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LCST phase behavior according to the Simha-Somcynsky theory: application to the n-hexane polyethylene system

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Abstract: Expressions for the free energy of mixing ΔG , including equation of state contributions, have been previously derived by Jain and Simha. However, the chemical potentials and compositional derivatives required for the description of phase behavior were approximated by polynomial fits to the theoretical ΔG for a particular case. Exact and general equations for a binary system are now derived. This opens the way for future analyses of phase equilibria, based on the Simha-Somcynsky (S-S) theory. The present application involves a *simulation* of the system n-hexane/polyethylene, previously treated by Jain and Simha. The analysis is extended now to a wide range of molar masses from 8 to 10^3 kg/mole and binodals as well as spinodals and critical conditions are computed over a wider range of pressures than previously. In the simulation the polymer samples are assumed to be monodispers. The phase boundaries differ significantly from the previous ones, as one should expect from the higher derivatives of polynomial fits. However, previous conclusions concerning an iso hole or free volume fraction difference between the constituents as a critical condition for the appearance of a lower critical solution temperature (LCST) stand. Moreover, and as an alternative, this condition can be expressed in terms of the excess free volume fraction h_{exc} of the mixture. Master curves for binodals and spinodals can be generated for different pressures over a reasonable temperature distance from the critical point. Similarly, h_{exc} at the binodal and spinodal condition can be represented by universal curves. Finally, we discuss the variation of the critical coordinates with chain length and conclude with an evaluation of the χ -function for different compositions, temperature, and pressure.

Key words: LCST phase behavior, χ parameter, hole theory, equation of state, polymer solution.

I. Introduction

The necessity to include equation of state contributions to the free energy of mixing was first pointed out by Prigogine, Mathot and Trappeniers [1]. Following applications by them, several authors have brought to bear various equation of state theories on the problem. The quantitative success of the S-S theory (S-S = Simha-Somcynsky) for single and multi-constituent polymers and oligomers has been extensively demonstrated. It was natural then to

proceed to the problem of phase equilibria. As a start, Jain and Simha [2, 3] set out to investigate LCST behavior in a particular solution, namely a homodisperse polyethylene in n-hexane. Here the requisite parameters for the two constituents had already been established. Numerical values for the interaction parameters were suggested by results for mixtures of n-paraffins.

The theory yields scaled thermodynamic functions. The scaling parameters appear as explicit functions of composition and include the competition

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between self- and cross-attraction energies and repulsion volumes. The required chemical potentials and their compositional derivatives involve lengthy algebraic manipulations. In order to obtain some initial results, Jain and Simha bypassed these by fitting quartic polynomials to the theoretical Gibbs free energy $\Delta G = G_m - (x_1 G + x_2 G_2)$. These, even if highly accurate, could not represent more than a first attempt. Quite apart from the issue of accuracy for the derivatives, exact analytical expressions are required for the future treatment of polymer solutions and polymer mixtures. The purpose of this paper is to derive exact analytical expressions for the chemical potentials and their pertinent compositional derivatives, required for the establishment of binodals, spinodals and critical coordinates as a function of pressure. The current results apply to a binary system, but form the basis for and point the way to future generalizations. These will be concerned with connections between UCST's and LCST's in polymer solutions [4, 5] and subsequently with phase equilibria in polymer mixtures.

The results are applied here to an analysis of the particular system studied in [2], i.e., ideal fractions of polyethylene in n-hexane. Binodals and, moreover, spinodals are obtained, now over a wider range of molar masses than previously, and the behavior of the χ -function in the LCST region is discussed. Finally, the results serve to gauge the numerical adequacy of the previous procedure.

Section II summarizes the pertinent results of the statistical theory and the basic thermodynamic relations. The new analytical expression for the change $\Delta\mu_i$ in chemical potential is also stated. The equations for the higher compositional derivatives are compiled in the Appendix. In Section III the results for the phase boundaries are presented. We continue with a discussion and conclusions in Sections IV and V.

II. Statistical and thermodynamic working equations

a. Single constituent

The theory of Simha-Somcynsky (S-S) models the chain molecular liquid by a quasi-lattice with sites occupied by one and only one segment or vacant. The configurational contribution F_i to the molar Helmholtz free energy of constituent i at a temperature T and volume V_i reads (2, 3):

$$F_i/(RT) = \ln(y_i/s_i) + s_i(1-y_i)/(y_i) \ln(1-y_i) \\ + (s_i - 1)(1 - \ln(z-1)) - c_i [\ln(v_{ii}^*(1 - \eta_i^3/Q_i)) \\ + 3/2 \ln(2\pi M_{oi}RT/(N_a h)^2) - y_i Q_i^2 (A Q_i^2 - 2B)/(2\tilde{T}_i)] \quad (1)$$

with:

y_i fraction of occupied lattice sites
 s_i number of segments per chain of molar mass M_i
 $3c_i$ number of external degrees of freedom per chain
 M_{oi} segmental molar mass M_i/s_i
 v_{ii}^* molar intermolecular repulsion volume between a segment pair of constituent i
 ϵ_{ii}^* maximum molar intermolecular attraction energy between a segment pair of constituent i
 A, B, z numerics equal to 1.011, 1.2045, 12 respectively.
 $Q_i = (y_i \tilde{V}_i)^{-1}$; $\eta_i = 2^{-1/6} y_i Q_i^{1/3}$ are dimensionless quantities.
 N_a, h Avogadro's number and Planck's constant, respectively.

The tildes signify scaled variables of state with the following scaling parameters:

$$T^*_i = q_i z \epsilon_{ii}^* / (c_i R) \quad (2.a)$$

$$P^*_i = q_i z \epsilon_{ii}^* / (s_i v_{ii}^*) \quad (2.b)$$

$$V^*_i = v_{ii}^* / M_{oi} \quad (2.c)$$

with

$q_i z = s_i(z-2)+2$ the number of intermolecular contact sites, and V^*_i a specific volume parameter per unit mass.

The scaled equation of state $\tilde{P}_i \tilde{V}_i / \tilde{T}_i = PV/(RTc_i)$ then is given by the following two coupled equations [6]:

$$\tilde{P}_i \tilde{V}_i / \tilde{T}_i = 1/(1 - \eta_i) + 2y_i Q_i^2 (A Q_i^2 - B) / \tilde{T}_i \quad (3)$$

with y_i the solution of the transcendental equation which expresses the minimization of the free energy, viz.

$$3c_i ((\eta_i - 1/3)/(1 - \eta_i) + y_i Q_i^2 (2B - 3A Q_i^2)/(6\tilde{T}_i)) \\ - s_i + 1 - s_i \ln(1 - y_i)/y_i = 0 \quad (4)$$

Equation of state data then yield the three scaling parameters, provided an additional relation between s_i and c_i is adopted. This amounts to a replacement of the ensemble of real chains by an ensemble of equivalent chains with the identical thermodynamic properties. The substitution $3c_i = s_i + 3$ employed implies an equivalent linear chain with unrestricted internal backbone bond rotations.

b. Binary mixture

The free energy F_m of the mixture has the following form [2, 3]:

$$\begin{aligned} F_m/(RT) = & x_1 \ln x_1 + x_2 \ln x_2 + \ln (y/<s>) \\ & + <s>(1-y) \ln (1-y)/y + (<s>-1)(1 - \ln (z-1)) \\ & - <c> [\ln (<v^*> (1-\eta)^3/Q) \\ & + 3/2 \ln (2\pi <M_0> RT/(N_d h)^2) \\ & - yQ^2(AQ^2-2B) (/2 \rightarrow 2)\tilde{T}] \end{aligned} \quad (5)$$

with $x_2 = 1-x_1$ the molar composition. The parameters now depend on x_i , the parameters of the constituents and the cross interactions ϵ_{12}^* and v_{12}^* . The explicit relations are stated in Appendix A. The brackets signify compositional averages.

Equations (1-5) determine the free energy changes ΔF and ΔG , whence we obtain the chemical potentials

$$\mu_i = (\partial F_m / \partial N_i)_{V,T,N_j} = (\partial G_m / \partial N_i)_{P,T,N_j} \quad (6)$$

and the corresponding $\Delta\mu_i$. Under heterogeneous equilibrium conditions, the compositions of the coexisting phases are determined by the set of equations

$$\mu_i' = \mu_i'', i = 1, 2, \quad (7)$$

where the primes indicate different phases.

Finally the conditions

$$(\partial^2 G_m / \partial x_2^2)_{P,T} = 0 \quad (8a)$$

$$(\partial^3 G_m / \partial x_2^3)_{P,T} = 0 \quad (8b)$$

define the critical composition, and the first equality determines the spinodal condition.

At this point we give the result of the statistical theory for the change $\Delta\mu_1$ of the solvent, derived by means of Eqs. (1-6), viz:

$$\begin{aligned} \Delta\mu_1/RT = & \ln (x_1 s_1 / <s>) + 1 - s_1 / <s> + \ln (y/y_1) \\ & + s_1(D - D_1) - c_1(E - E_1) + <c> s_1 \tilde{P}\tilde{V} / (\tilde{T} <s>) \\ & - c_1 \tilde{P}_1 \tilde{V}_1 / \tilde{T}_1 - <c> X_1 X_2 (\tilde{P}\tilde{V} / \tilde{T} - 1)(R_4 - R_2) / x_1 \\ & + (3/2) (c_1 (\ln (M_{01}/y <M_0>) \\ & + <c> s_1 s_2 x_2 (M_{02} - M_{01}) / (<s>^2 <M_0>) \\ & + UX_1 (1 + 2X_2(R_4 - 2R_2)) / x_1 - U_1, \end{aligned} \quad (9)$$

where $U = <c> y Q^2 (AQ^2 - 2B) / (2\tilde{T})$;

$$U_1 = c_1 y_1 Q_1^2 (AQ_1^2 - 2B) / (2\tilde{T}_1);$$

$$E = \ln (y V^* \tilde{V} (1-\eta)^3); \quad E_1 = \ln (y_1 V^* \tilde{V}_1 (1-\eta_1)^3);$$

$$D = (1-y)/y \ln (1-y);$$

$$D_1 = (1-y_1) \ln (1-y_1) / y_1;$$

$$R_k = (-X_1 \epsilon_{11}^* v_{11}^{*k} + (X_1 - X_2)$$

$$\epsilon_{12}^* v_{12}^{*k} + X_2 \epsilon_{22}^* v_{22}^{*k}) (<\epsilon^*> <v^*>^k).$$

The site fractions X_1, X_2 are defined by Eq. (A6) in Appendix A.

The derivatives in Eq. (8) are evaluated in Appendix B. Finally, we are able to complete the χ -function, so frequently discussed in the literature, and defined by the following equation:

$$\Delta\mu_1/RT = \ln \phi_1 + (1 - 1/m_2)\phi_2 + \chi\phi_2^2, \quad (10)$$

with ϕ_1, ϕ_2 the volume fractions of solvent and polymer, respectively, and $m_2 (= s_2 v_{22}^* / (s_1 v_{11}^*))$ the relative chain length of the polymer.

Table 1a. Segmental energy and volume parameters characterizing n-hexane, polyethylene, and mixtures thereof in the S-S theory. The intersegmental hard core volume v^*_{12} is computed according to: $v^*_{12} = ((v^*_{11})^{1/3} + v^*_{22})^{1/3}/2)^3$.

	n-Hexane	PE	Cross-interactions
ϵ^* [J/mol]	2.9325e + 03	2.7374e + 03	2.9325e + 03
ϵ^* [k]	3.5271e + 02	3.2924e + 02	3.5271e + 02
v^* [m ³ /mol]	4.3905e - 05	3.6215e - 05	3.88367e - 05

Table 1b. Molar mass characteristics (molar mass M , relative chain length s and external degrees of freedom c) of n-hexane and monodisperse polyethylene samples.

Sample code	M [kg/mole]	s	c
CH	0.086	2.5	1.833
PE ₁	8.00	252.2	85.07
PE ₂	10.00	315.3	106.08
PE ₃	50.00	1576.3	526.43
PE ₄	100.00	3152.5	1051.83
PE ₅	177.00	5579.9	1860.97
PE ₆	500.00	15762.5	5255.17
PE ₇	1000.00	31525.0	10509.33

III. Results

The numerical values of the interaction parameters for constituents and mixture are listed in Table 1, together with the molecular masses, corresponding chain lengths, and c -parameters of the former. Some of these differ slightly from those in [2, 3]. Hence the computations of the polynomial representations were repeated for purposes of comparison with the exact results. Figure 1 depicts the variation of $\Delta\mu_1$. Eq. (9) with mole fraction x_2 of polymer PE₁ at atmospheric pressure.

The differences between the two sets and the locations of the maxima are significant. In Fig. 2 the phase diagrams at three pressures are displayed. The differences from the polynomial spinodal at 1 bar (the dash-dot line) are pronounced. As a test of the analytical derivations and numerical calculations we note that the binodals and spinodals make contact at their extrema, in accordance with thermodynamic principles. Moreover, these extrema are also computed to represent the critical state, as they should.

Fig. 1a. Exact (—) and approximate (---) curves for the chemical potentials $\Delta\mu_1/RT$ vs composition for the system nH/PE_1 . b. shows part of plots in more detail.

Fig. 2. Exact calculated binodal (—), spinodal (---), and critical (■) conditions at different indicated pressures for the system *nH/PE*₁. Part of the approximate spinodal (— · —) at atmospheric pressure is also shown.

Fig. 3. Pressure dependence of critical temperature (—) and composition (---) up to 1000 bar for the system *nH/PE*₁.

IV. Discussion

a. Phase diagram: influence of pressure

In Fig. 3 the variation of the critical coordinates for polymer *PE*₁ is presented. Both composition and temperature increase with pressure. However, whereas the former tends to become practically constant above 600 bar, the latter increases significantly, indicating the enhanced compatibilization at elevated pressures. As has been recognized in the literature, this is a consequence of the fact that pressure tends to reduce the differences in the thermal and pressure properties of the low- and high-molar mass constituents [7, 8]. Jain and Simha [2, 3] concluded that this difference can be expressed solely in terms of the free volume functions $h = 1 - y$ of the constituents, at least over a moderate range of pressures. Specifically, at the critical point (LCST), $y_2 - y_1$ remains invariant to a very good approximation, although y_2 and y_1 , of course, increase with pressure. In other words, an iso-free volume difference condition applies. That this conclusion stands also on the basis of the exact expressions for the chemical potentials and higher derivatives, is illustrated in Table 2. The second column lists the differences $y_2 - y_1$ at the critical temperatures seen in the fourth column. Finally, we note the difference ΔT between the actual and an

Fig. 4. Representation of calculated $(T - T_{\text{crit}})$ vs $(x_2 - x_{2,\text{crit}})$ for binodal (—), spinodal (---) and critical (■) conditions at 1, 50 and 100 bar for the system *nH/PE*₁.

Fig. 5. Free volume difference $y_2 - y_1$ at the spinodal and consolute state vs temperature at different indicated pressures for the system nH/PE_1 .

Fig. 6. The calculated excess free volume h_{exc} for binodal (—), spinodal (---) and critical (■) conditions at different indicated pressures for the system nH/PE_1 . For moderate pressures up to 100 bar approximately universal curves can be defined.

estimated critical temperature. The estimate is obtained from the iso-postulate and the value of $y_2 - y_1$ for 1 bar. Below about 200 bar, the difference ΔT is acceptable. In this context we are led to an alternative function with compositional information, namely the excess hole fraction

$$h_{exc} = (1 - y)_{exc} = -(y_m - x_1 y_1 - x_2 y_2). \quad (11)$$

Table 2. The critical temperature T_{crit} , free volume difference ($y_2 - y_1$), and excess free volume h_{exc} as functions of pressure for the system nH/PE_1 . The temperature difference ΔT is defined in the text.

p [bar]	$y_2 - y_1$ at consolute state	$-h_{exc}$	T_{crit} [K]	ΔT [K]
1	0.186883	0.021924	402.25	0.00
50	0.186738	0.022291	413.32	0.19
100	0.186546	0.023789	424.84	0.56
200	0.186034	0.023151	448.60	1.70
500	0.184003	0.023680	526.80	9.34
1000	0.184400	0.022633	723.64	21.66

Table 2 indicates that similar conclusions can be reached as in terms of $y_2 - y_1$.

A minimum in ($y_2 - y_1$) and an oscillation in h_{exc} can be seen; we have no explanation to offer. However, we note that this is not the result of numerical inaccuracies in the determination of T_{crit} .

The spinodal and binodal curves in Fig. 2 can be transformed into a scaled representation of the difference $T - T_c$ vs $x_2 - x_{2c}$. Figure 4 shows approximate master curves. For practical purposes, a reduced spinodal curve extends over a range of about 20 K above T_c . For the binodals, superposition is less satisfactory. A narrowing of the miscibility gap at elevated pressures is noticeable. Next we show in Fig. 5 the temperature dependence of the free volume difference $y_2 - y_1$ for different pressures. The divergence from the common intercept at the respective critical temperatures remains small over a range of temperatures.

It is a well recognized notion that LCST phase separation results from differences in free volume quantities between the constituents [7, 8]. Such a difference is explicitly determined in terms of a special function inherent in the S-S theory. This can be expressed either as a simple difference between the two constituents (Fig. 5) or in terms of an excess function. The latter also serves to define approximate master curves as is seen in Fig. 6.

An extension of the calculations to still higher pressures and temperatures leads to a miscibility gap of the closed-loop type which eventually disappears. Experimentally, these conditions are not realizable, however, for the *n*H/PE pair. A further increase in pressure yields a new and very broad miscibility gap at low temperatures. Under these conditions, however, the square-well approximation to the cell potential employed in the S-S theory would no longer be adequate for a quantitative treatment.

b. Phase diagram: influence of molar mass

We have derived analogous results for all the molar masses listed in Table 1. As expected, location and shape of spinodal curves change. However, superposition of these for a given molar mass and different pressures is again accomplished. For high molar masses computations of binodals in terms of mole fractions present numerical problems. Hence the existence of master curves could not be verified. The important result concerning the behavior of the free volume function continues to be valid, as is seen in Table 3, which lists the critical coordinates and the values of $y_2 - y_1$ at the critical points.

Table 3. Critical conditions and free volume differences for indicated molar masses and pressures.

Sample	P	T_{cr}	$\chi_{2,cr}$	$(y_2 - y_1)$
code	[bar]	[K]	mole fraction	
PE ₁	1	402.25	1.30951e-03	0.186883
	50	413.32	1.35882e-03	0.186738
	100	424.84	1.40704e-03	0.186546
	200	448.60	1.50304e-03	0.186034
PE ₂	1	396.605	9.45450e-04	0.183495
	50	407.852	9.80950e-04	0.183242
	100	417.862	1.01566e-03	0.182927
	200	439.919	1.07961e-03	0.182143
PE ₃	1	373.229	8.59912e-05	0.169563
	50	381.431	8.91369e-05	0.168964
	100	389.724	9.22616e-05	0.168273
	200	405.976	9.82168e-05	0.166662
PE ₄	1	368.550	3.03309e-05	0.166768
	50	376.364	3.14268e-05	0.166121
	100	384.233	3.25190e-05	0.165378
	200	399.547	3.46610e-05	0.163661
PE ₅	1	365.874	1.28508e-05	0.165164
	50	373.475	1.33106e-05	0.164491
	100	381.113	1.37701e-05	0.163722
	200	395.922	1.46531e-05	0.161951
PE ₆	1	362.738	2.69628e-06	0.163270
	50	370.099	2.79178e-06	0.162572
	100	377.477	2.88721e-06	0.161776
	200	391.728	3.07435e-06	0.159953
PE ₇	1	361.430	9.51428e-07	0.162477
	50	368.694	9.85129e-07	0.161768
	100	375.967	1.01867e-06	0.160963
	200	389.985	1.08319e-06	0.159116

Fig 7. Shultz-Flory plot at indicated pressures for the critical temperatures shown in Table 2. The solid points are calculated critical temperatures, the lines are drawn to indicate extrapolations.

The variation of the characteristic free volume difference $y_2 - y_1$ over the wide range of molar masses from 8 to 10^3 kg/mole is comparatively small. This suggests that an iso-result derived here in respect to the critical temperature of a binary system, may also apply to the critical and threshold temperatures of polydisperse solutions.

Next we turn to the dependence of the critical coordinates on chain length. Although the lattice theory, as formulated by Staverman, Huggins, and by Flory [21, 22, 9–12] cannot account for the LCST phenomenon, it is instructive to make some comparisons. The variation of the critical volume fraction ϕ_{2c} with chain length is found to be in close agreement with the well known result of this theory, i.e.,

$$\phi_{2c} = 1/[1 + (s_2/s_1)^{1/2}]. \quad (12)$$

As for the critical temperatures, we plot in Fig. 7 our calculated T_c 's in the Shultz-Flory [13] representation

at a series of pressures. The intercepts are the reciprocal Θ -temperatures.

Significant departures from the linearity, predicted by the UCST theory in the absence of equation-of-state contributions to the free energy of mixing, on the low molar mass side and, thus, enhanced LCST miscibility are observed. For the pair cyclohexane/polystyrene, exhibiting both UCST and LCST behavior, a similar dependence of T_c on chain length is observed [4, 5]. Furthermore, in the *nH/PE* system, the predicted Shultz-Flory curves at different pressures are not superimposable for the small molar masses. These differences in miscibility behavior are not restricted to the consolute state, but extend to the complete phase diagram. All these phenomena must be related to the reduced difference in thermal and pressure characteristics between solute and solvent with decreasing molar mass of the former.

c. The χ -function

Application of Eqs. (9) and (10) in the homogeneous region at a series of temperatures and pressures is seen in Table 4. A similar increase of χ with polymer concentration has been observed experimentally for several polymer solution systems [14–19]. In the hole theory of S-S this dependence origi-

nates in the free volume contribution to the partition function [20]. A similar dependence for χ has been derived by Staverman [21, 22] and by Guggenheim [23]. In both cases, this is connected with the lattice energy and a refined evaluation of the number of segmental interaction contacts. The increase of χ with increasing temperature and decreasing pressure follows from the pattern seen in Fig. 2. A detailed discussion in terms of the S-S theory and comparison with experimental data will be postponed. We only recall here that accurate experimental data for the cyclohexane-polystyrene pair above and below the UCST Θ -temperature are available.

V. Conclusions

Exact expressions for the chemical potentials and their compositional derivatives, so far for a binary system, have been obtained. The way is now open to explore the predictions of the S-S theory for various types of mixtures, and to investigate the dependence of phase behavior on structural parameters. One particular type and application has been discussed here, i.e., a series of homodisperse polyethylenes in *n*-hexane and in the LCST region of temperatures and pressures. Numerical results obtained are specific of this particular simulation. However, certain observations should be of greater generality. These concern the influence of pressure and molecular mass, and the behavior of the hole or free volume fraction inherent in the S-S theory. We note:

1) Spinodals and binodals can be superimposed over a quite large temperature interval for moderate pressures. Deviations at greater distances from the respective critical temperatures are related to an enhanced improvement of miscibility at elevated pressures. It is worthwhile noting that a superposition of cloud point data for the system *nH/PE* has been realised before using a semiphenomenological approach [24].

2) Critical conditions are characterized by an invariant (iso) free volume difference, or alternatively by an invariant excess free volume fraction, again over a moderate pressure range. Within reasonable limits, moreover, the variation of this function along binodals and spinodals can be represented by universal curves.

3) The equation of state contribution to the free energy influences primarily the critical temperature for low molecular masses.

Table 4. Computed χ -values for the system *nH/PE*₁ in the homogeneous region of the phase diagram, at indicated compositions (segment fractions ϕ_2), pressure, and temperatures.

T		300 K	350 K	400 K
ϕ_2	P[bar]	χ	χ	χ
0.1	1	0.3763	0.4831	0.5915
	50	0.3727	0.4725	0.5688
	100	0.3699	0.4639	0.5508
	200	0.3668	0.4516	0.5253
0.2	1	0.4064	0.5083	0.6102
	50	0.4038	0.4992	0.5903
	100	0.4019	0.4918	0.5744
	300	0.4004	0.4816	0.5520
0.3	1	0.4465	0.5423	0.6373
	50	0.4448	0.5346	0.6200
	100	0.4440	0.5286	0.6061
	300	0.4442	0.5204	0.5866
0.4	1	0.4999	0.5880	0.6752
	50	0.4993	0.5818	0.6602
	100	0.4994	0.5770	0.6483
	200	0.5016	0.5710	0.6316

4) The temperature and pressure dependence of the χ -function follows from the above results for the changes in miscibility. The computed increase with polymer content appears to be in accord with experiment for several systems.

A detailed discussion of the predictions of the S-S hole theory in comparison with experiment remains to be presented in future research.

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Appendix A: Composition dependence of molecular parameters in the S-S theory

For a binary mixture of components 1 and 2, the molecular parameters become composition dependent according to [2, 3]

$$\langle s \rangle = x_1 s_1 + x_2 s_2 \quad (A1)$$

$$\langle qz \rangle = x_1(s_1(z-2)+2) + x_2(s_2(z-2)+2) \quad (A2)$$

$$\langle M_0 \rangle = (x_1 s_1 M_{01} + x_2 s_2 M_{02}) / \langle s \rangle \quad (A3)$$

$$\langle c \rangle = x_1 c_1 + x_2 c_2 \quad (A4)$$

$$\langle \varepsilon^* \rangle \langle v^* \rangle^2 = X_1^2 \varepsilon_{11}^* v_{11}^{*2} + X_2^2 \varepsilon_{22}^* v_{22}^{*2} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*2} \quad (A5)$$

$$\langle \varepsilon^* \rangle \langle v^* \rangle^4 = X_1^2 \varepsilon_{11}^* v_{11}^{*4} + X_2^2 \varepsilon_{22}^* v_{22}^{*4} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*4} \quad (A6)$$

$$\text{with } X_1 = (1-X_2) = x_1(s_1(z-2)+2) / \langle qz \rangle$$

$$T^* = \langle qz \rangle \langle \varepsilon^* \rangle / (\langle c \rangle R) \quad (A7)$$

$$P^* = \langle qz \rangle \langle \varepsilon^* \rangle / (\langle c \rangle \langle v^* \rangle) \quad (A8)$$

$$V^* = \langle v^* \rangle / \langle M_0 \rangle, \quad (A9)$$

where the parameters $\varepsilon_{12}^*, v_{12}^*$ refer to the cross pair interactions between segments of different components. The parameters $\varepsilon_{ii}^*, v_{ii}^*, s_i, M_{0i}$ and c_i characterize the pure component i .

Appendix B: Computational procedures

Equations (1–6) are complex functions of the principal variables $x_1, \tilde{P}, \tilde{T}$, and $\tilde{V}$. In order to make the derivatives manageable, some extra incidental variables I_s as functions of the principal variables are introduced. The Helmholtz free energy, the equation of state, and the minimization condition are considered to be functions of these incidental variables, viz.

the Helmholtz free energy

$$F = F_m / (RT) = F(x_1, y, \tilde{T}, Q, \eta, \langle s \rangle, \langle c \rangle, \langle M_0 \rangle, \langle v^* \rangle); \quad (B1)$$

the equation of state; and

$$E = E(y, \tilde{T}, Q, \eta, \tilde{V}, \tilde{P}) \quad (B2)$$

the minimization condition

$$M = M(y, \tilde{T}, Q, \eta, \langle s \rangle, \langle c \rangle). \quad (B3)$$

The compositional derivatives, defined in Eqs. (6) and (8) for the thermodynamic functions formulated in Eqs. (B1–B3) can be written in terms of the incidental variables. For the first derivative of a function Φ

$$(\partial \Phi / \partial x_1)_{P,T} = \sum_{i=1}^{n_I} (\partial \Phi / \partial I_i)_{I_{\#i}} (\partial I_i / \partial x_1)_{P,T} \quad (B4)$$

where Φ is a thermodynamic function, i.e., one of those appearing in Eqs. (B1–B3) and I_i is one of the n_i incidental variables. The second derivative reads

$$(\partial^2 \Phi / \partial x_1^2)_{P,T} = \sum_{i=1}^{n_1} \sum_{j=1}^{n_1} [(\partial(\partial \Phi / \partial I_i) / \partial I_j)_{I_i \neq I_j} / \partial I_i]_{I_i \neq I_j}^* \\ (\partial I_i / x_1)_{P,T} (\partial I_j / \partial x_1)_{P,T} + \sum_{i=1}^{n_1} (\partial \Phi / \partial I_i)_{I_i \neq I_i} (\partial^2 I_i / \partial x_1^2)_{P,T}. \quad (\text{B5})$$

The derivatives for the thermodynamic functions and the compositional derivatives of the incidental variables are summarized in the next paragraphs. Appropriate combination of the tabulated expressions produce the desired thermodynamic properties, e.g., chemical potentials, spinodals, etc. The variables y and $\tilde{V}$ and their derivatives deserve some comment. The structure factor y and the reduced volume $\tilde{V}$ are determined by solving the equation of state and the minimization condition for y and $\tilde{V}$. The derivatives $(\partial^k y / \partial x_1^k)_{P,T}$ and $(\partial^k \tilde{V} / \partial x_1^k)_{P,T}$ are determined by solving the set of equations formed by the k -th derivatives of the equation of state and the minimization condition.

Having determined y , $\tilde{V}$ and derivatives, all tabulated expressions and, consequently, thermodynamic properties can be computed in a straightforward manner. To determine the spinodal condition, Eq. (8a) is computed for given values of x_1 , P and T . Iterating the variable x_1 at constant P and T , the spinodal composition can be determined. The consolute state can be determined by solving Eqs. (8) iterating for example, x_1 and T at constant P . In the present work, Eq. (8b) is determined numerically from Eq. (8a). In principle, Eq. (8b) can be computed analytically.

The binodal conditions are given by the set of Equations (7). At given T and P , the compositions x_1' and x_1'' of the coexisting phases are determined in an iterative process, solving the equilibrium conditions (7). In terms of the compositional derivative (B4), the chemical potentials read

$$\mu_1 = G_m + x_2 (\partial G_m / \partial x_1)_{P,T} \quad (\text{B6})$$

$$\mu_2 = G_m - x_1 (\partial G_m / \partial x_1)_{P,T}. \quad (\text{B6}')$$

B.1 Compilation of the derivatives of the Helmholtz free energy.

First and second partial derivatives of the Helmholtz free energy function $F (= F_m/RT)$ with respect to the incidental variables are listed below. In the derivation all other incidental variables are assumed constant.

$$\frac{\partial F}{\partial x_1} = \ln x_1 - \ln x_2$$

$$\frac{\partial^2 F}{\partial x_1^2} = 1/x_1 + 1/x_2$$

$$\frac{\partial F}{\partial <s>} = \ln((z-1)/e) + (1-y)\ln(1-y)/y - 1/<s>$$

$$\frac{\partial^2 F}{\partial <s>^2} = 1/<s>^2$$

$$\frac{\partial^2 F}{\partial <s> \partial y} = -(\ln(1-y) + y)/y^2$$

$$\frac{\partial F}{\partial y} = -<s>(\ln(1-y) + y)/y^2 + 1/y + <c>Q^2(AQ^2 - 2B)/(2\tilde{T})$$

$$\frac{\partial^2 F}{\partial y^2} = 2<s>(\ln(1-y) + y)/y^3 + s/(y(1-y)) - 1/y^2$$

$$\frac{\partial^2 F}{\partial y \partial <c>} = Q^2(AQ^2 - 2B)/(2\tilde{T})$$

$$\frac{\partial^2 F}{\partial y \partial Q} = 2<c>Q(AQ^2 - B)/\tilde{T}$$

$$\frac{\partial F}{\partial y \partial \tilde{T}} = -<c>Q^2(AQ^2 - 2B)/(2\tilde{T}^2)$$

$$\frac{\partial F}{\partial <c>} = -\ln <v^*> + \ln Q - 3 \ln(1-\eta) - \frac{3}{2} \ln(2\pi <M_o> RT/(N_a h^2))$$

$$+ yQ^2(AQ^2 - 2B)/(2\tilde{T})$$

$$\frac{\partial^2 F}{\partial <c> \partial <v^*>} = -1/<v^*>$$

$$\frac{\partial^2 F}{\partial <c> \partial Q} = 1/Q + 2yQ(AQ^2 - B)/\tilde{T}$$

$$\frac{\partial^2 F}{\partial <c> \partial \eta} = 3/(1-\eta)$$

$$\frac{\partial^2 F}{\partial <c> \partial <M_o>} = -3/(2<M_o>)$$

$$\frac{\partial^2 F}{\partial <c> \partial y} = \frac{\partial^2 F}{\partial y \partial <c>}$$

$$\frac{\partial^2 F}{\partial <c> \partial \tilde{T}} = -yQ^2(AQ^2 - 2B)/(2\tilde{T}^2)$$

$$\frac{\partial F}{\partial <v^*>} = -<c>/<v^*>$$

$$\frac{\partial^2 F}{\partial <v^*>^2} = <c>/<v^*>^2$$

$$\frac{\partial^2 F}{\partial <v^*> \partial <c>} = \frac{\partial^2 F}{\partial <c> \partial <v^*>}$$

$$\frac{\partial F}{\partial Q} = <c>/Q + 2<c>yQ(AQ^2 - B)/\tilde{T}$$

$$\frac{\partial^2 F}{\partial Q^2} = -\langle c \rangle / Q^2 + 2\langle c \rangle y (3AQ^2 - B) / \tilde{T}$$

$$\frac{\partial^2 F}{\partial Q \partial \langle c \rangle} = \frac{\partial^2 F}{\partial \langle c \rangle \partial Q}$$

$$\frac{\partial^2 F}{\partial Q \partial y} = \frac{\partial^2 F}{\partial y \partial Q}$$

$$\frac{\partial^2 F}{\partial Q \partial \tilde{T}} = -2\langle c \rangle y Q (AQ^2 - B) / \tilde{T}^2$$

$$\frac{\partial F}{\partial \eta} = 3\langle c \rangle / (1 - \eta)$$

$$\frac{\partial^2 F}{\partial \eta^2} = 3\langle c \rangle / (1 - \eta)^2$$

$$\frac{\partial^2 F}{\partial \eta \partial \langle c \rangle} = \frac{\partial^2 F}{\partial \langle c \rangle \partial \eta}$$

$$\frac{\partial F}{\partial \langle M_o \rangle} = -3\langle c \rangle / (2 \langle M_o \rangle)$$

$$\frac{\partial^2 F}{\partial \langle M_o \rangle^2} = 3\langle c \rangle / (2 \langle M_o \rangle^2)$$

$$\frac{\partial^2 F}{\partial \langle M_o \rangle \partial \langle c \rangle} = \frac{\partial^2 F}{\partial \langle c \rangle \partial \langle M_o \rangle}$$

$$\frac{\partial F}{\partial \tilde{T}} = -\langle c \rangle y Q^2 (AQ^2 - 2B) / (2\tilde{T}^2)$$

$$\frac{\partial^2 F}{\partial \tilde{T}^2} = \langle c \rangle y Q^2 (AQ^2 - 2B) / (\tilde{T}^3)$$

$$\frac{\partial^2 F}{\partial \tilde{T} \partial \langle c \rangle} = \frac{\partial^2 F}{\partial \langle c \rangle \partial \tilde{T}}$$

$$\frac{\partial^2 F}{\partial \tilde{T} \partial y} = \frac{\partial^2 F}{\partial y \partial \tilde{T}}$$

$$\frac{\partial^2 F}{\partial \tilde{T} \partial Q} = \frac{\partial^2 F}{\partial Q \partial \tilde{T}}$$

$$\frac{\partial^2 M}{\partial \langle s \rangle \partial y} = -(\ln(1 - y) + y/(1 - y)) / y^2$$

$$\frac{\partial M}{\partial y} = -\langle s \rangle (\ln(1 - y) + y/(1 - y)) / y^2$$

$$-\langle c \rangle Q^2 (2B - 3AQ^2) / (2\tilde{T})$$

$$\frac{\partial^2 M}{\partial y^2} = 2\langle s \rangle (\ln(1 - y) + y/(1 - y)) / y^3 - \langle s \rangle / (y(1 - y)^2)$$

$$\frac{\partial^2 M}{\partial y \partial \langle s \rangle} = \frac{\partial^2 M}{\partial \langle s \rangle \partial y}$$

$$\frac{\partial^2 M}{\partial y \partial Q} = -2\langle c \rangle Q (B - 3AQ^2) / \tilde{T}$$

$$\frac{\partial^2 M}{\partial y \partial \langle c \rangle} = -Q^2 (2B - 3AQ^2) / (2\tilde{T})$$

$$\frac{\partial^2 M}{\partial y \partial \tilde{T}} = \langle c \rangle Q^2 (2B - 3AQ^2) / (2\tilde{T}^2)$$

$$\frac{\partial M}{\partial \langle c \rangle} = -3((\eta - 1/3)/(1 - \eta) + yQ^2 (2B - 3AQ^2) / (6\tilde{T}))$$

$$\frac{\partial^2 M}{\partial \langle c \rangle \partial \eta} = -2/(1 - \eta)^2$$

$$\frac{\partial^2 M}{\partial \langle c \rangle \partial y} = \frac{\partial^2 M}{\partial y \partial \langle c \rangle}$$

$$\frac{\partial^2 M}{\partial \langle c \rangle \partial Q} = -2yQ (B - 3AQ^2) / \tilde{T}$$

$$\frac{\partial^2 M}{\partial \langle c \rangle \partial \tilde{T}} = yQ^2 (2B - 3AQ^2) / (2\tilde{T}^2)$$

$$\frac{\partial M}{\partial \eta} = -2\langle c \rangle / (1 - \eta)^2$$

$$\frac{\partial^2 M}{\partial \eta^2} = -4\langle c \rangle / (1 - \eta)^3$$

$$\frac{\partial^2 M}{\partial \langle c \rangle \partial \eta} = \frac{\partial^2 M}{\partial \eta \partial \langle c \rangle}$$

$$\frac{\partial M}{\partial Q} = -2\langle c \rangle y Q (B - 3AQ^2) / \tilde{T}$$

$$\frac{\partial^2 M}{\partial Q \partial \tilde{T}} = 2\langle c \rangle y Q (B - 3AQ^2) / \tilde{T}^2$$

$$\frac{\partial^2 M}{\partial Q^2} = -2\langle c \rangle y (B - 9AQ^2) / \tilde{T}$$

B. 2 Compilation of derivatives of minimization condition.

The first and second derivatives of the minimization condition function M with respect to the incidental variables appear below. In the derivation all other incidental variables are assumed constant.

$$\frac{\partial M}{\partial \langle s \rangle} = 1 + \ln(1 - y) / y$$

$$\frac{\partial^2 M}{\partial Q \partial y} = \frac{\partial^2 M}{\partial y \partial Q}$$

$$\frac{\partial M}{\partial \tilde{T}} = yQ^2 < c > (2B - 3AQ^2) / (2\tilde{T}^2)$$

$$\frac{\partial^2 M}{\partial \tilde{T}^2} = -yQ^2 < c > (2B - 3AQ^2) / \tilde{T}^3$$

$$\frac{\partial^2 M}{\partial \tilde{T} \partial y} = \frac{\partial^2 M}{\partial y \partial \tilde{T}}$$

$$\frac{\partial^2 M}{\partial \tilde{T} \partial < c >} = \frac{\partial^2 M}{\partial < c > \partial \tilde{T}}$$

$$\frac{\partial^2 M}{\partial \tilde{T} \partial Q} = \frac{\partial^2 M}{\partial Q \partial \tilde{T}}$$

$$\frac{\partial^2 E}{\partial \eta \partial \tilde{P}} = \frac{\partial^2 E}{\partial \tilde{P} \partial \eta}$$

$$\frac{\partial^2 E}{\partial \eta^2} = 2\tilde{T} / (\tilde{P} (1 - \eta)^3)$$

$$\frac{\partial E}{\partial y} = 2Q^2 (AQ^2 - B) / \tilde{P}$$

$$\frac{\partial^2 E}{\partial y \partial \tilde{P}} = \frac{\partial^2 E}{\partial \tilde{P} \partial y}$$

$$\frac{\partial^2 E}{\partial y \partial Q} = 4Q(2AQ^2 - B) / \tilde{P}$$

$$\frac{\partial E}{\partial Q} = 4yQ(2AQ^2 - B) / \tilde{P}$$

B.3 Compilation of the derivatives of the equation of state.

First and second derivatives of the equation of state condition E with respect to the incidental variables are given below. In the derivation all other incidental variables are assumed constant

$$\frac{\partial E}{\partial \tilde{V}} = -1$$

$$\frac{\partial E}{\partial \tilde{P}} = -(\tilde{T} / (1 - \eta) + 2yQ^2 (AQ^2 - B)) / \tilde{P}^2$$

$$\frac{\partial^2 E}{\partial \tilde{P}^2} = 2(\tilde{T} / (1 - \eta) + 2yQ^2 (AQ^2 - B)) / \tilde{P}^3$$

$$\frac{\partial^2 E}{\partial \tilde{P} \partial \tilde{T}} = -1 / (\tilde{P}^2 (1 - \eta))$$

$$\frac{\partial^2 E}{\partial \tilde{P} \partial \eta} = -\tilde{T} / (\tilde{P} (1 - \eta)^2)$$

$$\frac{\partial^2 E}{\partial \tilde{P} \partial y} = -2Q^2 (AQ^2 - B) / \tilde{P}^2$$

$$\frac{\partial E}{\partial \tilde{T}} = 1 / (\tilde{P} (1 - \eta))$$

$$\frac{\partial^2 E}{\partial \tilde{T} \partial \tilde{P}} = \frac{\partial^2 E}{\partial \tilde{P} \partial \tilde{T}}$$

$$\frac{\partial^2 E}{\partial \tilde{T} \partial \eta} = 1 / (\tilde{P} (1 - \eta)^2)$$

$$\frac{\partial E}{\partial \eta} = \tilde{T} / (\tilde{P} (1 - \eta)^2)$$

$$\frac{\partial^2 E}{\partial \eta \partial \tilde{T}} = \frac{\partial^2 E}{\partial \tilde{T} \partial \eta}$$

$$\frac{\partial^2 E}{\partial Q \partial y} = \frac{\partial^2 E}{\partial y \partial Q}$$

$$\frac{\partial^2 E}{\partial Q \partial \tilde{P}} = \frac{\partial^2 E}{\partial \tilde{P} \partial Q}$$

$$\frac{\partial^2 E}{\partial Q^2} = 4y(6AQ^2 - B) / \tilde{P}$$

B.4 Compilation of the derivatives of the incidental variables.

First and second derivatives of the incidental variables with respect to the compositional variable x_1 are as follows:

$$\frac{\partial x_1}{\partial x_1} = 1; \quad \frac{\partial^2 x_1}{\partial x_1^2} = 0$$

$$\frac{\partial < s >}{\partial x_1} = s_1 - s_2; \quad \frac{\partial^2 < s >}{\partial x_1^2} = 0$$

$$\frac{\partial < c >}{\partial x_1} = c_1 - c_2; \quad \frac{\partial^2 < c >}{\partial x_1^2} = 0$$

$$\frac{\partial < M_0 >}{\partial x_1} = < M_0 > m'$$

$$\frac{\partial < M_0 >}{\partial x_1^2} = < M_0 > m'' + \frac{\partial < M_0 >}{\partial x_1} m'$$

with

$$m' = (s_1 M_{01} - s_2 M_{02}) / (s_1 M_{01} x_1 + s_2 M_{02} x_2) - \left(\frac{\partial < s >}{\partial x_1} \right) < s >$$

and

$$m'' = - \left((s_1 M_{01} - s_2 M_{02}) / (s_1 M_{01} x_1 + s_2 M_{02} x_2) \right)^2 + \left(\left(\frac{\partial \langle s \rangle}{\partial x_1} \right) / \langle s \rangle \right)^2 \quad \frac{\partial^2 \tilde{p}}{\partial x_1^2} = \tilde{p} p'' + \left(\frac{\partial \tilde{p}}{\partial x_1} \right) p'$$

$$\frac{\partial \langle \varepsilon^* \rangle < v^* \rangle^m}{\partial x_1} = 2 \left(\frac{\partial X_1}{\partial x_1} \right) \varepsilon' \quad m = 2, 4$$

$$\frac{\partial^2 \langle \varepsilon^* \rangle < v^* \rangle^m}{\partial x_1^2} = 2 \left(\frac{\partial^2 X_1}{\partial x_1^2} \right) \varepsilon' + 2 \left(\frac{\partial X_1}{\partial x_1} \right)^2 \varepsilon'' \quad m = 2, 4$$

$$\frac{\partial X_1}{\partial x_1} = (s_1(z-2) + 2)(s_2(z-2) + 2) / \langle qz \rangle^2$$

$$\frac{\partial^2 X_1}{\partial x_1^2} = \left(\frac{\partial X_1}{\partial x_1} \right) (s_1(z-2) - s_2(z-2)) / \langle qz \rangle^3 ;$$

with

$$\varepsilon' = X_1 \varepsilon_{11}^* v_{11}^{*m} + (1 - 2X_1) \varepsilon_{12}^* v_{12}^{*m} - X_2 \varepsilon_{22}^* v_{22}^{*m}$$

and

$$\varepsilon'' = \varepsilon_{11}^* v_{11}^{*m} - 2\varepsilon_{12}^* v_{12}^{*m} + \varepsilon_{22}^* v_{22}^{*m}$$

$$\frac{\partial \tilde{T}}{\partial x_1} = \tilde{T} p'$$

$$\frac{\partial^2 \tilde{T}}{\partial x_1^2} = \tilde{T} p'' + \frac{\partial \tilde{T}}{\partial x_1} p'$$

$$p' = \frac{\partial \langle c \rangle}{\partial x_1} / \langle c \rangle - \left(\frac{\partial \langle qz \rangle}{\partial x_1} / \langle \varepsilon^* \rangle + \langle qz \rangle \frac{\partial \langle \varepsilon^* \rangle}{\partial x_1} \right)$$

$$/ \langle qz \rangle < \varepsilon^* \rangle$$

$$p'' = - \left(\frac{\partial \langle c \rangle}{\partial x_1} / \langle c \rangle \right)^2 - \left(\left(\frac{\partial \langle qz \rangle}{\partial x_1} / \langle \varepsilon^* \rangle + \langle qz \rangle \frac{\partial \langle \varepsilon^* \rangle}{\partial x_1} \right) \right)^2$$

$$- \left(2 \left(\frac{\partial \langle qz \rangle}{\partial x_1} \right) \left(\frac{\partial \langle \varepsilon^* \rangle}{\partial x_1} \right) + \langle qz \rangle \frac{\partial^2 \langle \varepsilon^* \rangle}{\partial x_1^2} \right) / \langle qz \rangle < \varepsilon^* \rangle$$

$$\frac{\partial \tilde{p}}{\partial x_1} = \tilde{p} p'$$

with

$$p' = \left(- \left(\frac{\partial \langle qz \rangle}{\partial x_1} / \langle \varepsilon^* \rangle + \langle qz \rangle \frac{\partial \langle \varepsilon^* \rangle}{\partial x_1} \right) / \langle qz \rangle \right) + \left(\left(\frac{\partial \langle s \rangle}{\partial x_1} / \langle v^* \rangle + \langle s \rangle \frac{\partial \langle v^* \rangle}{\partial x_1} \right) / \langle s \rangle < v^* \rangle \right)$$

$$p'' = \left(\left(\left(\frac{\partial \langle qz \rangle}{\partial x_1} / \langle \varepsilon^* \rangle + \langle qz \rangle \frac{\partial \langle \varepsilon^* \rangle}{\partial x_1} \right) / \langle qz \rangle \right)^2 - \left(\left(\frac{\partial \langle s \rangle}{\partial x_1} / \langle v^* \rangle + \langle s \rangle \frac{\partial \langle v^* \rangle}{\partial x_1} \right) / \langle s \rangle < v^* \rangle \right)^2 - \left(2 \left(\frac{\partial \langle qz \rangle}{\partial x_1} \right) \left(\frac{\partial \langle \varepsilon^* \rangle}{\partial x_1} \right) + \langle qz \rangle \frac{\partial^2 \langle \varepsilon^* \rangle}{\partial x_1^2} \right) / \langle qz \rangle + \left(2 \left(\frac{\partial \langle s \rangle}{\partial x_1} \right) \left(\frac{\partial \langle v^* \rangle}{\partial x_1} \right) + \langle s \rangle \frac{\partial^2 \langle v^* \rangle}{\partial x_1^2} \right) / \langle s \rangle < v^* \rangle \right)$$

$$\frac{\partial Q}{\partial x_1} = -Q^2 q'$$

$$\frac{\partial^2 Q}{\partial x_1^2} = -2Q \left(\frac{\partial Q}{\partial x_1} \right) q' - Q^2 q''$$

with

$$q' = \tilde{V} \left(\frac{\partial y}{\partial x_1} \right) + y \left(\frac{\partial V}{\partial x_1} \right)$$

and

$$q'' = 2 \left(\frac{\partial \tilde{V}}{\partial x_1} \right) \left(\frac{\partial y}{\partial x_1} \right) + \tilde{V} \left(\frac{\partial^2 y}{\partial x_1^2} \right) + y \left(\frac{\partial^2 \tilde{V}}{\partial x_1^2} \right)$$

$$\frac{\partial \eta}{\partial x_1} = 2^{-1/6} \left(\left(\frac{\partial y}{\partial x_1} \right) Q^{1/3} + \frac{1}{3} y \left(\frac{\partial Q}{\partial x_1} \right) Q^{-2/3} \right)$$

$$\frac{\partial^2 \eta}{\partial x_1^2} = 2^{-1/6} \left(\left(\frac{\partial^2 y}{\partial x_1^2} \right) Q^{1/3} + \frac{2}{3} \left(\frac{\partial y}{\partial x_1} \right) \right)$$

$$\left(\frac{\partial Q}{\partial x_1} \right) Q^{-2/3} - \frac{2}{9} y \left(\frac{\partial Q}{\partial x_1} \right) Q^{-5/3} + \frac{1}{3} y \left(\frac{\partial^2 Q}{\partial x_1^2} \right) Q^{-2/3}$$