Fine ”mist” vs large droplets in phase separated manganites

L. Khomskii
St Edmund’s College, Cambridge University,
Cambridge CB3 0BN, UK

D. Khomskii
Laboratory of Solid State Physics,
Groningen University, Nijenborgh 4, 9747 AG Groningen,
The Netherlands

Abstract

The properties of phase-separated systems, e.g. manganites, close to a first order phase transition between charge-ordered insulator and ferromagnetic metal, are usually described by the percolation picture. We argue that the correlated occupation of metallic sites leads to the preferential formation of larger metallic clusters, which explains the often observed inverse, or “overshot” hysteresis in manganites (when the resistivity with increasing temperature is larger than with decreasing $T$). It also explains the recently discovered thermal cycling effect in manganites. Thus in treating this and similar systems in percolation picture, not only the total concentration of metallic phase, but also the distribution of metallic clusters by shape and size may significantly influence the properties of such systems.

PACS numbers: 71.10.w, 75.30.Kz

Phase separation seems to be the generic feature of doped strongly correlated systems such as manganites La$_{1-x}$M$_x$MnO$_3$ ($M =$ Ca, Sr). It is
observed in many situations experimentally and is obtained in many theoretical models [1, 2, 3], both at low doping range \((x < 1)\) and close to a half-doped case \((x \sim 0.5)\). Apparently one can speak of two different types of phase separation: microscopic phase separation, which is most often discussed by theoreticians and which is observed e.g. by the small-angle neutron scattering [4], and the large-scale, macroscopic phase separation. The later type is typically met close to a first-order phase transition and leads to a percolation-like behaviour of the system.

Two unusual effects were observed recently in studying the behaviour of certain manganites close to a first order insulator–metal transition — in \((\text{PrCa})\text{MnO}_3 \) [5], \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnCrO}_3 \) [6] and in some others [7]. In these systems there apparently occurs with decreasing temperature a transition from a charge-ordered (CO) insulator to a ferromagnetic metallic (FM) phase, accompanied by a sharp drop of resistivity. This drop has a large hysteresis. But with increasing temperature from the FM phase an inverse, or “overshot” hysteresis was observed in [5, 6, 7], schematically shown in fig. 1. The nature of this behaviour was not clarified; there were even suggestions [5] that there exist two different CO phases, one appearing with decreasing temperature, and another — when the temperature increases.

Another unusual phenomenon was found in one of these systems, \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnCrO}_3 \) [6]: when after the first decrease of the temperature it was increased and then the cycle was repeated, the resistivity, having the behaviour like the one shown in fig. 1, in each following cycle became higher and higher (if temperature was not increased beyond the shaded region of fig. 1). In some cases after several cycles the resistivity became insulating down to the lowest temperatures. Simultaneous magnetic measurements did not show any significant decrease of the total magnetization, i.e. the total fraction of the FM phase did not decrease strongly with such “training.”

We want to suggest here a simple explanation of these effects, introducing the notion generalizing the standard percolation picture. This idea was first put forth in 1999 [8]; closely related ideas were discussed recently in [9].

The main idea is the following. When there occurs a first order phase transition to a metallic phase with decreasing temperature, there appear FM droplets in a CO insulating matrix. With further decrease of temperature they grow and start to coalesce until a percolation limit is reached, after which the system behaves as a metallic one. During this process the metallic droplets are first formed close to some nucleation centres, so that there appear
Figure 1: Schematic behaviour of resistivity in certain manganites close to CO–FM transition [5–7]. Shaded is the region of “overshot” hysteresis.

many very small droplets — like a fog on a cold evening. With further decrease of temperature these droplets grow, and, as is well known, bigger droplets grow faster, gradually “consuming” smaller ones. This is caused by the larger vapour pressure above droplets with smaller curvature [10], or, in other words, by the tendency to reduce total surface energy. Finally the FM phase occupies (almost) the whole sample, which occurs at low temperatures.

With the following increase of the temperature the FM phase gradually starts to “evaporate”, but this process is accompanied by hysteresis — resistivity is initially lower than at the first decrease of temperature. However after a percolation metallic cluster is broken, there may occur an inverse situation — inverse, or “overshot” hysteresis, at which the resistivity is higher than at the first downward run. This is a natural consequence of different distribution of FM clusters by size and shape during decreasing and increasing temperature: whereas in going from the CO insulator phase we create a lot of small FM clusters (fine “fog”), in the opposite process, when we increase temperature starting from the FM phase occupying large part of the sample (big FM “pools”), these big droplets would survive even at high temperature. Thus at a given temperature (in the “shaded” region of fig. 1) the total volume of a FM phase may still be the same, but the distribution, the typical sizes of these FM clusters would be different: a lot of small droplets with decreasing $T$, and much smaller number of bigger droplets when we increase
temperature from the FM phase. This would naturally lead to an increase of resistivity in a reverse run — an overshot hysteresis: not only would FM droplets be bigger, but also insulating regions between them would increase, which would lead to larger resistivity.

One can illustrate this conclusion on a simple picture shown in fig. 2, in which we substituted random distribution of FM and CO phases by a regular stripe-like structure. A fine “fog” (large number of small FM and CO regions), realized with the decreasing $T$, is modelled by the situation of fig. 2a, and a situation which should be realized with the temperature increase is illustrated in fig. 2b. One immediately sees that the resistivity in the first case is given by the expression

$$\rho_{1a} = \rho_0 n e^{V/kT}$$

where $n$ is the number of insulating barriers (white stripes in fig. 2a), and $V$ is the value of each of these barriers (which for simplicity we take equal).

On the other hand, in the case of fig. 2b, instead of having $n$ small barriers, we have smaller number — in a limiting case only one barrier, but with the width $n$ times bigger. As a result we would get the resistivity

$$\rho_{1b} = \rho_0 e^{nV/kT}$$

— much larger than that given by Eq. (1).

Of course this model is strongly oversimplified, and in reality the difference between resistivities would be much smaller due to random distribution of different regions by size, shape and position; but the physics of “overshot
hysteresis” may be explained by the picture described above. Thus when considering the percolation conductivity, we have to take into account not only the relative volume, occupied by one or another phase, but also the distribution of these phases by the size. This is usually not done in a standard treatment of percolation; but, as we argued above, this may be a very important factor.

We checked this picture by a computer simulation. We modelled the percolation in phase-separated manganites by first randomly putting the “metallic atoms” (black points) on a $200 \times 200$ square lattice. The resulting distribution of metallic clusters for certain concentration $n_0$, smaller than the percolation threshold $n_c \sim 0.59$ (here for $n_0 = 0.125$) is shown in fig. 3a. This distribution is on the average the same for increasing and for decreasing $n$.

To model the physical situation described above (the preferable formation of large clusters) the algorithm was modified in such a way that the probability of adding new metallic atom at a certain cite is larger when there are already occupied sites adjacent to it (i.e. the probability to occupy the site is the larger, the more neighbouring sites are occupied). The resulting structures are shown in fig. 3b, 3c. Fig. 3b shows the distribution of occupied sites at $n_0 = 0.125$ reached by increasing occupation $n$ from zero with correlated occupation as explained above. Fig. 3c shows the distribution at the same concentration $n_0$ as in fig. 3b, but reached by first increasing $n$ from the situation of fig. 3b to $n \sim 0.75$ (above percolation threshold) and then decreasing $n$ down to 0.125; in reducing $n$ we used the same algorithm as when increasing it, i.e. the probability to remove an atom from a given site is larger when there are fewer occupied sites nearby.

As we see by comparing fig. 3a with 3b and 3c, the resulting distribution of metallic sites at the same total concentration (here 0.125) depends on whether we have random or correlated percolation: the clusters are bigger for correlated occupation. But more interestingly, the resulting distribution also depends on history: in accordance with our general expectations, for correlated occupation we indeed obtain many small clusters with increasing $n$ (or decreasing temperature), fig. 3b, and smaller number of bigger clusters, with bigger insulating barriers between them, with decreasing $n$ (increasing temperature), fig. 3c.

We can also add yet another ingredient in our computer modelling, imitating annealing: after several steps of adding particles, we allowed for their
Figure 3: Distribution of metallic clusters (black) for the filling $n_0 = 0.125$ reached at random occupation (3a) and for correlated occupation of metallic sites (3b–3c), see text. Fig. 3b corresponds to a state reached by increasing $n$ from 0 to $n_0$, and fig. 3c — by first increasing $n$ still further to $\sim 0.75$ and then reducing it back to $n_0$. Fig. 3d shows typical distribution of FM clusters at the same $n_0$ reached with annealing.
redistribution, removing and adding particles in the same correlated fashion, but keeping their total number fixed. This leads to some “rounding off” of the clusters, whose boundaries become smoother, and this annealing somewhat enhances the tendency described above: that for correlated occupation we obtain, on the average, larger droplets, see fig. 3d, and they become even larger at the reverse process of decreasing $n$.

One also sees in these simulations that the percolation limit $n_c$ itself does not depend on whether we increase or decrease $n$, even for correlated occupation; but the value of $n_c$ seems to decrease somewhat, from $\sim 0.593$ for the usual percolation [12] to about 0.576 for correlated occupation.

Thus our computer modelling confirms our general physical arguments and shows that in a more realistic picture of phase separation, which takes into account correlation in occupation of particles and which leads to the preferential formation of bigger clusters, the resulting picture depends on the history: we have many small clusters (fine “fog”) with increasing the fraction of metallic sites (decreasing temperature), and smaller number of bigger clusters with increasing $T$. As argued above, on the insulating side of the transition (below percolation threshold) this would lead to an increase of resistivity (inverse, or “overshot” hysteresis) which may explain the experimental observations of [3, 4, 7]. Thus, the correlated occupation of sites makes the system “more insulating” on the insulating side of the percolation transition and “more metallic” on the metallic side (the sharpening of the transition on the metallic side was also seen in the calculations of Ref. [9]). The most interesting feature of this picture is the dependence of it on the thermal history, shown above.

The picture suggested above may also explain the “training” effect observed in [3]. Indeed, one may expect that after the first cycle not all small droplets disappear. But with further cycling the larger and larger droplets will be formed, eventually with larger insulating barriers between them, which can lead to the behaviour observed in [3]. The requirement is that the upper temperature during cycling should fall within the “shaded” region of fig. 1a (and should not exceed it) so that the large droplets, which would serve as condensation centres during the next cycle, should not disappear.

Our computer modelling also confirms these qualitative considerations. In fig. 4a–d we show typical results of the distribution of FM (black) regions obtained after cycling. The procedure was first to increase $n$ from 0 to certain $n_0 < n_c$ (here again $n_0 = 0.125$), and then cycling $n$ several times.
between \( n_0 \) and \( n \sim 0.75 \). All the time we used the same algorithm as before (probability of adding and removing particles depending on the number of occupied neighbours). We see that, indeed, with increasing number of cycles the number of FM droplets for the same \( n_0 \) decreases, and their size and distance between them increase, which, according to the arguments leading to Eqs. (1)–(2), gives an increase of resistivity with “training”, even for the same concentration of the FM phase. This can explain the experimental results of Mahendiran et al. [6] (similar behaviour is also seen in the data of [5]).

Summarizing, we proposed that the properties of inhomogeneous systems like some manganites close to an insulator–metal transition may be explained if we add to the conventional percolation picture another ingredient — that not only the net concentration of metallic phase, but also the distribution of these metallic inclusions by size and shape may be different, which may strongly influence the properties. We argue that the metallic droplets formed with decreasing temperature take the form of a fine “fog” — a lot of small droplets formed at many different nucleation centres, whereas with increasing temperature, going from the metallic state, predominantly large metallic droplets survive. The picture we propose seems to be quite natural and agrees with what we know from other fields of physics and even from our everyday experience; it is also confirmed by our computer modelling. It can explain the “inverse hysteresis” and the change of properties during thermal cycling, observed in some manganites in the inhomogeneous phase close to an insulator–metal transition.

The general conclusion is that when treating the properties of inhomogeneous systems in percolation picture, not only the total fraction of one or another phase, but also distribution of these phases by size and shape may be crucial. It would be very interesting to verify the proposed picture experimentally, e.g. by small angle neutron scattering or by light scattering in manganites during thermal cycling.

We are grateful to E. Dagotto and M. Mostovoy for useful discussions and to Th. Lorenz and R. Mahendiran for informing us of their experimental results. This work was supported by the Netherlands Foundation for the Fundamental Study of Matter (FOM).
Figure 4: The effect of thermal cycling. The occupied metallic clusters (black) for $n_0 = 0.125$ after first increasing $n$ from 0 to $n_0$ (a), further increasing $n$ to 0.75 and then decreasing it back to $n_0$ (b) and after 2 (c) and 5 (d) cycles. (Figs. 4a and 4b correspond to figs. 3b and 3c.)
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