Transient Electronic Phase Separation During Metal-Insulator Transitions

Yin Shi* and Long-Qing Chen†
Department of Materials Sciences and Engineering,
Pennsylvania State University, University Park, PA 16802, USA

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From thermodynamic analysis we demonstrate that during metal-insulator transitions in pure matters, a nonequilibrium homogeneous state may be unstable against charge density modulations with certain wavelengths, and thus evolves to the equilibrium phase through transient electronic phase separation. This phase instability occurs as two inequalities between the first and the second derivatives of the free energy with respect to the order parameter are fulfilled. The dominant wavelength of the modulated phase is also derived. The computer simulation further confirms the theoretical derivation. Employing the pre-established phase-field model of VO$_2$, we show that this transient electronic phase separation may take place in VO$_2$ upon photoexcitation.

Phase separation widely exists in Nature. For example, a homogeneous liquid separates into a liquid-vapor mixture when it is mechanically unstable (the isothermal compressibility becomes negative); a homogeneous binary solution decomposes into two immiscible parts as the chemical instability is reached (the system is inside the spinodal curve) [1].

In multinary complex materials, the interplay among charge/spin/lattice degrees of freedom may lead to competing ground states with distinct electronic properties [2–5]. These states can coexist at low temperatures on microscopic length scale whereas any homogeneous phase is unstable, causing the electronic phase separation [2–5], e.g., the phase separation into metal-insulator mixtures underlying the colossal magnetoresistance [6, 7]. Like in the mechanical and the chemical phase separations, the electronic phase separation leads to stable phase mixtures. In this work we report a transient electronic phase separation into nonequilibrium metal-insulator coexistence during metal-insulator transitions (MITs) in pure matters. Based on thermodynamic analysis taking into account the influence of free charges on the intrinsic material $F_0$ and that from the additional free electrons and holes $F_f$,

$$F[T; \nu(r, t), n(r, t), p(r, t)] = F_0[T; \nu(r, t)] + F_f[T; \nu(r, t), n(r, t), p(r, t)],$$

where $T$ is the temperature and $n(r, t)$ and $p(r, t)$ are the free electron and hole density fields, respectively. $F_0$ is composed of a bulk energy term $f_b$ and a gradient energy term,

$$F_0 = \int \left[ f_b(T; \nu) + \frac{\kappa}{2} (\nabla \nu)^2 \right] d^3r,$$

where $\kappa$ is a positive constant.

$F_f$ can be constructed as follows. For simplicity, we assume that the energy gap symmetrically opens with respect to the Fermi level of the metallic phase during the MIT (which is the case for VO$_2$ [14]) and approximate the electron and the hole densities using the Boltzmann statistics. We shall follow the approximation adopted in the semiconductor physics that the conduction and the valence bands are effectively parabolic with effective densities of states $N_e$ and $N_v$, respectively [15]. Hereafter the energy reference is chosen at the midpoint of the gap. Then the electron and the hole densities are expressed as $n = N_e \exp[-(E_g/2 - \mu_e)/k_BT]$ and $p = N_v \exp[-(E_g/2 - \mu_h)/k_BT]$, respectively, where $E_g$ is the gap, $\mu_{e(h)}$ is the (quasi-) chemical potential of the electrons (holes), and $k_B$ is the Boltzmann constant [15]. $F_f$ is thus calculated as

$$F_f = \int \left[ \int_0^\infty (\mu_e)_{TV} dn + \int_0^p (\mu_h)_{TV} dp \right] d^3r - F_i$$

$$= \int k_B T \left( n \ln \frac{n}{N_e} - n + p \ln \frac{p}{N_v} - p \right).$$
\[ V = \frac{1}{2} (n + p) \] \[ + E_g (n + p) \] \[ d^3r - F_i, \] (3)

where \( V \) indicates the volume. \( F_i = -2 \int k_B T n_i \) \[ d^3r \] is the equilibrium intrinsic free energy of the free electrons and holes, where \( n_i \) is the equilibrium intrinsic carrier density. Hence \( F_i = 0 \) at the equilibrium intrinsic case. Naturally the energy gap \( E_g \) is related to the order parameter \( \nu \). Since \( E_g \) is a scalar invariant with respect to the reverse of the sign of \( \nu \), the symmetry-allowed expansion for \( E_g \) on the lowest order of \( \nu \) is \( E_g = \gamma \nu^2 \), where \( \gamma \) is a positive constant.

The kinetics of the MIT is described by the Allen-Cahn equation for the non-conserved order parameter \( \nu \), \( \dot{\nu} = -L \delta F/\delta \nu \), and the diffusion equation for \( n \), \( \dot{n} = \nabla \cdot [(Mn/e) \nabla (\delta F/\delta n)] \) [16]. Here we assume charge neutrality everywhere \( (n = p \) always and thus no net electric field produced) and that the timescale of the transient electronic phase separation is much shorter than the lifetime of the free carriers (the source in the diffusion equation is ignored within the timescale considered).

The overdot represents the time derivative, \( L \) is a constant related to the interface mobility, \( M \) is the mobility of the electrons, and \( e \) is the elementary charge. We assume that the phase transition happens faster than the diffusion process of the electrons (that is, \( \nu \) is in equilibrium at any moment for a given distribution of \( n \)). In one dimension, these equations are then

\[ \frac{\partial f_b}{\partial \nu} - \kappa \nu'' + 2 \nu \nu(n - n_i) = 0, \] (4)

\[ M \gamma e (\nu \nu' + n \nu' + \nu n') + \frac{M k_B T}{e} n'' = \ddot{n}, \] (5)

where the prime represents the spatial derivative along the \( x \) dimension.

We now examine the stability of Eqs. (4-5) against infinitesimal fluctuations. First, one can solve \( n \) out as a function of \( \nu \) from Eq. (4), and substitute it into Eq. (5) to obtain a differentiation equation of \( \nu \) only. Then one may consider the solution to be a uniform value \( \ddot{\nu} \) plus an infinitesimal fluctuation with a wavenumber \( k \),

\[ \nu = \ddot{\nu} + \psi_k(t) \exp(ikx), \] (6)

where \( \psi_k \) is an infinitesimal amplitude. This is also equivalent to an infinitesimal modulation of the electron (hole) density field. Substitution of Eq. (6) into Eqs. (4-5) gives, to the first order of \( \psi_k \),

\[ \dot{\psi}_k = R(k) \psi_k, \] (7)

with

\[ R(k) = - \frac{M h_1 k^2 + h_2 k^4}{h_3 + h_4 k^2}, \] (8)

where

\[ h_1 = \frac{k_B T}{\gamma} \left[ \frac{\partial^2 f_b}{\partial \dot{\nu}^2} \right]_{\dot{n}} + \left( \frac{\dot{\nu} - k_B T \gamma}{\gamma \dot{n}} \right) \left[ \frac{\partial f_b}{\partial \nu} \right]_{\dot{n}}. \] (9a)

\[ h_2 = \frac{k_B T \kappa}{\gamma}, \] (9b)

\[ h_3 = \frac{2 \gamma \nu^2 \dot{n}_i}{k_B T} + \frac{1}{\gamma} \left[ \frac{\partial^2 f_b}{\partial \dot{\nu}^2} \right]_{\dot{n}} - \frac{1}{\gamma} \left[ \frac{\partial f_b}{\partial \nu} \right]_{\dot{n}} \] (9c)

\[ h_4 = \frac{\kappa}{\gamma}. \] (9d)

\( \ddot{n}_i = n_i \) at \( \ddot{\nu} \). The solution to Eq. (7) is just \[ \psi_k(t) = \exp[R(k)t] \]. Hence \( R < 0 \) indicates that \( \psi_k \) vanishes with time and Eqs. (4-5) are stable against small fluctuations, while \( R > 0 \) indicates that \( \psi_k \) grows exponentially with time, and Eqs. (4-5) are unstable against small fluctuations.

For small \( k \), we can expand Eq. (8) to the fourth order of \( k \),

\[ R(k) \approx -\frac{M}{e} \left( \frac{h_1 k^2 + h_2 h_3 - h_1 h_4 k^4}{h_3^2} \right). \] (10)

If \( h_1/h_3 > 0 \) and \( h_2 h_3 - h_1 h_4 > 0 \), \( R(k) \) in Eq. (10) is always nonpositive, which corresponds to the stable regime. One can check that the equilibrium case \([\left( \partial f_b/\partial \nu \right)_{\nu = 0} = 0, (\partial^2 f_b/\partial \nu^2)_{\nu = 0} = 0, \nu = \bar{\nu} \] is included in the stable regime, as expected. On the other hand, if \( h_1/h_3 < 0 \) and \( h_2 h_3 - h_1 h_4 > 0 \), or equivalently,

\[ \left| \frac{1}{\gamma} \left( \partial^2 f_b / \partial \nu^2 \right)_{\nu = 0} \right| < \left( 1 - \frac{\gamma \ddot{\nu}^2}{k_B T} \right) \left| \frac{\partial f_b}{\partial \nu} \right|_{\nu = 0}, \] (11)

\( R(k) \) in Eq. (10) has a shape as shown in Fig. 1(a). As can be seen, the unstable range of \( k \), i.e., those \( k \) yielding \( R(k) > 0 \), is

\[ |k| < \sqrt{-\frac{h_1 h_3}{h_2 h_3 - h_1 h_4}}, k \neq 0. \] (12)

Inequalities (11) thus correspond to the unstable regime. \( R(k) \) has two positive maxima at \( \pm k_0 \), with \( k_0 \) calculated to be \( \sqrt{-h_1 h_3/(2(h_2 h_3 - h_1 h_4))} \). Since \( \psi_k \) grows exponentially with the time at the rate \( R(k) \), the dominant \( \psi_k \)'s are those at \( k = \pm k_0 \), which leads to a modulation of \( \nu \) with the wavelength

\[ \lambda_0 = \frac{2\pi}{k_0} \approx 2\pi \sqrt{\frac{2(h_2 h_3 - h_1 h_4)}{-h_1 h_3}}. \] (13)

Therefore, for a \( \ddot{\nu} \) satisfying condition (11), the initial homogeneous phase with the order parameter \( \ddot{\nu} \) will spontaneously separate to the mixture of a metal-like phase and an insulator-like phase.

To confirm the above derivation, we numerically solve Eqs. (4-5) with periodic boundary conditions for both \( \nu \) and \( n \). We use the standard Landau polynomial for \( f_b \), \( f_b = -4f_0(\tau \nu^2/2 + \nu^4/4) \) with \( \tau = (T - T_0)/T_0 \), which describes a second-order phase transition at a critical temperature \( T_0 \). \( f_0 \) is the equilibrium free energy density at \( T = 0 \) K. The parameters are chosen to be \( f_0 = -0.25k_B T_0 N_c, k = 8k_B T_0 N_c^{1/3} \) and \( \gamma = 5k_B T_0 \).
The calculation result at temperature $\tau = -0.5$ is shown in Fig. 1(b-c). Initially $\nu$ has a value $\tilde{\nu} = -0.5$ plus a random noise ranging from $-0.005$ to $0.005$. This $\tilde{\nu}$ is inside the unstable regime (11). Indeed, the noise grows with the time with a dominant wavelength, which is shown clearly in the Fourier transformation of $\nu$ at $t = 1.8 \times 10^5 e/M k_B T_0 N^2_{e}/3$. The inset in (b) lists the times in units of $\nu = 0$. The calculation result at temperature $T = 0.1$ shows clearly in the Fourier transformation of $\nu$ (10). At $t = 8$, the noise shrinks and that the system directly evolves to the equilibrium insulator-like phase (valleys of $\nu$) at later stages (not shown). If adding to Eq. (5) the source term representing the electron-hole recombination process (the process for $n$ to approach $n_0$), we see that the transient metal-insulator mixture eventually evolves to the equilibrium homogeneous insulator with $\nu = -\sqrt{-\tau} = -1/\sqrt{2}$. The simulation of the cases inside the stable regime shows that the initial noise shrinks and that the system directly evolves to the equilibrium homogeneous insulator.

In the spinodal decomposition in binary solutions, the solute-concentration modulation with a finite wavelength rises from the interaction of the concentration (the gradient energy) [17]. In the transient electronic phase separation, however, the free energy of free electrons and holes in Eq. (3) does not possess the gradient energy; rather, the coupling of Eq. (4) and Eq. (5) gives rise to an effective interaction of the free-electron and free-hole densities.

In the above derivation, it is seen that the electronic phase separation occurs only when the initial state is nonequilibrium. We expect that the ultrafast photoexcitation may possibly lead to this electronic phase separation, since it can drive a system away from equilibrium. As an example we will examine the photoinduced MIT in VO$_2$.

The MIT in VO$_2$ can be described by two order parameter fields $\eta(r, t)$ and $\nu(r, t)$, which characterize the structural and the electronic phases, respectively [11–13, 18]. The R and the M1 phases correspond to $\nu = 0, \eta = 0$ and $\nu \neq 0, \eta \neq 0, \nu \eta < 0$, respectively. Like in obtaining Eqs. (4-5), the kinetics of the phase transitions in VO$_2$ under photoexcitation is governed by the Allen-Cahn equations for $\eta$ and $\nu$ and the diffusion equations for $n$ and $p$,

\[
\dot{\eta}(r, t) = - L_1 \frac{\delta F_{VO_2}}{\delta \eta(r, t)},
\]

\[
\dot{\nu}(r, t) = - L_2 \frac{\delta F_{VO_2}}{\delta \nu(r, t)},
\]

\[
\dot{n}(r, t) = \nabla \cdot \left[ \frac{M_e n(r, t)}{e} \nabla \frac{\delta F_{VO_2}}{\delta n(r, t)} \right] + \Gamma(r, t),
\]

\[
\dot{p}(r, t) = \nabla \cdot \left[ \frac{M_h p(r, t)}{e} \nabla \frac{\delta F_{VO_2}}{\delta p(r, t)} \right] + \Gamma(r, t),
\]

which are closed by the Poisson equation for the self-consistent determination of the electric potential $\Phi(r, t)$,

\[
- \nabla^2 \Phi(r, t) = \frac{e[p(r, t) - n(r, t)]}{\epsilon_r \epsilon_0}.
\]

Here $F_{VO_2} = F_{VO_2}[\Phi(r, t); \eta(r, t), \nu(r, t), n(r, t), p(r, t)]$ is the Landau free energy of VO$_2$ [18]. $\Gamma(r, t)$ represents the photoexcitation rate of free electron-hole pairs. $L_1$ and $L_2$ are constants related to the interface mobility, and $M_{e(h)}$ is the electron (hole) mobility. $\epsilon_e$ and $\epsilon_0$ are the relative permittivity of VO$_2$ and the vacuum permittivity, respectively. The electron-hole recombination process can be ignored here since the lifetime of free electrons and holes in VO$_2$ ($\sim 10$ µs [14]) is found to be much longer than the timescale of the transient electronic phase separation. For a monochromatic light with an angular frequency $\omega$ and an intensity $I$, $\Gamma$ can be derived from the Fermi’s golden rule [18],

\[
\Gamma = \sqrt{2\pi N_e N_c e^2 E_{g} I} \left( 1 + \frac{m^*}{m_h} \right) \sqrt{\frac{\hbar \omega - E_g}{k_B T}}
\]

\[
\times f \left( \frac{-\hbar \omega}{2} + \mu_h \right) \left[ 1 - f \left( \frac{\hbar \omega}{2} - \mu_e \right) \right].
\]

where $m^*_h$ is the effective mass of holes in VO$_2$, $c$ is the speed of light in the vacuum, $m$ is the electron mass,
\( h \) is the Planck constant divided by 2\( \pi \), and \( f(\varepsilon) = [1 + \exp(\varepsilon/k_B T)]^{-1} \) is the Fermi distribution function. 
\( I \) is a Gaussian-type function of both the space and the time controlling the illumination range and duration of the pump laser pulse: in the 1D case \( I(x,t) = \sqrt{I_0} g_\delta(x-x_0)g_\zeta(t-t_0) \), where \( g_\delta(\varepsilon) = \exp(-\varepsilon^2/2\sigma^2) \) and \( I_0 \) is defined as the intensity of the laser pulse. The illumination width and the pulse duration are defined as \( 4\delta \) and \( 2\zeta \), respectively. \( x_0 \) and \( t_0 \) are the position and the moment of the peak of the laser pulse, respectively.

The simulation setup is sketched in the inset in Fig. 2(b). We consider a VO\(_2\) nanobeam (1D system) with its two ends connected to the ground. The corresponding boundary conditions for Eqs. (14-18) are that \( \Phi \) is zero and \( n, p \) have their equilibrium values at the two ends. We assume Neumann boundary conditions (zero spatial derivatives) for \( \eta \) and \( \nu \) at that two ends. Figure 2 presents the calculation results for the photoexcited VO\(_2\). Inside the illuminated region, the photoexcitation produces free electron-hole pairs, which screen the electron-electron repulsion. This eventually leads to the closure of the gap, resulting in the transition from the insulator to the metal inside the illuminated region. On the other hand, the free electrons and holes diffuse outside the illuminated region, inducing a nonequilibrium state there. As can be seen clearly, a phase and a charge density modulations with a wavelength of \( \sim 11 \) nm take place around \( x \sim 70 \) nm several picoseconds after the incidence of the laser, inducing coexistence of the metal-like (high carrier density) and the insulator-like (low carrier density) phases. A wave-like ionic displacement field (represented by \( \eta \)) also develops around \( x \sim 70 \) nm due to the coupling between the electronic and the structural order parameters. The metal-like and the insulator-like phases coarsen at later stages.

We further calculate the wavelength of the phase modulation at various temperatures, as shown in Fig. 3. The wavelength increases with elevating temperature, and reaches the maximum of \( \sim 14 \) nm near \( T_c \). At low temperatures the modulation wavelength may be calculated to be sub-nanometers. This should be considered as invalid since the Landau theory is essentially not applicable to the lengthscale comparable to the lattice constant.

In summary, we have shown theoretically that in materials exhibiting MIT, a homogeneous state away from equilibrium may be unstable against charge density modulations with a certain range of wavelengths. Hence the homogeneous state evolves to the equilibrium phase not homogeneously, but through transient electronic phase separation with a dominant wavelength. The criterion for the onset of this phase instability has something to do with both the first and the second derivatives of the free energy with respect to the order parameter.

Employing the phase-field model of VO\(_2\) that has been extended to the photoexcitation problem, we have shown that the transient electronic phase separation may emerge in photoexcited VO\(_2\) at the edge of the illuminated region, which is accompanied by a transient wave-like ionic displacement field at the same place. Further experiments may pay attention to detecting the transient

![FIG. 2. Transient electronic phase separation in a 300-nm-long VO\(_2\) nanobeam at \( T = 320 \) K photoexcited by an 800-nm laser pulse (\( I_0 = 10^7 \) W/cm\(^2\), \( \delta = 25 \) nm, \( x_0 = 150 \) nm, \( \zeta = 0.1 \) ns, \( t_0 = 0.2 \) ns). (a), (b) and (c) are the temporal evolution of \( \nu \), \( \eta \) and \( n \), respectively. The inset in (b) is the schematic of the simulation setup. We only show the results on half of the sample (\( 0 \leq x \leq 150 \) nm) [the shaded region in (a) indicates the half of the illuminated region]. The results on the other half are symmetrical with the shown results about the \( x = 150 \) nm mirror plane.](image)

![FIG. 3. Wavelength of the phase modulation as a function of the temperature in the photoexcited VO\(_2\). The fixed conditions are the same as in Fig. 2. The line is guide to eyes.](image)
electronic phase separation and the modulated charge density and ionic displacement fields in VO₂ and other materials exhibiting MIT.

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* yxs187@psu.edu
† lqc3@psu.edu

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[18] See Supplemental Material for a detailed description of the Landau free energy of VO₂ and a detailed derivation of the photoexcitation rate of free electron-hole pairs.