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Fluctuations and universality in a catalysis model with long-range reactivity

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Abstract

The critical properties of the Ziff-Gulari-Barshad (ZGB) model with the addition of long-range reactivity [C. H. Chan and P. A. Rikvold, Phys. Rev. E **91**, 012103 (2015)] are further investigated. The scaling behaviors of the order parameter, susceptibility, and correlation length provide additional evidence that the universality class of the ZGB system changes from the two-dimensional Ising class to the mean-field class with the addition of even a weak long-range reactivity mechanism.

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1. Model and Motivation

In 1986, Ziff, Gulari, and Barshad introduced a lattice-gas model (known as the ZGB model) to simulate the nonequilibrium process of the oxidation of carbon monoxide on a Pt catalyst (Ziff 1986). The catalyst surface is modeled as a $L \times L$ square lattice, and a random site is chosen L^2 times in each time step (MCSS, Monte Carlo step per site). Adsorption of the gas species can take place only if the chosen site is empty. CO is adsorbed with probability y, which is proportional to its partial pressure in the supplied gas. Adsorption of oxygen is attempted with probability $1 - y$, but is successful only if a randomly chosen nearest-neighbor site is also empty. O_2 then dissociates into two adsorbed O atoms. After the adsorption, the adsorbed species checks its four nearest-neighbor sites. If the opposite species is found, the pair forms carbon dioxide (CO_2) and leaves the surface immediately. It has further been noticed in experiments that adsorbed species can desorb from the surface without reacting, and that the desorption rate of carbon monoxide is much higher than that of oxygen (Ehsasi 1986). Therefore, the desorption rate of CO (k) is often added to the model as a second control parameter, in addition to the CO partial pressure (y) (Brosilow 1992, Tomé 1993). In this work, we choose desorption with probability k. The desorption rate can be considered as a proxy for temperature as thermal fluctuations would make the adsorbed particle break its bond with the catalyst surface more easily.

If the CO desorption rate (k) is not very high, simulations show that the catalyst surface can be in one of three phases, depending on the value of the CO partial pressure (y): 1. CO poisoned phase, which has CO covering most of

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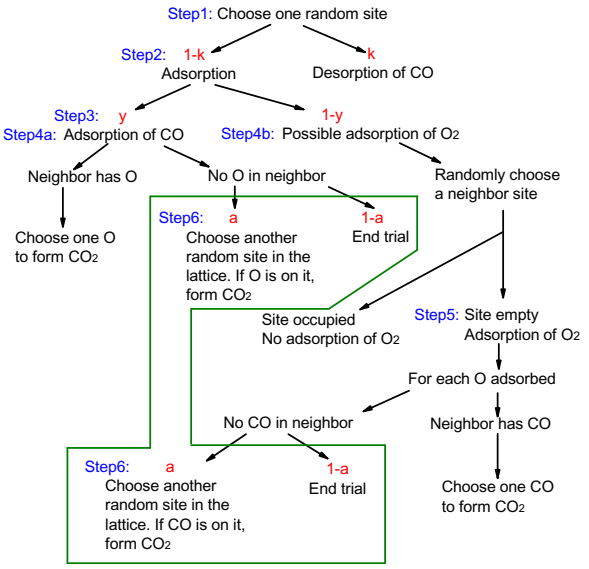

Figure 1. Flow chart for the reaction process. The algorithm is based on that used in (Machado 2005) for the ZGB model with CO desorption. The framed region contains the added long-range reactivity of strength a. (From Chan 2015).

the surface with some scattered empty sites. It is observed when y is large. 2. O-poisoned phase, which has oxygen covering the whole surface when the CO partial pressure (y) is sufficiently low (not observed in experiments). 3. mixed phase, in which the catalyst surface is covered by a mixture of O, CO, and empty sites. It is observed for intermediate values of y. The order parameter of the system is the CO coverage (θ_{CO}), which is defined as the proportion of the lattice sites occupied by CO. A first-order phase transition line separates the mixed phase and the CO poisoned phase. Similar to an equilibrium lattice-gas system, moving along this first-order transition line in the phase diagram eventually leads to a critical point. It has been found that this critical point belongs to the two-dimensional equilibrium Ising universality class (Tomé 1993).

Recent studies of adding non-zero long-range interactions in an equilibrium Ising ferromagnet (Nakada 2011) showed that the universality class of the critical point changed abruptly from Ising to mean-field. Motivated by this result, we recently modified the ZGB model by introducing an adjustable probability (a) that an O atom and a CO molecule adsorbed far apart on the surface can react to form CO_2 and desorb (Chan 2015). This move is attempted only if the adsorbed species cannot find an opposite species within its four nearest-neighbor sites. If the two sites contain opposite species, CO_2 will be formed and the two sites will become empty. Details of the implementation are shown in Fig. 1. While our recent work (Chan 2015) has shown that the universality class of the critical point changes from the Ising class to the mean-field class using fourth-order cumulants, here we look at the fluctuations of the order parameter (CO coverage) at the critical point through two quantities, the 'susceptibility' and the time average of the absolute difference of the CO coverage from its mean value. The results further confirm the change of the universality class of the critical point from Ising to mean-field upon introducing long-range reactivity.

2. Results

Figure 2(a) shows a Ln-Ln scaling relation between the time average of the absolute difference of the CO coverage from its mean ($\langle|\theta_{\mathrm{CO,c}} - \langle\theta_{\mathrm{CO,c}}\rangle|\rangle$) at the critical point, and the system size (L). The critical points were found in our recent work (Chan 2015), using cumulant crossing. The negatives of the slopes of these lines represent the critical exponent ratio β/ν and are plotted in Fig. 2(b). Without long-range reactivity ($a = 0$), we obtain 0.0977 ± 0.0007, which is close to the exact Ising value of $\beta = 1/8$ and $\nu = 1$. For the case with long-range reactivity ($a > 0$), the weighted average is 0.564 ± 0.008, consistent with the exact mean-field result of $\beta = 1/2$ and $\nu = 1$.

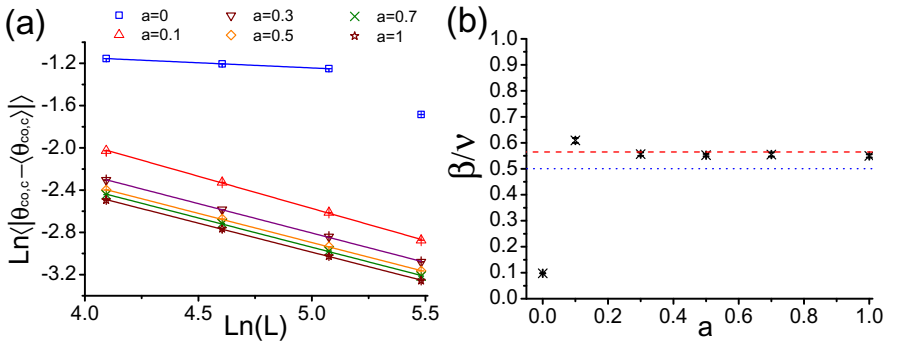

Figure 2. (a) Natural logarithm of the time average of the difference of the CO coverage from its mean, shown vs the natural logarithm of the size of the system for $L = 60$, 100, 160, and 240. 10^7 MCSS were used for non-zero long-range reactivity ($a = 0.1, 0.3, 0.5, 0.7$ and 1), and 10^8 MCSS were used without long-range reactivity ($a = 0$), when the system was near the corresponding critical point (e.g, the data point for $L = 100$ was taken at the 100/60 cumulant crossing point). The negative of the slopes of these lines are the critical exponent ratio β/ν and are plotted in (b). For $a = 0$, it gives 0.0977 ± 0.0007, which is close to the exact Ising value of $1/8 = 0.125$. For $a > 0$, the weighted average value is 0.564 ± 0.008 (dashed line), which is close to the exact mean-field value of 1/2 (dotted line).

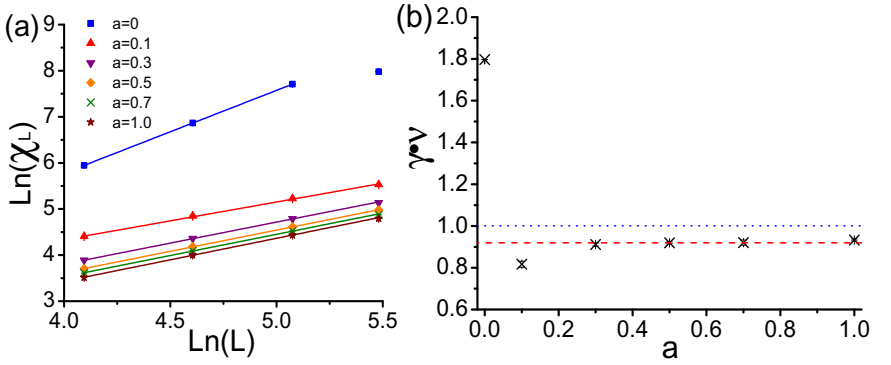

Figure 3. (a) Natural logarithm of the susceptibility (χ_L), shown vs the natural logarithm of the system size (L) for $L = 60$, 100, 160, and 240 near their corresponding critical points with $a = 0$, 0.1, 0.3, 0.5, 0.7, and 1. 5×10^7 MCSS were used for $a > 0$ and 10^8 MCSS for $a = 0$. The slopes of the fitting lines for different long-range reactivities (a) are the critical exponent ratio γ/ν, plotted in (b). For the Ising case ($a = 0$), we obtain $\gamma/\nu = 1.7967 \pm 0.0001$, which is close to the exact Ising value of 7/4. For the mean-field case ($a > 0$), we get a weighted average of $\gamma/\nu = 0.92 \pm 0.01$ (dashed line), which is close to the exact mean-field value of 1 (dotted line).

We define a nonequilibrium analog of equilibrium magnetic susceptibility or fluid compressibility as

$$\chi_L = L^2(\langle\theta^2_{\mathrm{CO},L}\rangle - \langle\theta_{\mathrm{CO},L}\rangle^2) \tag{1}$$

for a $L \times L$ system, which for simplicity we call 'susceptibility.' It is well suited to measure the strong fluctuations of the order parameter near the nonequilibrium critical point (Machado 2005). Figure. 3(a) shows the natural logarithm of the susceptibility (χ_L) vs the natural logarithm of the system size (L). The slopes of the fitting lines represent the critical exponent ratio γ/ν (Nakada 2011) and are shown in Fig. 3(b). For $a = 0$, we obtain $\gamma/\nu = 1.7967 \pm 0.0001$, which is close to the exact Ising value of 7/4. For $a > 0$, we get a weighted average of $\gamma/\nu = 0.92 \pm 0.01$, which is close to the exact mean-field value of 1.

We define the CO disconnected correlation function as $c(r) = \langle\sigma_i\sigma_j\rangle$, where σ_i is 1 if site i is occupied by CO and is 0 otherwise, r is the distance between site i and site j, and the spatial average is taken along the horizontal and vertical directions. The critical correlation length was estimated by integration as

$$\xi(L) = \frac{\int_0^{L/2}[\langle c(r)\rangle - \langle c(L/2)\rangle]rdr}{\int_0^{L/2}[\langle c(r)\rangle - \langle c(L/2)\rangle]dr} \tag{2}$$

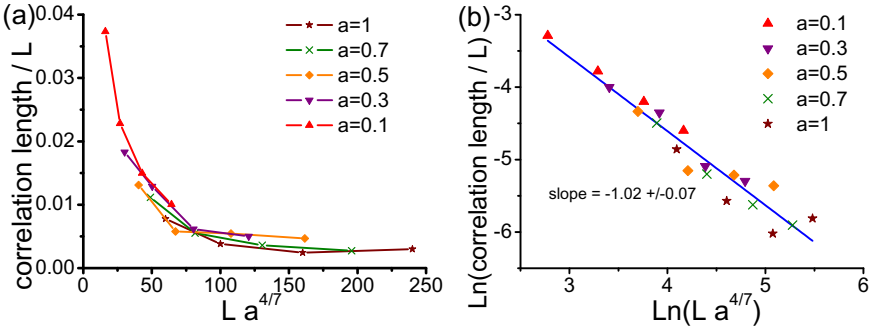

Figure 4. (a) Scaling plot of the correlation length at the corresponding critical points with a scaling index of 4/7 for $a > 0$, using 10^7 MCSS. Scaling index values of 0.435, 0.448, 0.499, 0.45 and (4/7)/1.3 were also tried but not shown, as 4/7 gives the best result, i.e., the data points fall most closely onto one curve. A log-log plot of the results in (a) are shown in (b). The data points lie along a straight line of slope close to −1, which justifies the use of 4/7 as the scaling index.

as in (Nakada 2011) and (Chan 2015). In the study of an Ising model with long-range interactions of strength α (Nakada 2011), Nakada *et al.* suggested the scaling relation $\xi(L) = Lf(L\alpha^{\nu/\gamma})$. They plotted $\xi(L)/L$ against $L\alpha^{\nu/\gamma}$ using the Ising value of $\nu/\gamma = 4/7$ and verified that the data points all fell onto one curve (Nakada 2011). When α was not too small, the log-log plot of the graph had a slope of −1. Here we tried the same procedure with our long-range reactivity a, also using $\nu/\gamma = 4/7$, and obtained Fig. 4(a). Although the data points do not lie perfectly on one curve, in a Ln-Ln plot, we also obtain a straight line with slope close to −1, as shown in Fig. 4(b). Using $\nu/\gamma = 1/1.7967$ as obtained in Fig. 3, gives nearly exactly the same graphs, just with the slope in (b) changed from −1.02 to −1.03. So it is justified to claim $\nu/\gamma = 4/7$.

In our recent work (Chan 2015), we also tried to obtain ν/γ by looking at the scaling relation between the change in critical desorption rate with the change in long-range reactivity, as well as the scaling relation between change in critical CO partial pressure with the change in long-range reactivity. We obtained $k_{c,\infty}(a) - k_{c,\infty}(0) \propto a^{0.448}$ and $y_{c,\infty}(a) - y_{c,\infty}(0) \propto a^{0.499}$ and expected that one of these values should be ν/γ of the $a = 0$ case, as we know that for the 2D equilibrium Ising model with long-range interaction of strength α, the change in critical temperature against the change in long-range interaction strength α is known to behave as $T_c(\alpha, \infty) - T_c(0, \infty) \propto \alpha^{\nu/\gamma}$ with ν/γ obtained from the $a = 0$ case, i.e. 4/7 (Nakada 2011).

The index values of 0.499 and 0.448, both deviate significantly from 4/7. We therefore suggested in (Chan 2015) that a might not be linearly related to α, but rather as $a \propto \alpha^{1.3}$. However, Fig. 4(b) suggests that the relation for the equilibrium system, $\xi(L) = Lf(L\alpha^{\nu/\gamma})$, still holds for our model with α replaced by a, which means $a \propto \alpha$. Both Fig. 3(b) and Fig. 4(b) suggest that $\nu/\gamma = 4/7$ for $a = 0$. Thus it seems that the indices obtained from $k_{c,\infty}(a) - k_{c,\infty}(0)$ vs a and $y_{c,\infty}(a) - y_{c,\infty}(0)$ vs a are not ν/γ. We currently have no satisfactory explanation for this result.

3. Summary

We present numerical evidence that the addition of non-zero long-range reactivity to the ZGB model changes the universality class of the critical point from Ising to mean-field. Estimates for the exponent ratios β/ν and γ/ν are obtained and compared to the value for γ/ν obtained in our previous published work (Chan 2015).

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