 and 100,000 and the initial rise is small, so it was felt that the additional steeper rise was due to the effect known as LCST or lower critical solution temperature; this was noted in Jennings and Middleman. There is some data for polystyrene/benzene solutions of various molecular weights that was gathered by Prud'homme and Gregory (1985) using a similar apparatus to Jennings and Middleman. The data from Prud'homme and Gregory do not show a very straight linear rise of temperature with respect to molecular weight and at high molecular weight the temperature of nucleation drops off to a considerable degree, so their data cannot be compared with the final equation in this paper.

3. Theory

According to Blander and Katz there is the following expression for the rate of nucleation J (number of bubbles formed per cm³ per second).

$$J \approx 3.73 \ (10^{35}) \ [d^2 \ \sigma \ / \ M^3 \ B]^{1/2} \ exp \ [-1.182 \ (10^5) \ \sigma^3 \ /(T \ (P_V - P_L)^2) \]$$
(1)

d is the liquid density, σ is the surface tension, M is the molecular weight of solvent, B is a correction factor (equation (6) below), T is the temperature in degrees Kelvin, P_V is the vapor pressure of the escaping gas molecules and P_L is the hydrostatic pressure on the droplet of solution.

The polymer is non-volatile and the "bubble surface gains or loses molecules" of molecular weight M (Blander and Katz). At a certain value of J nucleation takes place at the limit of superheat T_1 and we would expect J to be equal among the four molecular weights of polymer as the concentration of polymer approaches zero. This treatment proves that only what happens on the surface of the nucleating bubble matters. Blander and Katz say there is a Poynting correction factor δ that relates the vapor pressure of the superheated liquid, P_V , to the equilibrium vapor pressure, Pe, for small values of P_L , which is in this case atmospheric pressure. For this system, Pe = 17.433 atm and $P_L = 1$ atm, so this is satisfied, as $P_L / Pe = 0.057$. The Poynting correction factor is δ .

$$\delta = (\mathbf{P}_{\mathrm{V}} - \mathbf{P}_{\mathrm{L}}) / (\mathbf{P}\mathbf{e} - \mathbf{P}_{\mathrm{L}})$$
(2)

Assuming the gas is ideal in the equation, $d_G = Pe MW_1/RT_1$, and

$$\delta \approx 1 - V_L / Ve + \frac{1}{2} (V_L / Ve)^2$$

= 1 - d_G / d + 0.5 (d_G / d)² (3)

where the volumes and densities are for the liquid and gas in equilibrium. Blander and Katz give a proof for equation (3) and say it is generally accurate up to one atmosphere pressure, the condition in which the data was collected by Jennings and Middleman.

When considering bubble nucleation for polymer solutions it seems that one should only look at the surface layer from which the solvent molecules are either escaping or adhering. Accordingly, the density would be the volume fraction weighted sum at the surface of the respective densities and the equilibrium vapor pressure would be directly proportional to the volume fraction of solvent at the surface. In polymer solutions, nucleation depends only on what is happening near the surface, so the density is essentially the density of the solvent and the equilibrium vapor pressure follows Raoult's Law.

$$d = d_1 \phi_{1S} + d_2 \phi_{2S} = d_1 + (d_2 - d_1) \phi_{2S}$$
(4)

$$Pe = Pe(0) \phi_{1S} = Pe(0) (1 - \phi_{2S})$$
(5)

 ϕ_{1S} and ϕ_{1} and are the surface and interior volume fractions of solvent (the subscript 2 refers to the polymer). This is because the surface is the only thing the nucleating bubble "sees" and the rest of the interior could be regarded as having the same concentration as the surface. According to calculations made by Siow and Patterson (1973), for preferential solvent adsorption, $\sigma_2 > \sigma_1$, the adsorption isotherm (in their Fig. 1) hardly changes with molecular weight above molecular weight 2500, so the surface volume fraction of polymer is essentially zero all the way up to $\varphi_2 =$ 0.3. When $\sigma_2 - \sigma_1 \approx 22$ dyne/cm there obtains preferential solvent adsorption, so in that case "there is little qualitative difference between the surface thermodynamics of a polymer solution and a mixture of spherical molecules". (The data that Jennings and Middleman gathered was only up to about weight fraction 0.3 and above that for high MW it was felt that the LCST phenomenon took over.) Below in Eq. (10) this is made quantitative.

In the equation for $J = A \exp(K)$ there is also a correction factor B which has little effect on the limit of superheat because for J large errors in the prefactor A "lead to very small errors in predictions of the superheats needed to cause homogeneous nucleation" (Blander and Katz).

$$B \approx 1 - 1/3 (1 - P_L/P_V)$$
 (6)

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The B factor accounts for the fact that the bubble is in mechanical equilibrium, is close to 2/3, and for the purposes of its calculation, $P_V = Pe$, as it has a negligible effect on the temperature of nucleation. The δ correction factor is needed because the nucleating droplet is under pressure $P_L = 1$ atm pressure (other than its equilibrium vapor pressure Pe) and must be included as it is in the exponent. It will be seen later that δ and the equilibrium vapor pressure drop out of the calculation for these polymer solutions.

The following two equations apply for the athermal case (dT = 0) by the theory of Siow and Patterson for polymer solutions, where a = surface area of the solvent molecule and r = ratio of the molar volume of the polymer to that of the solvent. Eq. (7) gives the surface tension and Eq. (8) relates the surface and interior volume fractions.

$$(\sigma - \sigma_1) a / kT = \ln (\phi_{1S} / \phi_1) + ((r - 1) / r) (\phi_{2S} - \phi_2)$$
(7)

$$\ln[(\phi_{2S} / \phi_2)^{1/r} / (\phi_{1S} / \phi_1)] = (\sigma_1 - \sigma_2) a / kT$$
(8)

Near $\varphi_2 = 0$, Eq. (7) becomes

$$\partial \sigma / \partial \phi_2 = \mathbf{k} \mathbf{T} / \mathbf{ra}$$
 (9)

Near $\varphi_2 = 0$, Eq. (8) becomes

$$\varphi_{2S} = \varphi_2 \exp\left[r\left(\sigma_1 - \sigma_2\right)a / kT\right]$$
(10)

Putting in the numbers, $\partial \phi_{2S} / \partial \phi_2 \approx 10^{-38}$ (for MW = 2000, r = 13.4) and even less for higher MW. Thus, polymer is present in vanishingly small volume fraction in the surface for $w_2 \leq 0.3$ for which there is data. That is why the density and vapor pressure only apply to what is at the surface. The gas molecules escape or adhere to the surface of a bubble nucleating in the interior of the rising droplet of solution.

So, the following equations are true: $\partial \delta / \partial \phi_2 = 0$, $\partial d / \partial \phi_2 = 0$, $\partial P e / \partial \phi_2 = 0$, and $\partial B / \partial \phi_2 = 0$ for w_2 near 0. The rate of nucleation is of the form $J = A \exp(K)$ and $(\partial \ln A / \partial w_2)/(\partial K / \partial w_2)$ and $(\partial \ln A / \partial T)/(\partial K / \partial T)$ are both small near the origin (0, T₁). It turns out that they both are about 0.2% and that establishes for any ray emanating from the origin, $\Delta J = J \Delta K$, so $\Delta J = 0 \rightarrow \Delta K = 0$. Therefore K can be taken as a constant where the 2000, 4000, 50,000 and 100,000 curves meet. An expression for $\partial T / \partial w_2$ can be derived from the fact that K dominates in nucleation and that is done in this theory.

For the weight fraction, this ratio is independent of the molecular weights and surface area of the solvent molecule. It is simply:

$$\lim w_2 \rightarrow 0 \ (\partial \ln A / \partial w_2) / (\partial K / \partial w_2) = 1 / (6K) = -0.24\%$$
(11)

In the temperature direction, there are a number of terms, as each parameter depends on temperature. These expressions are for $T \rightarrow T_1$. See Appendix for values of parameters and partial derivatives.

$$\partial \ln A / \partial T = (\partial d_1 / \partial T) / d_1 + 0.5 (\partial \sigma / \partial T) / \sigma$$

- 0.5 (\delta B / \delta T) / B = - 0.01251
$$\partial K / \partial T = -1.182 x 10^5 [3\sigma^2 (\partial \sigma / \partial T) / (T \delta^2 (Pe - P_L)^2) - \sigma^3 / (T^2 \delta^2 (Pe - P_L)^2) - 2\sigma^3 (\partial \delta / \partial T) / (T \delta^3 (Pe - P_L)^2)$$

$$\frac{5^{3}}{(1\delta^{2} (\text{Pe} - \text{P}_{\text{L}})^{3})(\partial \text{Pe}/\partial 1)] = 6.488$$

$$\lim T \rightarrow T_1 (\partial \ln A / \partial T) / (\partial K / \partial T) = -0.19\%$$

The reason these two ratios do not agree exactly must be mainly in the estimation for the surface tension. It is extrapolated far beyond the data up near the critical point. The pressure is close, except the Poynting correction may be off a bit. Otherwise, the approximation that K = const. is good, so it would hold for all the data.

Neglecting the change in the coefficient one can easily derive an expression for $\lim \phi_2 \rightarrow 0$ for $\partial T / \partial \phi_2$ where ϕ_2 is the volume fraction of polymer in the interior of the droplet. The exponent is then taken constant.

$$K = -1.182 \times 10^5 \sigma^3 / T (P_V - P_L)^2$$
(13)

So, solving for T, then differentiating (using partial derivatives throughout this paper).

$$\lim \varphi_{2} \rightarrow 0 \ \partial T / \partial \varphi_{2} = T_{1} ((3 / \sigma_{1}) \ \partial \sigma / \partial \varphi_{2}$$
$$- (2 / (P_{V} - P_{L})) \ \partial P_{V} / \partial \varphi_{2})$$
(14)

In Siow and Patterson's theory for polymer solutions, the surface volume of solvent and interior volume of solvent are used here in the simple athermal (dT = 0) case. Their theory is for the surface tension of a polymer solution against a liquid and in the experimental conditions the droplet rose in a column of heated glycerol where the temperature rises as the droplet ascends in the column. This surface tension is taken to be the surface tension of the nucleating bubble within the droplet. Substituting (2) into (14) and using the fact that $\partial \delta / \partial \varphi_2 = 0$ for w₂ near 0:

$$\lim \varphi_{2} \rightarrow 0 \quad \partial T / \partial \varphi_{2} = T_{1} \left(\left(3 / \sigma_{1} \right) \partial \sigma / \partial \varphi_{2} \right)$$
$$- \left(2 / \left(\text{Pe} - \text{P}_{L} \right) \right) \partial \text{Pe} / \partial \varphi_{2} \right)$$
(15)

The result (using (9) and (15)) along with the fact that $\partial Pe/\partial \phi_2 = 0$ near $\phi_2 = 0$ is:

$$\lim \varphi_2 \rightarrow 0 \quad \partial T / \partial \varphi_2 = 3 k T_1^2 / \sigma_1 r a \tag{16}$$

where k = Boltzmann constant, $T_1 = limit$ of superheat of cyclohexane, $\sigma_1 =$ surface tension of cyclohexane at T_1 , r = ratio of molar volume of polymer to molar volume of solvent at T_1 and a = surface area of the solvent molecule at T_1 .

One adjustment made to Siow and Patterson was in the calculation of the surface area of the cyclohexane molecule, according to the formulas for a sphere

$$a = (4 \pi / (4 \pi / 3)^{2/3}) V^{2/3} = 4.836 V^{2/3}$$
(17)

where V is the molar volume of cyclohexane at T_1 divided by Avogadro's number, N_o , 6.0225x10²³ molecules/mole.

The data for surface tensions of cyclohexane (Jasper, 1972) (extrapolated) and polystyrene (Wu, 1970), the densities for cyclohexane (Kerimov and Apaev, 1972) (extrapolated) and polystyrene (Bernardo and Vesely, 2007), and the vapor pressure of cyclohexane (CRC, 44th) were taken from the indicated sources. The polystyrene (Mukherji and Ahuja, 1981) was from Pressure Chemical Co. (erratum in Jennings and Middleman). Density data for cyclohexane was from the Internet by (DDBST). See Appendix for details on data calculations.

4. Results

(12)

Following is a table comparing theory with experiment. In this simplified equation, all quantities are at the limit of superheat for the solvent.

$$\lim w_2 \rightarrow 0 \ \partial T / \partial w_2 = (MW_1 / MW_2) (3kT_1^2 / \sigma_1 a)$$
(18)

Table 1. Theory vs. experiment for polystyrene in cyclohexane.

<i>jetemente</i> t				
Molecular	2000	4000	50,000	100,000
weight				
$\partial T/\partial w_2$ T in				
°C				
Theory	52.58	26.29	2.10	1.05
Experiment	48.48	28.78	3.62	2.66
ΔT in °C for	+0.82	-0.50	-0.30	-0.32
$w_2 = 0.2$				

Eq. (18) does reasonably well at predicting the limit of superheat for all the data. The average deviation in the slope for the two lower MWs is about 8%, but since the temperature rise is only about 10-15 °C at 30 weight percent, if the athermal slope is used, the prediction gives an error of 0.5 or 0.8 °C at 20% weight fraction between theory and experiment. Notice that as the MW of polymer grows large, the temperature rise from this phenomenon is much less; that is what is found for the data in Jennings and Middleman for low weight fraction and higher molecular weight. However, the slope is more accurate at low molecular weight.

5. Conclusions

The athermal version of a theory for surface thermodynamics of polymer solutions by Siow and Patterson is used along with classical nucleation theory to predict the limit of superheat of polystyrene-cyclohexane solutions from 2000 to 100,000 molecular weight at one atmosphere pressure collected by Jennings and Middleman. Eq. (18) fairly well predicts the limit of superheat for all the data. However, the slope is more accurate at low molecular weight. As the molecular weight of polymer grows large, the temperature rise from this phenomenon is much less.

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Nomenclature (see Appendix for units)

- a surface area of solvent molecule
- B factor $\approx 2/3$
- d density of liquid
- d_i density of solvent (1) or polymer (2)
- d_G density of gas at equilibrium vapor pressure
- k Boltzmann constant
- M molecular weight of solvent molecule
- MW_i molecular weight of solvent or polymer
- No Avogadro's number
- Pe equilibrium vapor pressure of gas in bubble
- P_L ambient pressure on solution droplet
- P_V vapor pressure of gas in bubble
- r ratio of molar volume of polymer to molar volume of solvent
- T_1 temperature of limit of superheat for pure solvent at 1 atm

V _i W ₂	molar volume of solvent (L) or vapor (e) i equilibrium weight fraction polymer	n 4. Polystyrene Research Sum Middleman, MA	in cyclohexane: data are from UCSD mary Jan. 11, 1983 (Jennings and CROMOLECULES Vol. 18, No. 11, 1985).		
δ	Poynting correction factor	NUM 2000	NUV 2000		
σ_1	surface tension of solvent	MW = 2000	V There Carting 1		
σ_2	surface tension of polymer	X = wt fract. PS	Y = 1 degrees Centigrade		
ϕ_i	volume fraction of solvent or polymer in interior of	of 0	219.6		
(0	solution of solvent or polymer on surface of	0.030 of 0.026	221.55		
ψ_{iS}	solution	0.0825	222		
	solution	0.0825	223.4		
Д РР	FNDIX - Data for calculations of temperature rise i	n 0.180	223.7		
supe	rheat	0.180	228.2		
sape	indu	0.302	234.2		
DAT	A PERTAINING TO EOUATION (18)	0.302	234.65		
		Deg Centigrade	= 219.697 + (48.484)(weight fraction		
MW	$M_1 = 84.161$ MW ₂ = 2000-100,000	polystyrene), r =	0.999		
$\sigma_1 =$	4.0904 dyne/cm $\sigma_2 = 26.329$ dyne/cm				
$T_1 =$	492.75 K $d_1 = 0.5386$ g/cc $a = 196.73 \times 10^{-16}$ cm ²	MW = 4000			
$\mathbf{k} = 1$	$1.3805 \ge 10^{-16} \text{ erg/deg}$	X = wt fract. PS	Y = I degrees Centigrade		
		0	219.6		
1.	Formulas for σ , Pe, d, δ for pure cyclohexane T_l	= 0.03	220.2		
492.	75 Kelvin	0.03	220.7		
		0.044	220.4		
$\sigma_1 =$	$= 60.8402(1-T/553.55)^{11/9}$ dyne-cm (Jasper	$(1) 0.043 \\ 0.002$	220.7		
$\mathbf{B} =$	0.6858	0.092	222.1		
		0.091	222.5		
R =	82.056 cm ³ atm deg ⁻¹ mole ⁻¹	0.095	221.55		
MW	$I_1 = 84.161$ (cyclohexane)	0.137	221.7		
		0.142	223.1		
Pe =	$0.0079473 \exp(0.015613 \text{ T}) \text{ atm}$	0.211	225.8		
(CR	C, 44th ed.)	0.210	225.0		
		0.219	225.5		
δ =	$1 - d_G/d_1 + 0.5 (d_G/d_1)^2 = 0.9349$	0.219	225.95		
(Bla	nder and Katz)	0.230	226.2		
1		0.230	226.9		
$d_G =$	= (Pe/R1) MW ₁ = 0.03629 g/cc	0.288	227.0		
idea.	gas in equilibrium with liquid	0.288	228.05		
L	0.597226 alas at 465.22 Valuin	0.311	227.55		
$a_1 =$	0.587520 g/cc at 403.52 Kelvin	0.310	228.7		
and $0.5/02/0$ g/cc at 4/5 Keivin - 1.2569 0.001/2282 T (DDPST)		Deg Centigrade	a = 219.440 + (28.779)(weight fraction		
_	(DDDS1)	polystyrene), r =	0.99		
2 Г	Data at limit of superheat of cyclohexane	MW - 50.000			
2. D	and at time of supernear of cyclonexane	X - wt fract PS	V – T degrees Centigrade		
d1 =	$= 0.5386 \text{ g/cc}$ $d_2 = 0.9571 \text{ g/cc}$	A = wt fidet. I S	219.6		
$\sigma_1 =$	$= 4.0904 \text{ dyne/cm} \sigma_2 = 26.329 \text{ dyne/cm}$	0.036	220.05		
- 1	······································	0.036	219.7		
Pe =	$= 17.433 \text{ atm}$ $P_{\rm L} = 1 \text{ atm}$	0.106	220.05		
		0.106	220.04		
3. N	leed to calculate partial derivatives at	Deg Centigrade	e = 219.682 + (3.621)(weight fraction		
$T_l =$	492.75 Kelvin	polystyrene), r =	0.78		
		1 5 5 77			
$\partial \sigma_1 /$	$\partial T = -0.1343 (1 - T_1 / 553.55)^{2/9} = -0.08223$	MW = 100,000			
		X = wt fract. PS	Y = T degrees Centigrade		
∂Pe/	$\partial T = 0.00012408 \exp(0.015613 T_1) = 0.2722$	0	219.2		
		0	219.7		
$\partial\delta$ /	$\partial T = - ((\partial Pe_1 / \partial T) MW_1 / (RT d_1) - PeMW_1 / (RT^2 d_1))$	- 0.038	219.25		
(Pe MW ₁ / (RT(d ₁) ²)) ($\partial d_1 / \partial T$)) (1 - d _G /d ₁)		0.038	219.6		
= - (0.001021	0.089	219.45		
		0.089	219.85		
$\partial d_1 /$	$\partial T = -0.001439$	0.118	219.6		
	2	0.118	220.0		
∂B /	$\partial T = -(1/3) P_L / (Pe)^2 (\partial Pe / \partial T) = -0.0002986$	0.154	219.6		
(P _V i	s approximated as Pe because this is small)	0.154	219.95		

Deg Centigrade = 219.408 + (2.662)(weight fraction polystyrene), r = 0.57

5. Density of cyclohexane (extrapolated)

 $d_1 = 0.5386$ g/cc The following data are from Kerimov and Apaev (1972).

T (K) Pressure Density = d_1 283.15 101.300 kPa 0.7891 g/cc (laboratory pressure) 348.15 101.300 kPa 0.7265 g/cc 283.15 1082.00 kPa 0.7900 g/cc

348.15 1082.00 kPa 0.7276 g/cc

for 283.15 K $\Delta d_1/\Delta kPa = (0.79-0.7891)/(1082-101.3) = 0.00000091771$ for 348.15 K $\Delta d_1/\Delta kPa = (0.7276-0.7265)/(1082-101.3) = 0.00000112165$

Extrapolating, get $\Delta d_1 / \Delta k Pa$ for T = 492.75 K between the pressures. $\Delta d_1 / \Delta k Pa = 0.0000091771 + ((0.00000112165-0.00000091771)/(348.15-283.15))(492.75-283.15)$ = 0.000001575

Then, this is used to extrapolate the following data down to 760 mmHg = 101.3 kPa.

First, interpolate between the two temperatures for T = 492.75 K.

Then, extrapolate between the pressures.

 $d_1(101.3 \text{ kPa}, 492.75\text{K}) = 0.54015 + (0.000001575)(101.3-1082) = 0.5386 \text{ g/cc}$

6. Surface tension of cyclohexane (extrapolated)

$$\begin{split} &\sigma_1 = 4.0904 \; dyne/cm \; at \; T = 492.75K \\ & \text{The following data are from Jasper (1972) - cyclohexane} \\ & \text{surface tension: dyne-cm } (\pm 0.01), \; T \; in \; degrees \; Centigrade. \\ & 40^\circ \quad 50^\circ \quad 60^\circ \quad 70^\circ \\ & 22.87 \quad 21.68 \quad 20.49 \quad 19.30 \end{split}$$

The well-known empirical formula for surface tension near the critical point is

 $\sigma = \sigma_0 (1 - T/T_c)^{11/9}$ where T is in Kelvin

Values for σ_o are calculated for $T = 40^\circ$, 50° , 60° , 70° Centigrade and then σ_o is extrapolated to $T = 219.6 \ ^\circ\text{C}$, $T_c = 553.55\text{K}$.

 $\sigma_1 = 60.8402(1 - T/553.55)^{11/9}$

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