A PRACTICAL EQUATION OF STATE VALID IN THE CRITICAL REGION FOR PURE COMPOUNDS

Gustavo A. Iglesias-Silva
Departamento de Ingeniería Química
Instituto Tecnológico de Celaya
Celaya, Guanajuato, CP 38010
(México)

and

Kenneth R. Hall
Chemical Engineering Department
Texas A&M University
College Station, TX 77843
(USA)

Abstract

A simple, analytic expansion about the critical point appears capable of adequate representation for the compression factor in the single phase region near the critical point. The equation requires T_c, P_c, V_c, and ω to predict the compression factor, and we have used it to represent the behavior of methane, argon, carbon dioxide, and ethylene. The scaling hypothesis would indicate that this expansion is invalid, however the data seem to be susceptible of such treatment. The equation can also represent phase behavior in the critical region.

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Introduction

The behavior of pure fluids in the region of their critical points has received considerable attention recently ranging from the classical description discussed by Landau and Lifshitz (1959) to the development of scaling hypothesis as evidenced by the works of Griffiths (1965), Fisher (1967) and Levelt Sengers (1970). Confirmation of these latter methods requires high quality experimental data. In this work, we present a functional representation of the compression factor valid near the critical point in the single phase region. The function resembles the classical description of Landau and Lifshitz (1959), but it is explicit in the compression factor.

Development

The critical point imposes conditions which are useful for development of equations of state. These conditions in mathematical form are:

$$\left(\frac{\partial P}{\partial V}\right)_T\bigg|_{CP} = \left(\frac{\partial P}{\partial \rho}\right)_T\bigg|_{CP} = 0 \tag{1}$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T\bigg|_{CP} = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T\bigg|_{CP} = 0 \tag{2}$$

where P is pressure, T is temperature, V is molar volume and ρ is density. Higher order derivatives may be zero also as discussed by Baher (1963). Equations of state are usually written as

$$P = f(T, V \text{ or } \rho) \quad \text{or} \quad Z = f(T, V \text{ or } \rho) \tag{3}$$

where Z (=$P/\rho RT$) is the compression factor and R is the gas constant, because these forms require fewer terms than forms explicit in P and T. The first and second derivatives of P with respect to ρ expressed in terms of Z and its derivatives are:

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \rho RT\left(\frac{\partial Z}{\partial \rho}\right)_T + ZRT \tag{4}$$

and

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = \rho RT\left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T + 2RT\left(\frac{\partial Z}{\partial \rho}\right)_T . \tag{5}$$

In general, the nth derivative is:

$$\left(\frac{\partial^n P}{\partial \rho^n}\right)_T = \rho RT\left(\frac{\partial^n Z}{\partial \rho^n}\right)_T + nRT\left(\frac{\partial^{n-1} Z}{\partial \rho^{n-1}}\right)_T \qquad n \geq 1 \tag{6}$$

Often it is convenient to express Equation 6 as the derivative of Z with respect to ρ:

$$\left(\frac{\partial^n Z}{\partial \rho^n}\right)_T = \frac{Z}{P}\sum_{i=0}^{n}(-1)^{i+1}\frac{n!}{i!}\frac{1}{\rho^{n-i}}\left(\frac{\partial^i P}{\partial \rho^i}\right)_T \tag{7}$$

where n = 1, 2,..., ∞. Because density and temperature are inverse variables with respect to Z, the derivative of Z with respect to T at constant ρ is:

$$\left(\frac{\partial^n Z}{\partial T^n}\right)_\rho = \frac{Z}{P}\sum_{i=0}^{n}(-1)^{i+1}\frac{n!}{i!}\frac{1}{T^{n-i}}\left(\frac{\partial^i P}{\partial T^i}\right)_\rho . \tag{8}$$

The cross derivative of Z with respect to temperature and density is:

$$\left[\frac{\partial^m}{\partial T}\left(\frac{\partial^n Z}{\partial \rho^n}\right)\right] = \frac{Z}{P}\sum_{k=0}^{m}\sum_{i=0}^{n}(-1)^{k+n-i}\frac{m!}{(m-k)!}\frac{n!}{i!}\frac{1}{T^k\rho^{n-i}}\left[\frac{\partial^{m-k}}{\partial T^{m-k}}\left(\frac{\partial^i P}{\partial \rho^i}\right)\right] \tag{9}$$

For n = 1, 2 at the critical point, Equation 7 becomes:

$$\left(\frac{\partial Z}{\partial \rho}\right)_T = -\frac{Z_C}{\rho_C} \tag{10}$$

and

$$\left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T = 2\frac{Z_C}{\rho_C^2} \tag{11}$$

***T*-*ρ* Plane.**

On the T-ρ plane, isobars have shapes similar to isotherms on the P-ρ plane such that:

$$\left(\frac{\partial T}{\partial \rho}\right)_P\bigg|_{CP} = \left(\frac{\partial^2 T}{\partial \rho^2}\right)_P\bigg|_{CP} = 0 \tag{12}$$

Following the same procedure as used for the P-ρ plane, we obtain:

$$\left(\frac{\partial Z}{\partial \rho}\right)_P\bigg|_{CP} = -\frac{Z_C}{\rho_C} \tag{13}$$

$$\left(\frac{\partial^2 Z}{\partial \rho^2}\right)_P\bigg|_{CP} = 2\frac{Z_C}{\rho_C^2} \tag{14}$$

Thus, the derivatives at the critical point are the same on both the T-ρ and P-ρ planes.

***P*-*T* Plane.**

On the P-T plane, the slope of the critical isochore equals the slope of the vapor pressure curve at the critical point of a pure component. The slope of the vapor pressure at the critical point is proportional to the Reidel constant:

$$\alpha_k \equiv \frac{T_C}{P_C}\left(\frac{dP}{dT}\right)^{\sigma}\Bigg|_{CP} = \frac{T_C}{P_C}\left(\frac{\partial P}{\partial T}\right)_{\rho}\Bigg|_{CP} \approx 5.808 + 4.917\omega \tag{15}$$

where superscript σ denotes the saturation curve (vapor pressure) and ω is the acentric factor. In addition, the critical point is an inflection point for the vapor pressure/critical isochore line:

$$\left(\frac{d^2P}{dT^2}\right)^{\sigma}\Bigg|_{CP} = \left(\frac{\partial^2 P}{\partial T^2}\right)_{\rho}\Bigg|_{CP} = 0 \tag{16}$$

Equations 7 - 9 at the critical point are:

$$\frac{\partial^k Z}{\partial \rho^k}\Bigg|_{CP} = \frac{Z_C k!}{\rho_C^k}\left\{(-1)^k + \sum_{i=3}^{k}(-1)^{k-i}\beta_{i0}\right\} \tag{17}$$

$$\frac{\partial^k Z}{\partial T^k}\Bigg|_{CP} = \frac{Z_C k!}{T_C^k}\left\{(-1)^k(\alpha - 1) + \sum_{i=3}^{k}(-1)^{k-i}\beta_{0i}\right\} \tag{18}$$

and

$$\frac{\partial^n Z}{\partial T^j \partial \rho^{n-j}}\Bigg|_{CP} = \frac{Z_C j!(n-j)!}{\rho_C^{n-j} T_C^j}\left\{\sum_{k=0}^{j-2}(-1)^{k+n-j}\beta_{0,j-k} + \sum_{k=0}^{j-2}\sum_{l=1}^{n-j}(-1)^{k+n-j-l}\beta_{l,j-k}\right.$$

$$\left. + \sum_{l=3}^{n-j}(-1)^{n-l}\beta_{l,0} + \sum_{l=1}^{n-j}(-1)^{n-l-1}\beta_{l,1} + (\alpha-1)(-1)^{n-1}\right\} \tag{19}$$

where the β denote cross partial derivatives of P with respect to t and ρ in reduced form.

An Equation of State for the Critical Region

If we assume that the equation of state is analytic in the single phase region (which is possible even if the critical point is non-analytic in the two phase region) it is possible to make a Taylor series expansion of $Z = Z(T, \rho)$ about the critical point:

$$Z = Z_C + \sum_{n=0}^{\infty} \sum_{j=1}^{n} \frac{1}{j!(n-j)!} \left[\frac{\partial^n Z}{\partial T^j \partial \rho^{n-j}} \right]_{CP} (T - T_C)^j (\rho - \rho_C)^{n-j} \tag{20}$$

which becomes through the second derivative terms:

$$\begin{aligned} Z = Z_C &+ \left(\frac{\partial Z}{\partial \rho} \right)\bigg|_{CP} (\rho - \rho_C) + \left(\frac{\partial^2 Z}{\partial \rho^2} \right)\bigg|_{CP} \frac{(\rho - \rho_C)^2}{2!} + \\ &\left(\frac{\partial Z}{\partial T} \right)\bigg|_{CP} (T - T_C) + \left(\frac{\partial^2 Z}{\partial T^2} \right)\bigg|_{CP} \frac{(T - T_C)^2}{2!} + \left(\frac{\partial^2 Z}{\partial T \partial \rho} \right)\bigg|_{CP} (T - T_C)(\rho - \rho_C) + \ldots \end{aligned} \tag{21}$$

Substituting Equations 10, 11, 15 and 16 into Equation 21 results in:

$$\begin{aligned} \frac{Z - Z_C}{Z_C} = &-\left(\frac{\rho - \rho_C}{\rho_C} \right) + \left(\frac{\rho - \rho_C}{\rho_C} \right)^2 + \\ &(\alpha - 1)\left[\left(\frac{T - T_C}{T_C} \right) - \left(\frac{T - T_C}{T_C} \right)^2 + \left(\frac{\beta_{\rho T}}{\alpha - 1} - 1 \right)\left(\frac{T - T_C}{T_C} \right)\left(\frac{\rho - \rho_C}{\rho_C} \right) \right] \end{aligned} \tag{22}$$

Equation 22 is the simplest form of a Taylor's expansion which could fit data in the critical region. Obviously, higher derivative terms, if included, could extend the applicability of the equation over a wider range.

Results

To test the applicability of this method, we have applied Equation 22 as well as the corresponding equations including through 4th and 6th derivatives to predict the compression factor of argon, carbon dioxide, and ethene, methane and nitrogen. Data sources are from Gilgen *et al.* (1994), Duschek *et al.* (1990), Wagner (1997), Kleinrahm and Wagner (1987) and Wagner (1997) for argon, carbon dioxide, ethene, methane and nitrogen respectively.

Table 1 contains the properties of the substances used in this work. Tables 2 - 6 contain the values (and standard deviations) of the cross derivatives obtained from fits of the data using Taylor's expansions through the 2nd, 4th and 6th derivatives. In each case, the range of data has been restricted such that the deviations are random and within the experimental error estimate. For these data sets, the estimated standard deviation is 0.02 %. Therefore, we have restricted the data such that the fits replicate about 60 - 70 % of the data within 0.02 % and all of the data within 0.06 %. Interestingly, it does not appear that the third derivative of pressure with respect to density is zero although, in some cases, the fourth derivative is zero and in all cases it is near zero.

Figures 1 - 3 illustrate the fits for Ar. Figures 4 and 5 demonstrates the ability of the 4th and 6th derivative equations to correlate phase behavior near the critical point. Figure 6 illustrates the ability of the 6th derivative equation to fit the values of Z along the saturation curve.

Conclusions

A Taylor's expansion in temperature and density appears capable of correlating compression factor data in the near critical region for pure substances within experimental error. Depending upon the number of derivatives included in the expansion, the reduced density range varies from about 0.9 - 1.02 up to 0.55 - 1.3. The first non-zero derivative of pressure with respect to density appears to be the third. The expansion can describe both single and two phase data.

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Table 1. Critical Parameters.

Substance	T_C K	P_C MPa	ρ_C kg·m^{-3}	ω
Argon	150.687	4.8630	535.60	0.0000
Carbon Dioxide	304.128	7.3773	467.60	0.2210
Ethene	282.350	5.0418	214.24	0.0865
Methane	190.551	4.5992	162.66	0.0120
Nitrogen	126.192	3.3958	313.30	0.0380

Table 2. Values of the parameters used in the Equation of State for argon.

Parameter	Estimate	Standard Error	Estimate	Standard Error	Estimate	Standard Error
β_{11}	5.888	0.08	5.811	0.08	5.803	0.04
β_{12}			12.066	1.8	15.456	0.88
β_{13}			-56.29	8.4	-105.86	6.9
β_{14}					-14	24
β_{15}					471	36
β_{21}			-9.615	0.43	-9.537	0.13
β_{22}			14.33	4.2	25.38	2.1
β_{23}					-259	16
β_{24}					427	36
β_{31}			13.08	1.8	16.709	0.44
β_{32}					-69.1	4.4
β_{33}					4	12
β_{41}					13.36	1.2
β_{42}					-77.05	5.4
β_{51}					10.84	1.6
β_{03}			3.241	0.82	3.165	0.43
β_{04}			-64.62	5.6	-96.56	5.0
β_{05}					165	19
β_{06}					94	18
β_{30}			-0.858	0.08	-0.809	0.02
β_{40}			-0.519	0.51	0.012	0.07
β_{50}					3.408	0.26
β_{60}					3.507	0.97

Note: $\beta_{ij} = \dfrac{\rho_C^i T_C^j}{i!\, j!\, P_C} \left(\dfrac{\partial^{i+j} P}{\partial \rho^i \partial T^j} \right)_{CP}$

Table 3. Values of the parameters used in the Equation of State for carbon dioxide.

Parameter	Estimate	Standard Error	Estimate	Standard Error	Estimate	Standard Error
β_{11}	6.341	0.30	6.392	0.09	6.310	0.05
β_{12}			32.34	2.6	41.78	2.2
β_{13}			-179	16	-362	39
β_{14}					-274	290
β_{15}					8778	1413
β_{21}			-11.166	0.33	-12.950	0.10
β_{22}			3.72	4.1	49.32	3.8
β_{23}					-907	99
β_{24}					4097	671
β_{31}			18.13	1.2	23.657	0.38
β_{32}					-175	13
β_{33}					450	83
β_{41}					17.419	0.72
β_{42}					-146.03	9.0
β_{51}					-22.381	0.71
β_{03}			29.42	1.4	63.11	3.3
β_{04}			-272	13	-1105	83
β_{05}					4966	661
β_{06}					-3146	1709
β_{30}			-0.823	0.03	-0.821	0.00
β_{40}			-0.143	0.16	0.212	0.01
β_{50}					2.737	0.03
β_{60}					0.906	0.03

Note: $\beta_{ij} = \dfrac{\rho_C^i T_C^j}{i!\,j!\,P_C}\left(\dfrac{\partial^{i+j} P}{\partial \rho^i \partial T^j}\right)_{CP}$

Table 4. Values of the parameters used in the Equation of State for ethene.

Parameter	Estimate	Standard Error	Estimate	Standard Error	Estimate	Standard Error
β_{11}	5.655	0.70	5.751	0.06	5.708	0.05
β_{12}			26.93	1.7	31.38	1.5
β_{13}			-1234	11	-232	17
β_{14}					10	82
β_{15}					3221	139
β_{21}			-9.851	0.26	-10.921	0.24
β_{22}			12.05	3.5	34.81	5.5
β_{23}					-440	43
β_{24}					1329	112
β_{31}			16.08	1.3	23.74	1.1
β_{32}					-137	14
β_{33}					107	41
β_{41}					25.42	2.9
β_{42}					-181	18
β_{51}					-7.72	5.4
β_{03}			31.51	1.0	50.10	1.3
β_{04}			-276.55	9.9	-800	26
β_{05}					3550	151
β_{06}					-3515	204
β_{30}			-0.824351	0.01	-0.932	0.01
β_{40}			0.115	0.04	0.057	0.03
β_{50}					5.097	0.30
β_{60}					8.29	1.1

Note: $\beta_{ij} = \dfrac{\rho_C^i T_C^j}{i!\,j!\,P_C}\left(\dfrac{\partial^{i+j} P}{\partial \rho^i \partial T^j}\right)_{CP}$

Table 5. Values of the parameters used in the Equation of State for methane.

Parameter	Estimate	Standard Error	Estimate	Standard Error	Estimate	Standard Error
β_{11}	5.000	0.22	5.082	0.07	5.107	0.04
β_{12}			39.21	2.3	42.85	1.9
β_{13}			-241	16	-340	46
β_{14}					-1699	522
β_{15}					26345	3565
β_{21}			-9.488	0.28	-10.549	0.09
β_{22}			30.76	4.4	64.45	4.0
β_{23}					-1044	86
β_{24}					4792	590
β_{31}			19.41	1.4	25.259	0.42
β_{32}					-201.26	9.2
β_{33}					396	64
β_{41}					23.688	0.77
β_{42}					-270	12
β_{51}					-30.81	1.5
β_{03}			32.48	1.7	110.56	8.7
β_{04}			-305	18	-2786	326
β_{05}					22770	3570
β_{06}					-49705	9731
β_{30}			-0.803	0.01	-0.828	0.00
β_{40}			0.042	0.09	0.109	0.01
β_{50}					3.283	0.02
β_{60}					2.104	0.07

Note: $\beta_{ij} = \dfrac{\rho_C^i T_C^j}{i!\,j!\,P_C}\left(\dfrac{\partial^{i+j} P}{\partial \rho^i \partial T^j}\right)_{CP}$

Table 6. Values of the parameters used in the Equation of State for nitrogen

Parameter	Estimate	Standard Error	Estimate	Standard Error	Estimate	Standard Error
β_{11}	5.530	0.18	5.684	0.06	5.683	0.03
β_{12}			23.60	1.4	25.33	0.87
β_{13}			-109.99	7.9	-182	8.5
β_{14}					123	33
β_{15}					1244	48
β_{21}			-9.658694	0.24	-11.256	0.16
β_{22}			17.80	2.8	52.53	3.2
β_{23}					-415	21
β_{24}					779	48
β_{31}			12.77	1.7	20.975	0.83
β_{32}					-60.48	6.4
β_{33}					-147	19
β_{41}					34.41	2.5
β_{42}					-135.57	9.3
β_{51}					13.61	3.6
β_{03}			11.799	0.51	20.052	0.57
β_{04}			-127.46	4.3	-349.75	9.7
β_{05}					1339	50
β_{06}					-1032	55
β_{30}			-0.805	0.01	-0.935	0.01
β_{40}			0.089	0.03	-0.150778	0.02
β_{50}					5.893	0.18
β_{60}					10.886	0.58

Note: $\beta_{ij} = \dfrac{\rho_C^i T_C^j}{i!\,j!\,P_C}\left(\dfrac{\partial^{i+j} P}{\partial \rho^i \partial T^j}\right)_{CP}$

Figure Captions

Figure 1. Correlation of Ar data with 2nd derivative equation.

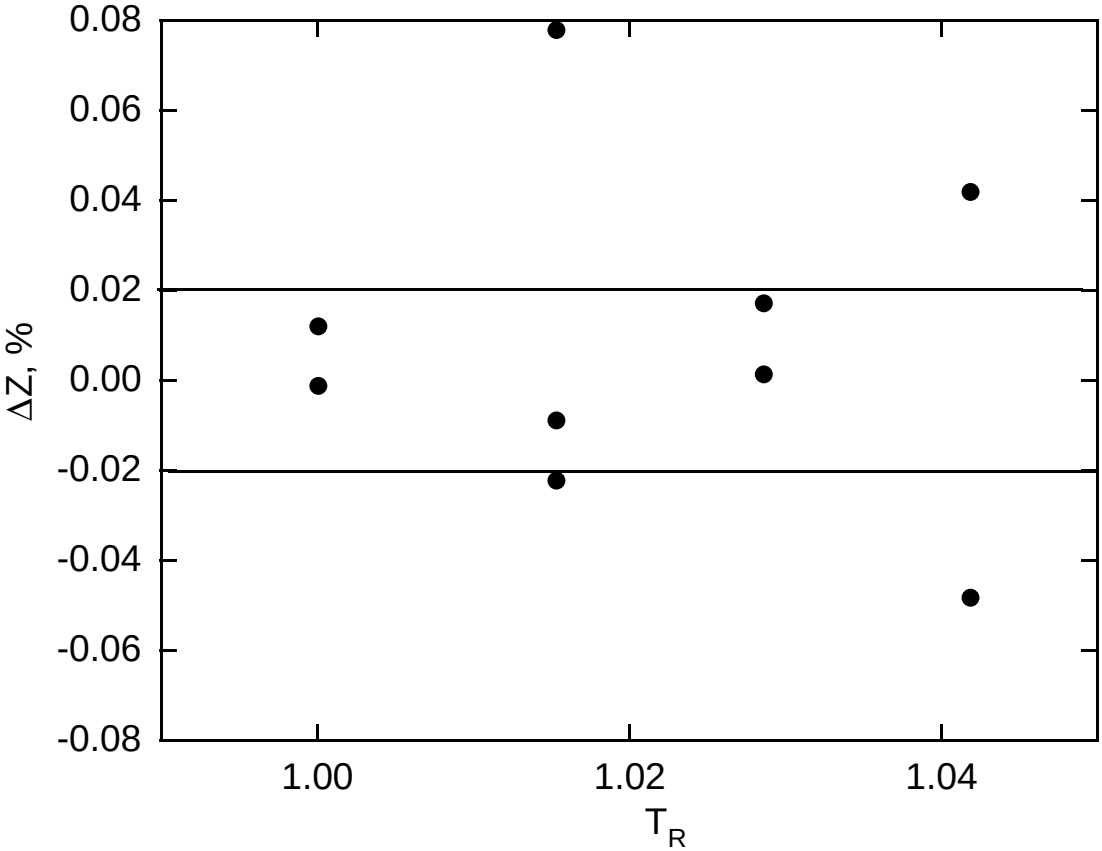
Figure 2. Correlation of Ar data with 2nd derivative equation.

Figure 3. Correlation of Ar data with 2nd derivative equation.

Figure 4. Representation of two phase data using the 4th derivative expansion. Solid circles are saturated vapor and filled circles are saturated liquid.

Figure 5. Representation of two phase data using the 6th derivative expansion. Solid circles are saturated vapor and filled circles are saturated liquid.

Figure 6. Representated of the saturated values for Z using the 6th derivative expansion.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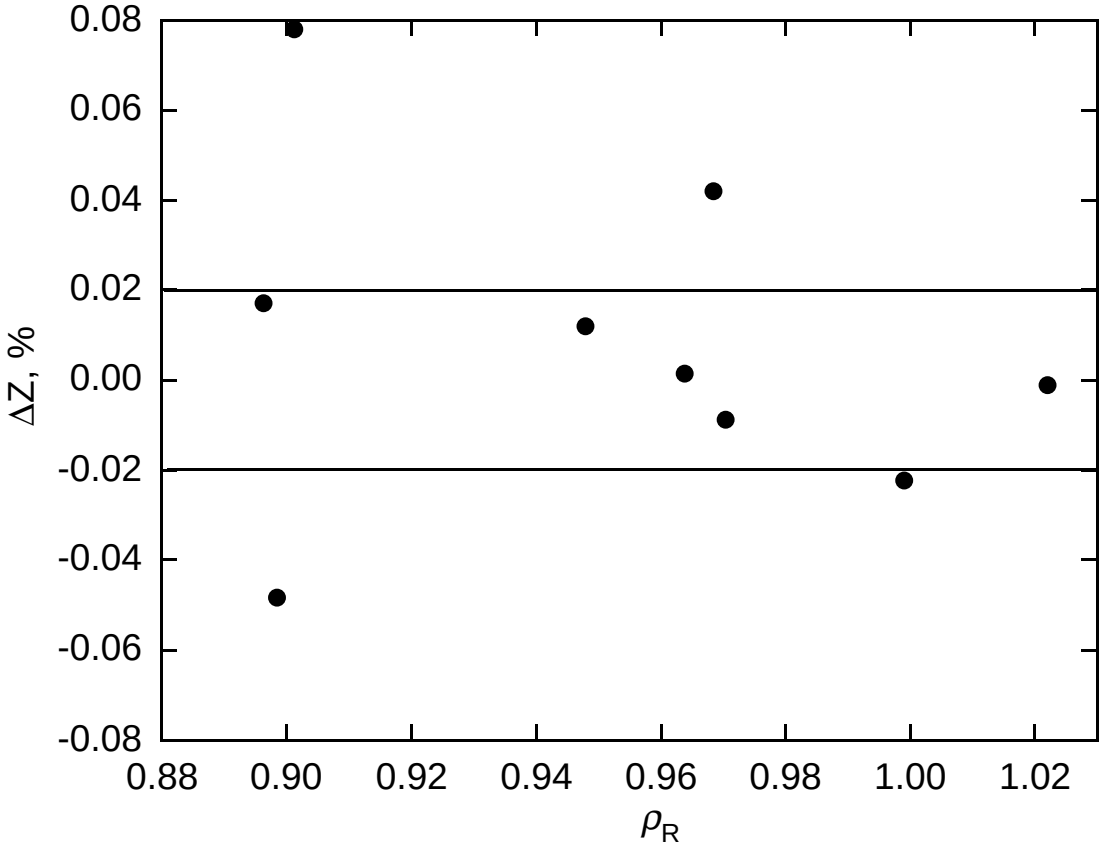
1.04
T_R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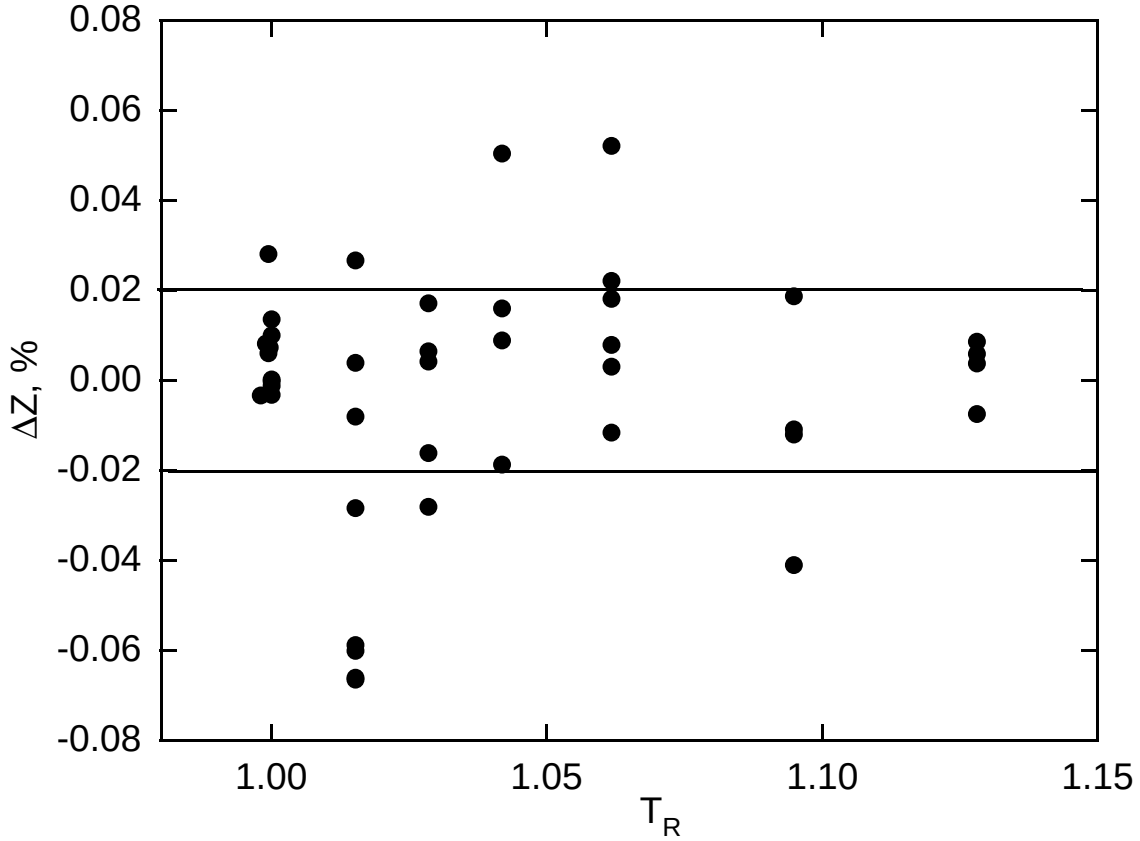
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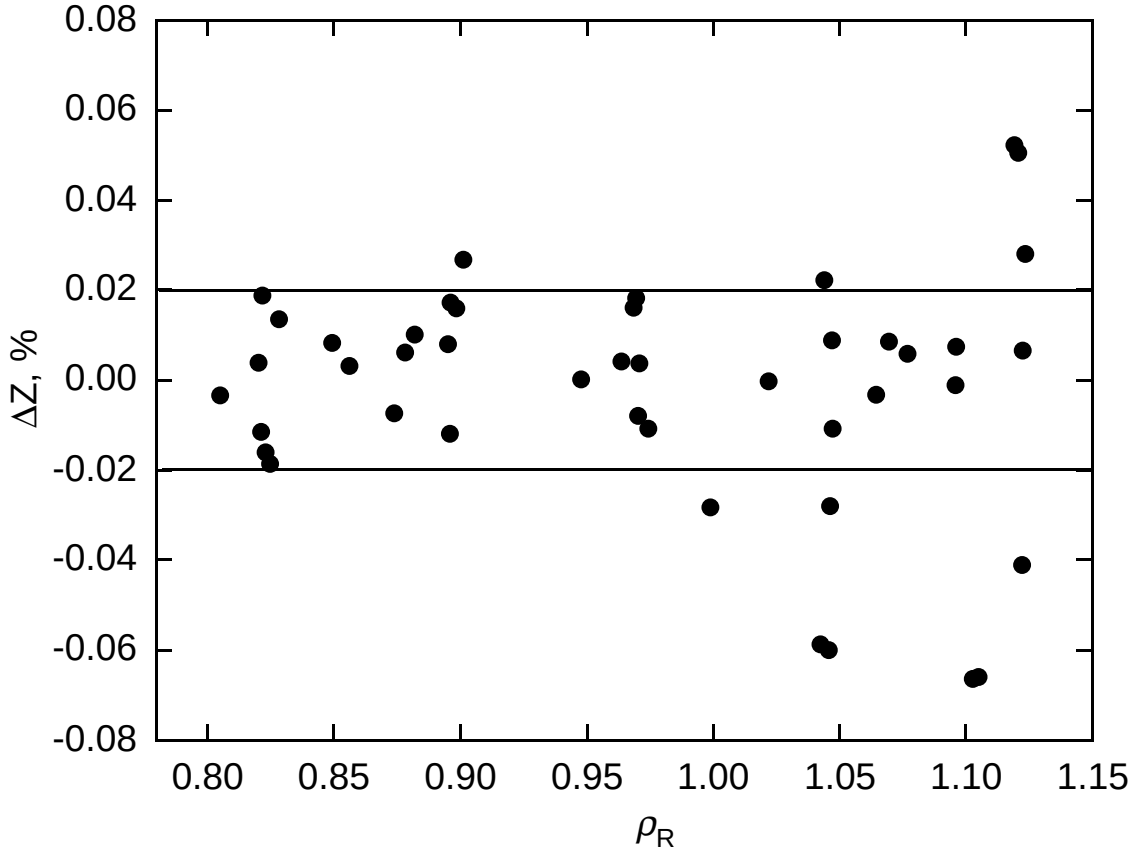
T_R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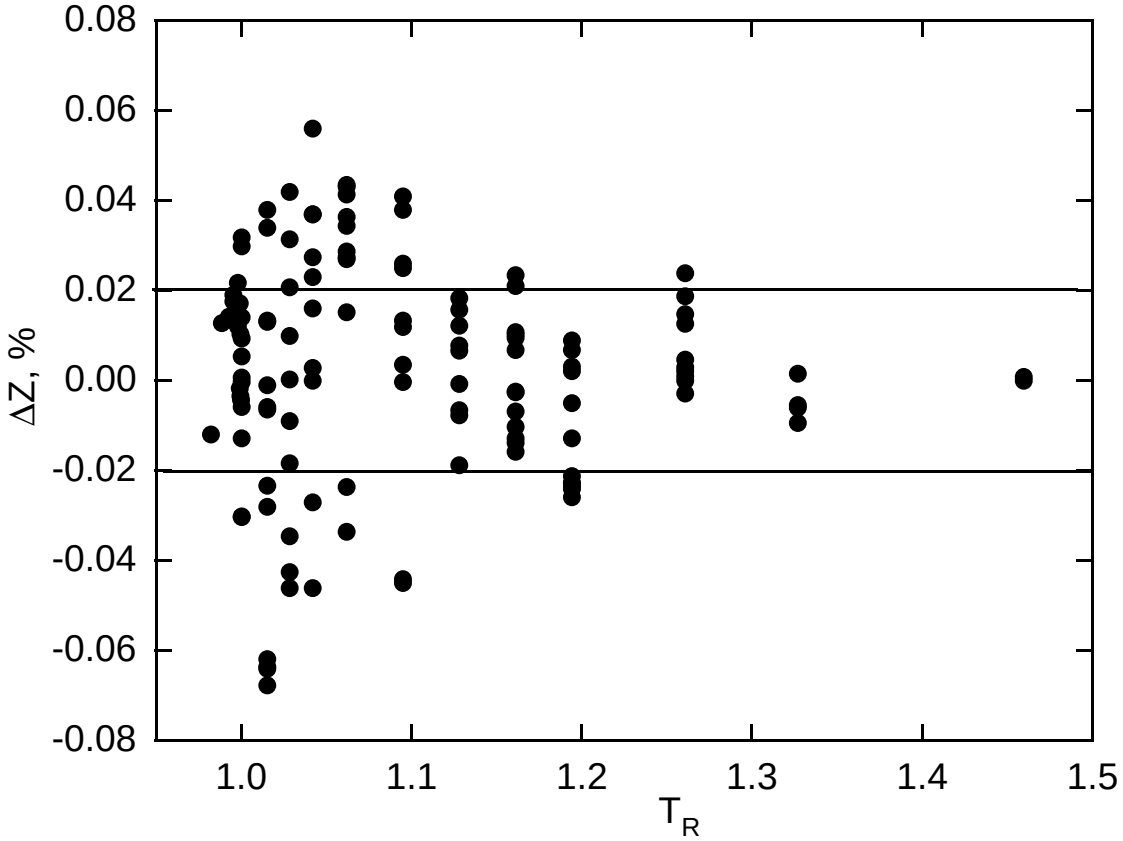
ρ_R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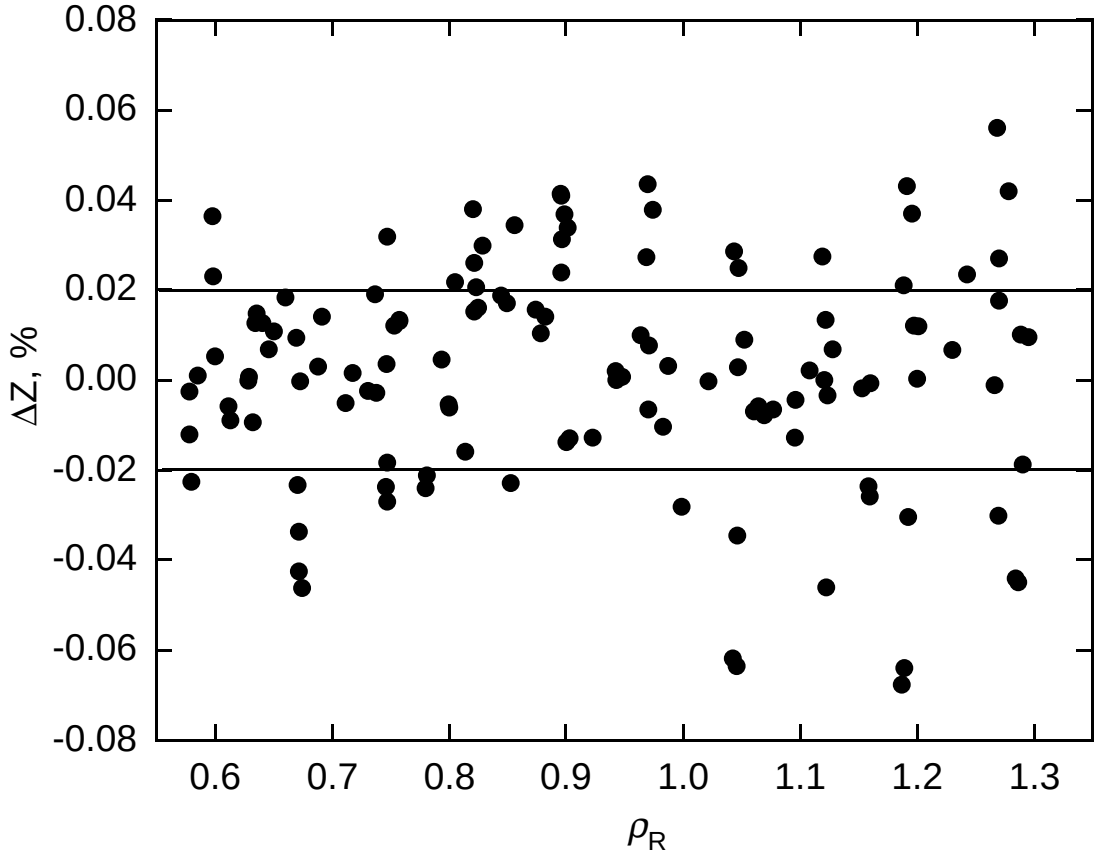
T_R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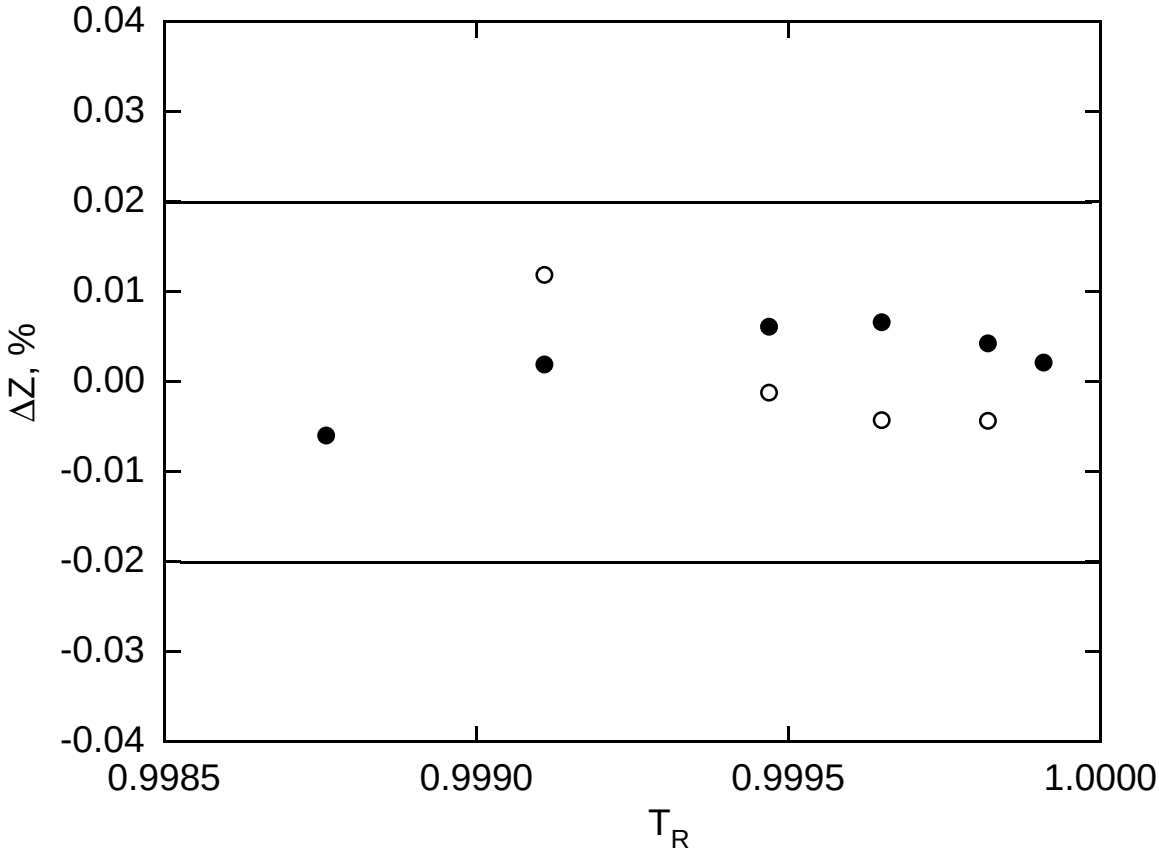
ρ_R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ΔZ, %
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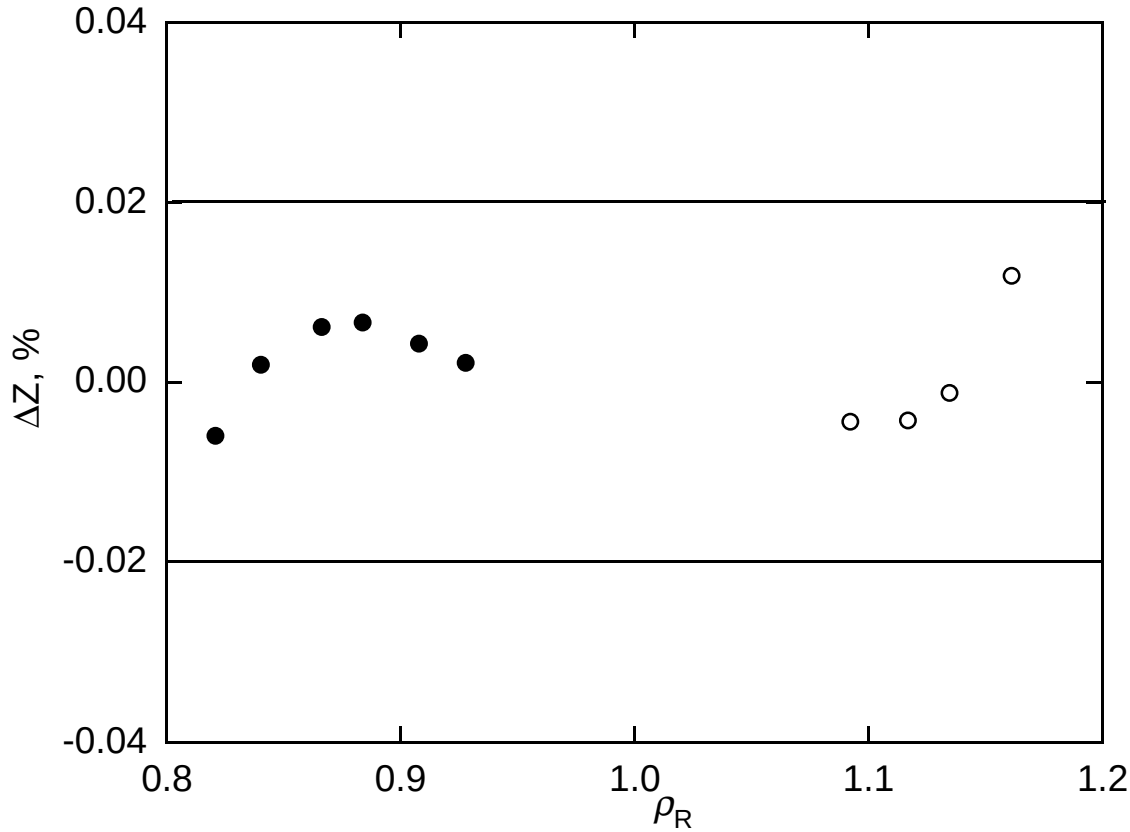
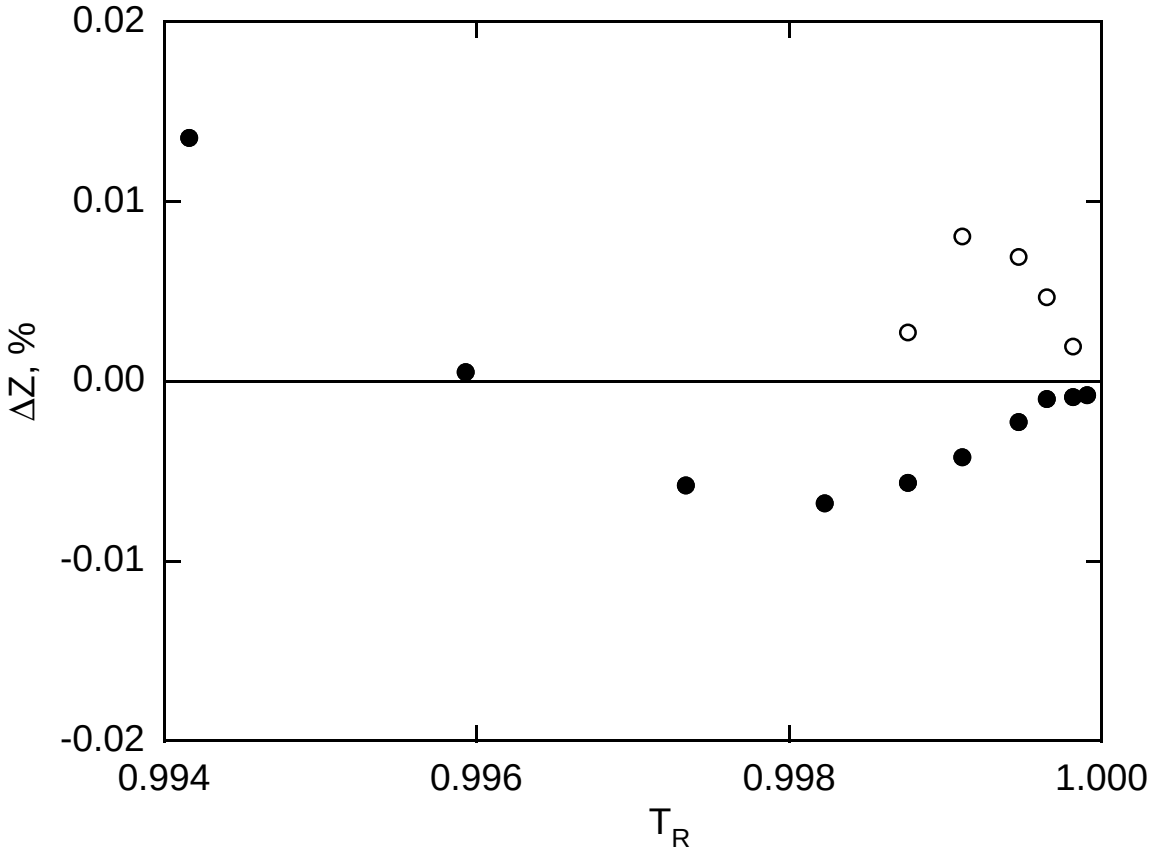
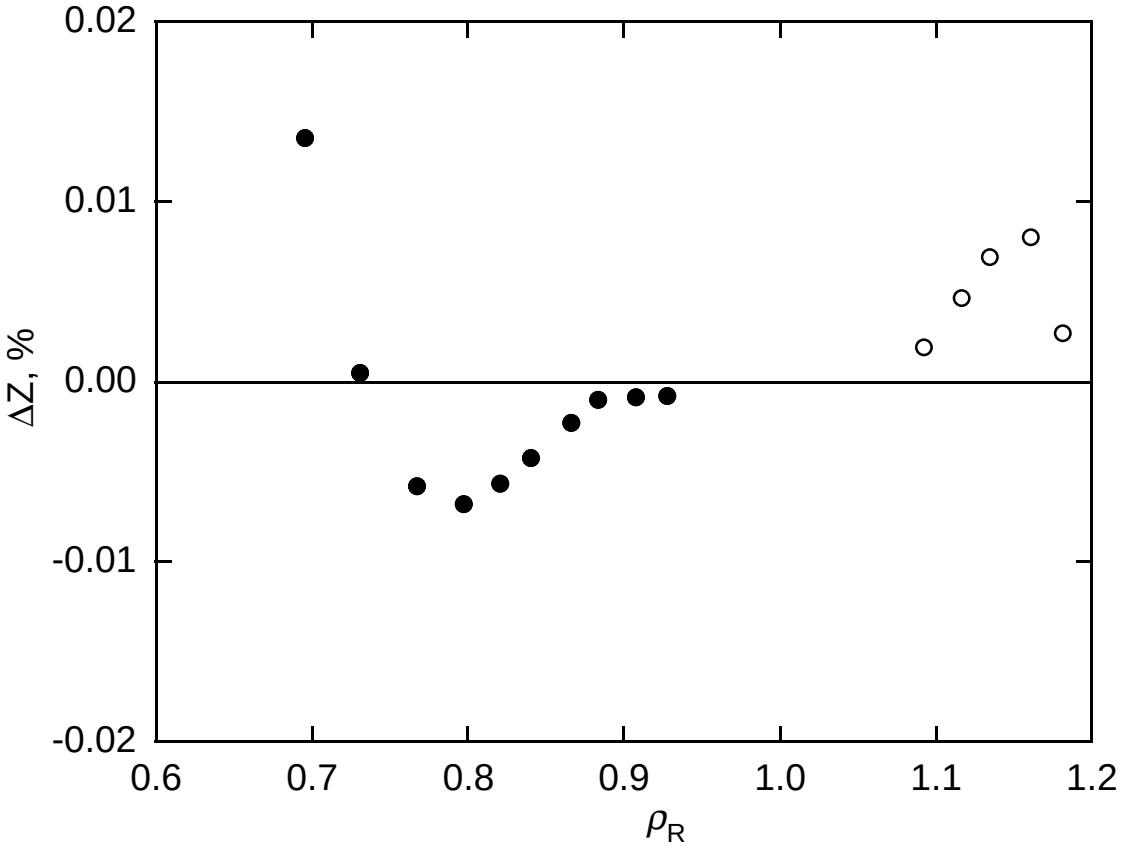
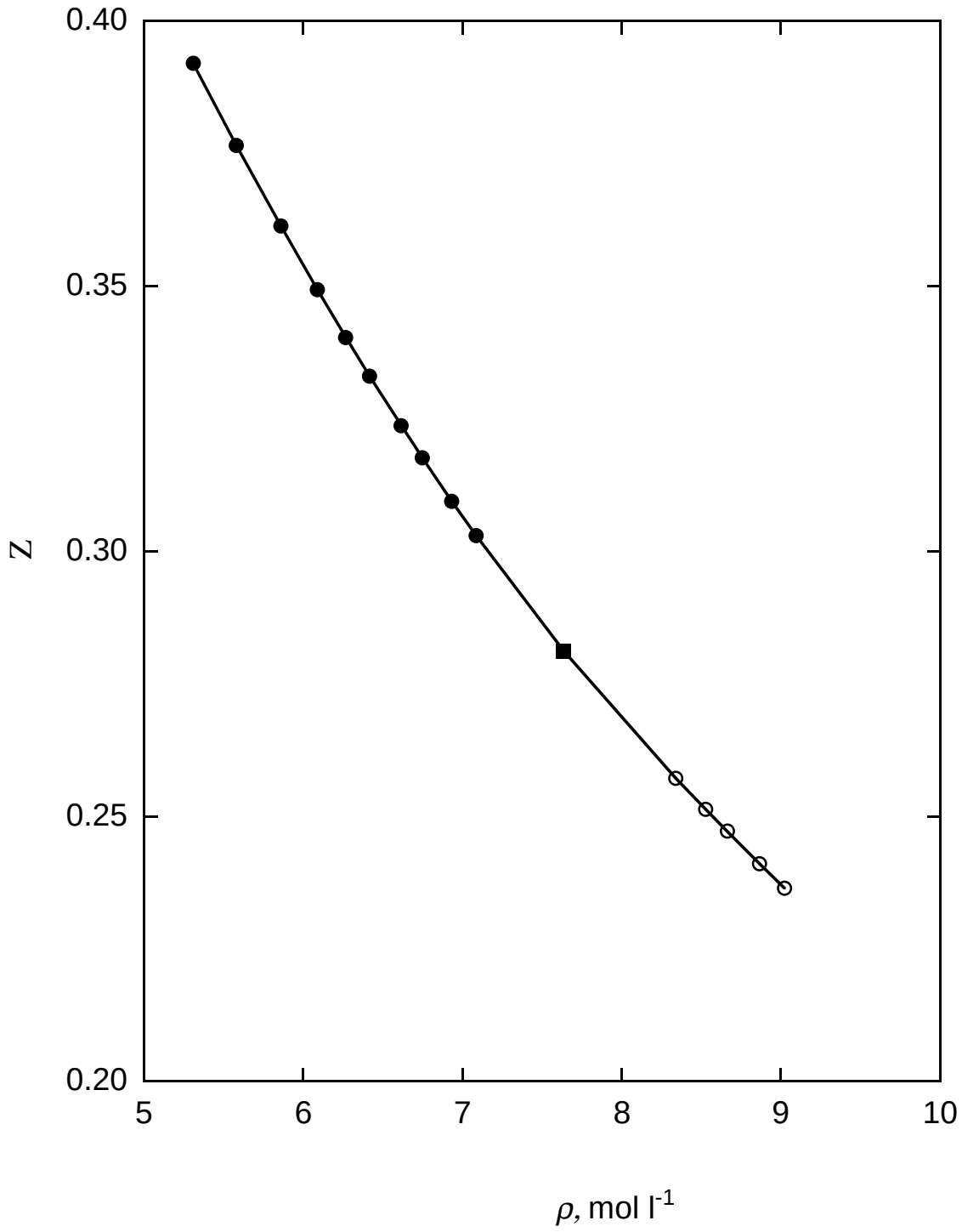
1.0000
T_R


0.04
0.02
0.00
-0.02
-0.04
ΔZ, %
0.8
0.9
1.0
1.1
1.2
ρ_R


0.02
0.01
0.00
-0.01
-0.02
ΔZ, %
0.994
0.996
0.998
1.000
T_R


0.02
0.01
0.00
-0.01
-0.02
ΔZ, %
0.6
0.7
0.8
0.9
1.0
1.1
1.2
ρ_R


0.40
0.35
0.30
0.25
0.20
Z
5
6
7
8
9
10
ρ, mol l-1