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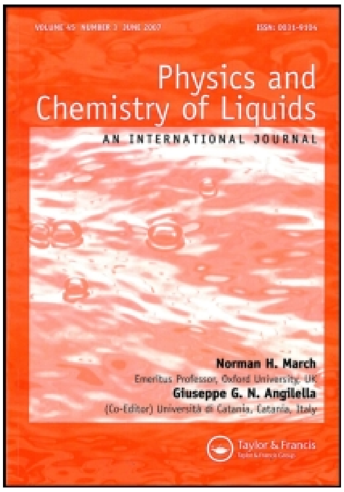

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

A Quasi-lattice Model for the Thermodynamic Properties of Au-Zn Liquid Alloys

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To cite this Article Prasad, L. C. and Singh, R. N.(1990) 'A Quasi-lattice Model for the Thermodynamic Properties of Au-Zn Liquid Alloys', Physics and Chemistry of Liquids, 22: 1, 1 — 9

To link to this Article: DOI: 10.1080/00319109008036406

URL: http://dx.doi.org/10.1080/00319109008036406

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Phys. Chem. Liq., 1990, Vol. 22, pp. 1-9
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A QUASI-LATTICE MODEL FOR THE THERMODYNAMIC PROPERTIES OF Au–Zn LIQUID ALLOYS

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(Received 15 November 1989)

The quasi-lattice model developed by Bhatia and Singh[1-2] has been applied to understand the alloying behaviour of Au–Zn liquid alloys. The large negative values of ordering energy and chemical short range order parameter indicate heterocoordination in Au–Zn melt. The dip in concentration fluctuations in long wavelength limit and larger negative value of excess free energy of mixing at $C = \frac{1}{2}$ suggest the existence of 1-1 type of complexes (AuZn) in the liquid alloys. This makes us believe that Au–Zn liquid alloys with symmetrical properties of mixing belong to strong interacting system.

KEY WORDS: Short range order parameter, binary alloys.

1 INTRODUCTION

The thermodynamic properties of strong interacting binary liquid alloys can be successfully explained by quasi-lattice model developed by Bhatia and Singh[1-2]. The model, in essence, assumes the existence of chemical complexes, $A\mu B\nu$ [$\mu A + \nu B \equiv A\mu B\nu$, μ and ν are small integers and A and B are constituent species] which are in chemical equilibrium with the unassociated atoms of the alloy. Further, they have considered that the energy of a given nearest neighbour bond is different if it belongs to the complex than if it does not. The model has already been used to explain the asymmetry of the properties of mixing of systems like Li–Pb, Mg–Bi, Ag–Al etc. Special attention has been given to concentration fluctuations [Scc(0)] in the long wavelength limit, and the chemical short range order parameter (CSRO).

Recently, Gerling and Predel[3] carried out an experimental investigation on Au–Zn system. It is different from other strong interacting systems in that the excess free energy of mixing (G_M^{xs}) is as low as -20.907 KJ/mol but G_M^{xs} and heat of mixing are almost symmetrical around the equiatomic composition. Their results reveal an existence of $1-1(\mu = \nu = 1)$ type of association of medium strength in the molten state. However, this could better be understood if one considers Scc(0) and CSRO. We plan here to apply the quasi-lattice model of Bhatia and Singh[1] to understand the alloying behaviour of Au–Zn liquid alloys. We apply it to compute activity, excess free energy of mixing (G_M^{xs}), excess entropy of mixing (S_M^{xs}), concentration fluctuations in the long wavelength limit [Scc(0)] and the chemical short range order parameter (α_1) as a function of concentration and temperature.

In Section 2, the general expressions of quasi-lattice model are briefly summarised and are reduced to simple expressions for $\mu = \nu = 1$. Numerical values of the thermodynamic properties including Scc(0) and CSRO have been presented in Section 3 and are discussed in the light of experimental observations$^{3-4}$. A short conclusion is provided in Section 4.

2 FORMULATION

For strong interacting binary liquid alloys, Bhatia and Singh[1] assumed the existence of appropriate privileged group or chemical complexes $A\mu B\nu$, all in chemical equilibrium with unassociated atoms A and B of binary alloy. The grand partition function was solved by assuming that the energy of a given nearest neighbour bond is different if it belongs to the complex than if it does not. This has allowed them to obtain an expression for the activity ratio $\gamma[=\gamma_A/\gamma_B$ where γ_A and γ_B are activity coefficients of A atom and B atom respectively],

$$\ln \gamma = Z \ln 6 + (Z/2K_B T)(P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}) + \phi \tag{1}$$

where Z is the coordination number and ϕ is a constant independent of concentration but may depend upon temperature and pressure. P_{ij} denote the probability that i–j bond is a part of the complex and is given by

$$P_{AB} = C^{\mu-1}(1 - C)^{\nu-1}[2 - C^{\mu-1}(1 - C)^{\nu-1}] \tag{2}$$

$$P_{AA} = C^{\mu-2}(1 - C)^{\nu}[2 - C^{\mu-2}(1 - C)^{\nu}],\ \mu \geqslant 2 \tag{3}$$

$$P_{BB} = C^{\mu}(1 - C)^{\nu-2}[2 - C^{\mu}(1 - C)^{\nu-2}],\ \nu \geqslant 2 \tag{4}$$

ε_{ij} denote the energy of i–j bond if it is free bond and $[\varepsilon_{ij} + \Delta\varepsilon_{ij}]$ denote its energy if the i–j bond is one of the bonds in the complex $A\mu B\nu$. The first term in Eq. (1) is given by

$$Z \ln 6 = \tfrac{1}{2} z \ln \frac{1 - C}{C} \frac{\beta + 2C - 1}{\beta - 2C + 1} \tag{5}$$

β has been set as follows,

$$\beta = [1 + 4C(1 - C)(\eta^2 - 1)]^{1/2} \tag{6}$$

where

$$\eta = \frac{(\rho_{AA}\rho_{BB})^{1/2}}{\rho_{AB}} \tag{7}$$

ρ_{ij} in Eq. (7) stand for

$$\rho_{ij} = e^{-[\varepsilon_{ij} + P_{ij}\Delta\varepsilon_{ij}]/K_B T} \tag{8}$$

In view of Eqs (7) and (8), we may write

$$\eta^2 = \exp[2\omega/ZK_B T] \exp\left[\frac{2P_{AB}\Delta\varepsilon_{AB} - P_{AA}\Delta\varepsilon_{AA} - P_{BB}\Delta\varepsilon_{BB}}{K_B T}\right] \tag{9}$$

where

$$\omega = Z[\varepsilon_{AB} - \tfrac{1}{2}\varepsilon_{AA} - \tfrac{1}{2}\varepsilon_{BB}] \tag{10}$$

which is usually termed as ordering energy. The above expressions simplify considerably if one considers that the likely complexes to be formed are of AB type ($\mu = \nu = 1$). Eq. (2) to (4) become

$$P_{AB} = 1 \quad \text{and} \quad P_{AA} = P_{BB} = 0 \tag{11}$$

and expression (9) reduces to

$$\eta^2 = \exp\left[\frac{2(\omega + Z\Delta\varepsilon_{AB})}{ZK_B T}\right] \tag{12}$$

The expression for activity ratio γ simplifies as

$$\ln \gamma = z \ln 6 = \tfrac{1}{2}\ Z \ln \frac{1 - C}{C} \frac{\beta + 2C - 1}{\beta - 2C + 1} \tag{13}$$

Bhatia and Singh[1] further noted that there exists an exact relation between γ and G_M^{xs} i.e.

$$f'(c) = \ln \gamma,\ f(c) = \frac{G_M^{xs}}{NK_B T} \tag{14}$$

where prime indicates first differential with respect to C. Therefore,

$$\begin{aligned} \frac{G_M^{xs}}{NK_B T} &= \int_0^C Z \ln \sigma \\ &= \tfrac{1}{2}Z\left[c \ln \frac{\beta + 2C - 1}{C(\beta + 1)} + (1 - C) \ln \frac{\beta - 2C + 1}{(1 - C)(\beta + 1)}\right] \end{aligned} \tag{15}$$

This leads to expressions for activity as

$$a_A = C\left[\frac{\beta + 2C - 1}{C(\beta + 1)}\right]^{1/2Z} \tag{16}$$

$$a_B = (1 - C)\left[\frac{\beta - 2C + 1}{(1 - C)(\beta + 1)}\right]^{1/2Z} \tag{17}$$

The expression for entropy of mixing can easily be obtained from Eq. (15) and by using standard thermodynamic relation,

$$S_M = -\left(\frac{dG_M}{dT}\right)_P \tag{18}$$

and

$$S_M^{xs} = -R[C \ln \gamma_A + (1 - C) \ln \gamma_B] - \frac{8RC^2(1 - C)^2\eta^2}{(\beta + 2C - 1)(\beta - 2C + 1)(\beta + 1)} \times \left[\frac{1}{K_B}\frac{d(\omega + Z\Delta\varepsilon_{AB})}{dT} - \frac{\omega + Z\Delta\varepsilon_{AB}}{K_B T}\right] \tag{19}$$

The concentration fluctuations in the long wave length limit thus becomes

$$\mathrm{Scc}(0) = N(\overline{\Delta C})^2 = NK_B T\left(\frac{d^2G_M}{dC^2}\right)^{-1} T, P, N \tag{20}$$

Equations (20) and (15) yield,

$$\mathrm{Scc}(0) = C(1 - C)\left[1 + \tfrac{1}{2}Z\left(\frac{1}{\beta} - 1\right)\right]^{-1} \tag{21}$$

Finally, the expression of Warren–Cowley short range order (SRO) parameter[5–6], α_1, for the nearest neighbour site simplifies to

$$\frac{\alpha_1}{(1 - \alpha_1)^2} = C(1 - C)\left[\exp\left(\frac{2(\omega + Z\Delta\varepsilon_{AB})}{ZK_B T}\right)^{-1}\right] \tag{22}$$

3 RESULTS AND DISCUSSION

3.1 *Activity*

The numerical values of activity (a_{Zn}) have been obtained from Eq. (16) where the energy term ($w + Z\Delta\varepsilon_{AB}$) and the coordination number Z are basic inputs. In liquid and amorphous state, the atoms are randomly distributed in a nearly closed packed structure and therefore the coordination number for nearest neighbour shell is about 10 (See Waseda[7]). So far as the energy term is concerned there is no well defined method to determine it. In principle, it can be determined by using pairwise interactions of pseudo-potential method[8–9] but very little progress has been done in this direction. We further note that both w and $\Delta\varepsilon_{AB}$ are independent of concentration but may depend on temperature and pressure. Therefore, we express ($w + Z\Delta\varepsilon_{AB}$) as W, an energy parameter. For want of better information, we suggest that W can be determined from observed free energy of mixing at equiatomic composition i.e.

$$G_M^{xs}/NK_B T = \ln 2^{z/2}[1 + \exp(-W/ZK_B T)]^{-1/2Z} \tag{23}$$

The observed data of Gerling and Predel[3] for Au–Zn liquid alloys suggests that $W/K_B T$ is equal to -7.2789 at 1173°K. On the other hand, the data by Hultgren *et al.*[4] at $C = 1/2$ yield $W/K_B T = -7.6936$ at 1080°K. We therefore simply express

$$W = A + BT \tag{24}$$

where the coefficients A and B are $-12.509428\ K_B T$ and $0.0044591\ K_B$ respectively.

Table 1 Activity of Zn(a_{Zn}) of Au-Zn liquid alloys.

C_{Zn}	a_{Zn}		
	Theory		*Experimental*[4]
	T = 1080°K	*T = 1173°K*	*T = 1080°K*
0.1	0.00011	0.00016	0.00012
0.2	0.00056	0.00080	0.00051
0.3	0.00257	0.00349	0.00312
0.4	0.01185	0.01493	0.01360
0.5	0.05090	0.05860	0.05350
0.6	0.16822	0.17979	0.17200
0.7	0.38483	0.39465	0.39000
0.8	0.64146	0.64628	0.65000
0.9	0.85931	0.86042	0.85600

The computed values of activity at $T = 1080°K$ and $T = 1173°K$ have been tabulated in Table 1 along with the experimental values of Hultgren *et al*[4]. From Table 1 it is apparent that the theoretical and the experimental values are in good agreement. Our values suggest that activity is very sensitive to temperature and the magnitude of a_{Zn} increases with the increase in temperature.

We may recall that the activity is one of those thermodynamic functions which can be measured directly from the experiment and therefore, can be used with greater confidence to check the validity of the theoretically derived expressions.

3.2 Excess Free energy of mixing (G_M^{xs}) and concentration fluctuations in the long wave length limit [Scc(0)]

Equation (15) has been used to compute excess free energy of mixing G_M^{xs} as a function of concentration at 1080°K and 1173°K. The energy parameter is same as that used in the computation of activity. The computed values of G_M^{xs} are plotted in the lower part of Figure 1, and are compared with the experimental observations[3-4]. The theoretical and experimental values are in good agreement.

We observe that G_M^{xs} of Au-Zn liquid alloys is quite symmetrical around $C = 1/2$ and exhibits minimum around equiatomic composition. It is as low as -20.907 KJ/mol. which is close to the values for other strong interacting liquid alloys namely Mg-Bi ($G_M^{xs} \simeq -21.79$ KJ/mol) and Li-Pb ($G_M^{xs} \simeq -22$ KJ/mol). This indicates that Au-Zn liquid alloys belong to a very strong-interacting system.

With this in mind, we have computed Scc(0) which is widely used to explain the nature of interactions[10] in binary liquid alloys. The same energy parameter has been used in Eq. (21) to compute Scc(0) as a function of concentration. These are plotted in the upper part of Figure 1. The computed results are also compared with the values obtained directly from the activity data i.e.

$$\mathrm{Scc}(0) = \frac{C_{\mathrm{Au}} a_{\mathrm{Zn}}}{(\partial a_{\mathrm{Zn}}/\partial C_{\mathrm{Zn}})_{T,P,N}} \tag{25}$$

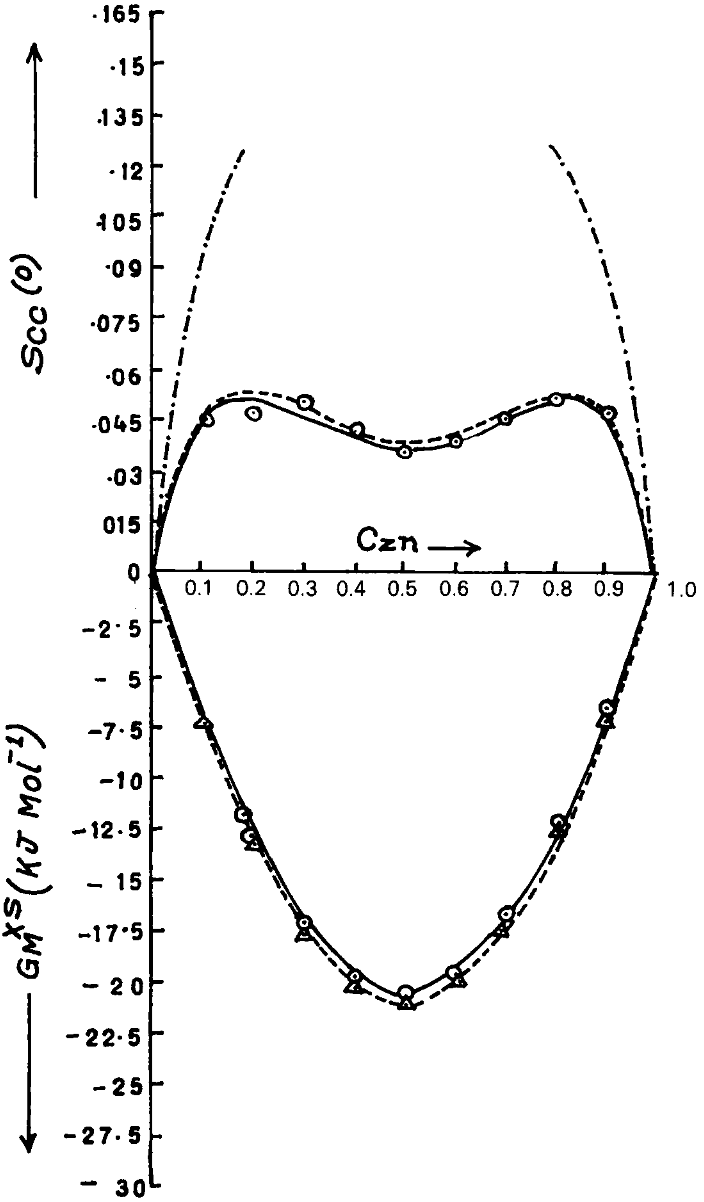

Figure 1 Lower part: Excess free energy of mixing (G_M^{xs} KJ mol^{-1}) of Au–Zn liquid alloys at different temperatures. (———) theory at 1080°K, (- - - - -) theory at 1173°K, (⊙⊙⊙⊙) refer to experimental[4] values at 1080°K and (△△△△) denote experimental[3] points at 1173°K. Upper Part: Concentration fluctuations at $q = 0$ [Scc(0)] of Au–Zn liquid alloys at different temperatures (———) theory at 1080°K and (- - - - - -) theory at 1173°K. (⊙⊙⊙⊙) refer to experimental[4] values at 1080°K and (–·–·–·–) denote Scc^{id}(0).

Scc(0) computed from Eq. (25) are usually termed as experimental values. Though it can be measured directly from small angle scattering measurements, but due to involved complexities no such measurements exist.

Scc(0) computed from theoretical expression (21) and that from Eq. (25) are in good agreement. The figure shows a distinct minimum at equiatomic composition with maximum on either side. It clearly indicates that 1–1 complex (Au–Zn) exists in the molten state. Obviously, the stability is maximum at $C = 1/2$. Singh[10] has pointed out that the point of inflection in Scc(0) corresponds to $W/K_BT \simeq -2.6$ for $Z = 8$ and $W/K_BT \simeq -3.3$ for $Z = 12$. There is no minimum in Scc(0) for W/K_BT greater than these values but exhibits only maximum at $C = 1/2$. It may be noted that the value of W/K_BT for Au–Zn is much smaller ($\simeq -7.69$) than the values assigned to obtain inflection in Scc(0). This simply indicates that the bonding between nearest unlike atom is quite strong around the equiatomic composition.

3.3 Chemical short range order parameter (α_1)

Warren–Cowley short range order parameter[5–6] is widely used to understand the nature of ordering in nearest neighbour shell of binary liquid alloys. Since the work by Bhatia and Singh[1], it has become possible to compute α_1 as a function of concentration from the knowledge of ordering energy and the coordination number. Recently Singh[10] has discussed in detail the nature of order parameter and the impact of W and Z on α_1. We therefore, have used Eq. (22) to compute α_1 for Au–Zn liquid alloys. The energy parameter W and the coordination number Z are same as used in the derivation of activity, G_M^{xs} and Scc(0). The computed values at 1080°K and 1173°K are plotted in Figure 2. We observe that α_1 is negative at all concentrations

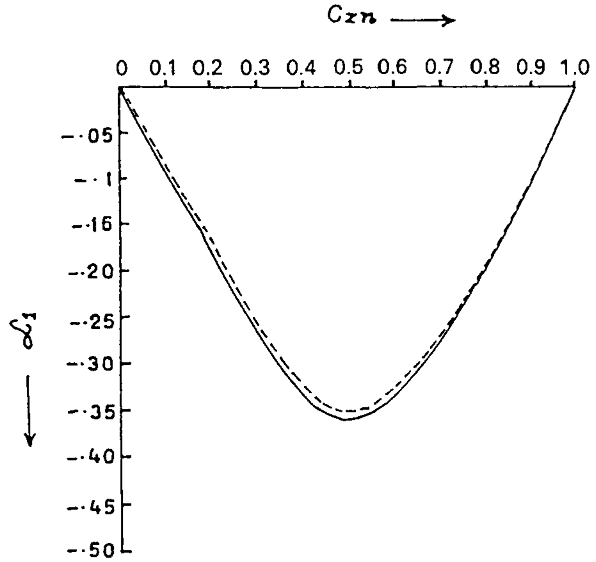

Figure 2 Chemical short range order parameter (α_1) of Au–Zn liquid alloys at different temperatures (———) theory at 1080°K and (-----) theory at 1173°K.

and symmetrical at $C = 1/2$. The maximum hetero-coordination (preference of unlike atoms as nearest neighbours) occurs at equiatomic composition. α_1 at $C = 1/2$ has been found to be equal to -0.366 at 1080°K and -0.348 at 1173°K. We may recall that for complete ordering α_1 is -1 at equiatomic composition. Our computed values suggest that at 1080°K the ordering is only of the order of 37% and thus hetero-coordination is not complete in the nearest neighbour shell.

3.4 Excess entropy of mixing (S_M^{xs})

Lastly, we used Eq. (19) to compute excess entropy of mixing S_M^{xs}, as a function of concentration. Here, one requires the value of dW/dT. At first place, we have tried to determine it from Eq. (24) which was in turn used to determine S_M^{xs}. We found that a simple relation like Eq. (24) cannot be used successfully to explain S_M^{xs}. In this connection we may refer to the work by Singh *et al.*[11] who have also experienced a similar problem while working with Li–Mg system. Contrary to this, they have suggested that dW/dT should be determined from the observed heat of mixing at $C = 1/2$ i.e.

$$\frac{H_M}{RT} = -0.5\left[1+\exp\left(\frac{W}{ZK_BT}\right)\right]^{-1}\left[\frac{1}{K_B}\frac{dW}{dT}-\frac{W}{K_BT}\right] \qquad (26)$$

We have used the observed value of H_M at $C = 1/2$ of Gerling and Predel[3] to determine $1/K_B(dW/dT)$ from above equation. The latter is then used in Eq. (19) to compute S_M^{xs} as a function of concentration. These are plotted in Figure 3 and are

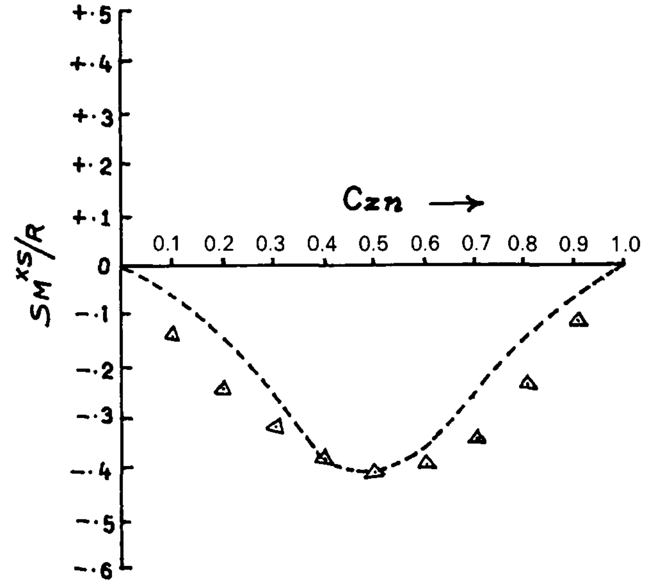

Figure 3 Excess entropy of mixing (S_M^{xs}/R) of Au–Zn liquid alloys at $T = 1173$°K. (-----) theory and (△△△△) refer to experimental[3] values.

compared with the experimental values[3]. The two are in reasonable agreement with one another likewise other thermodynamic properties. S_M^{xs} is also symmetrical about $C = 1/2$ and exhibits minimum at equiatomic composition.

4 CONCLUSION

The quasi-lattice model for compound forming molten alloys successfully explains the thermodynamic properties like activity, excess free energy of mixing, concentration fluctuations in the long wavelength limit, short range order parameter and excess entropy of mixing of Au–Zn liquid alloys. The large negative values of W and α_1 indicate heterocoordination in the Au–Zn melt. Scc(0) exhibits maximum stability around the equiatomic composition. Scc(0) has a distinct dip at $C = 1/2$ with maxima on either side. The large negative values of G_M^{xs} and the dip in Scc(0) suggest the existence of complexes Au–Zn in the vicinity of equiatomic composition. The minimum values of S_M^{xs} and α_1 at $C = 1/2$ further substantiate the above observation. Au–Zn liquid alloys have been found to be different from other strong interacting systems because most of the properties of mixing are symmetrical around $C = 1/2$, which is usually not found in other strong interacting systems.

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