Reversible thermal fusing model of carbon black current-limiting thermistors

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Composites of carbon black particles in polyethylene exhibit an unusually rapid increase in resistivity as the applied electric field is increased, making this material commercially useful as current-limiting thermistors, also known as automatically resettable fuses. In this application the composite is in series with the circuit it is protecting: at low applied voltages the circuit is the load, but at high applied voltages the composite becomes the load, limiting the current to the circuit. We present a simple model of this behavior in terms of a network of nonlinear resistors. Each resistor has a resistance that depends explicitly and reversibly on its instantaneous power dissipation. This model predicts that in the soft fusing, or current-limiting, regime, where the current through the composite decreases with increasing voltage, a platelike dissipation instability develops normal to the applied field, in agreement with experimental observations, which is solely due to fluctuations in the microstructure.

INTRODUCTION

The electrical conductivity of composites of conducting carbon-black particles dispersed in a solid insulating polymeric matrix is of significant interest because of the widespread applications of this material, such as current-limiting thermistors, self-regulating heating elements, xerographic inks, static electricity dissipation devices, electrical cable sheathing, etc. A novel property of this material is its extremely large, positive thermal coefficient of resistance, which is roughly understood as follows. At sufficiently high concentrations of carbon black, percolating paths of particles exhibit a dc conductivity that is sensitively dependent on the poly(ethylene)-filled gaps between particles. When the temperature of the composite is increased the polymer expands, increasing the gaps only slightly, yet greatly increasing the composite resistivity. (For a review of this phenomena see Carmana.[1]) Experiments on the temperature dependence of the conductivity,[2,3] measured on isothermal samples with a very small current density, show a very abrupt increase in the resistance at ~133 °C, which is related to the sudden specific volume increase that accompanies melting of the semicrystalline poly(ethylene) matrix. In fact, when the resistance is plotted against the thickness of the sample, a smooth, faster-than-exponential dependence of the resistivity is found.[2]

When a carbon black composite is used as a current limiting thermistor, self-heating can lead to nonisothermal temperature fields, which can develop into pronounced electric field and dissipation instabilities within the device. In a typical application, the thermistor is electrically in series with a circuit it is protecting. Under normal operating conditions, the resistance of the circuit is greater than that of the thermistor, so the voltage drop across the thermistor is small. However, should a serious circuit short occur, the resistance of the thermistor will become much greater than the remaining electrical path to ground and the predominate voltage drop V will eventually occur across the composite. If the remaining shorted circuit inductance L is significant, the rate of current rise, V/L, can be sufficiently low that the thermal diffusion length will greatly exceed the average separation of the highly dissipative fraction of the carbon black phase before current limiting occurs. This can be referred to as a *slow fusing* regime. In this circumstance a continuum model of the composite should be accurate, and this has been pursued in the work of Dougal[4] and of Loser *et al.*[5] who have modeled both the temperature and electric fields in a one dimensional thermistor, during a current limiting transient.

On the other hand, if the remaining shorted circuit inductance is small the current rise rate is high, and if the current density through the composite is sufficiently large, the temperature distribution within the granular composite will have large local variations, so that a smooth temperature field is not attained. In this regime the granularity of the composite can lead to large electric field instabilities that can precipitate breakdown, so this might be an operating condition that is impractical, but interesting nonetheless.

For the heating rate to be rapid enough for the composite granularity to generate instabilities, we require a significant temperature rise in the particle gaps, relative to the surrounding media. This circumstance can cause current limiting to occur before thermal diffusion smooths local temperature variations, which we define as *fast fusing*. Fast fusing is favored by low thermal conductivity of the surrounding medium, and a high Joule heating in the gaps, as discussed in detail below. This rapid heating regime is probably more likely when the carbon black particles form aggregated domains of appreciable size, and is especially important when the carbon black phase is near the percolation threshold. Because these materials are often manufactured to be close to the percolation threshold, the relevant length scale for thermal diffusion to eliminate the effects of composite granularity is probably of the order of the spatial correlation length of the so-called conducting backbone, under the assumption that the occurrence of ''hot bonds'' scales with this length.

The conducting backbone[6] is that fraction of the carbon black phase that contributes to current conduction, and is of much lower dimensionality than the percolating fraction of the carbon black, defined as the volume fraction of carbon black attached to the infinite cluster. This length scale becomes arbitrarily large as one approaches the percolation threshold.

In both the fast and slow fusing regimes instabilities can develop, but for quite different reasons. Dougal[4] treated the slow switching case by finite difference computations of a one-dimensional device, using the material parameters of the composite, including the dependence of the electrical conductivity on temperature and the heat of fusion of poly(ethylene). The device was modeled under normal steady state operating conditions and the temperature field determined, which had a maximum at the center of the composite, midway between the electrodes, which were of relatively high thermal conductivity. A circuit short was then introduced, causing the inductance-limited current to gradually increase through the composite. Because of the initial nonuniform temperature distribution, an instability then developed at the middle of the sample, due to the positive feedback in this system. As current limiting developed, the middle of the sample became much hotter, and therefore more resistive, so that essentially all of the voltage drop was across this narrow region, causing an increase in the field there. When the same simulation was run from an initially isothermal condition, this field instability was far less focused, extending throughout the sample. In operating conditions where the remaining circuit inductance is very high, and the actual device is very thin, this instability will be significantly broadened.

In this paper we explore the regime where the current rise is so fast, and the heating rate is so high, that structural and resistivity fluctuations in the composite drive the development of instabilities. In this regime the Joule heating produced at the resistive contacts between carbon black particles will significantly raise the gap temperature relative to the surrounding material, causing runaway contact resistance. Our three-dimensional model of these composites is rudimentary. First, a real carbon black composite is treated as randomly distributed hard spheres and mapped onto a network of nonlinear resistors; second, the resistivity rise at particle contacts is taken to be a nonlinear, reversible function of the *instantaneous local Joule heating*, a nonobvious assumption (at least to us) which follows from the considerations given below. The resistance changes propagate electrically through the network, not thermally.

The expression that relates the contact resistance explicitly to the dissipation has an exponent that is a free parameter. We find that when this exponent is just large enough to cause current limiting behavior, a two-dimensional, platelike instability develops orthogonal to the applied field. The location of this instability is due to structural and contact resistance fluctuations in the disordered composite, and the width is determined by the proximity to the percolation threshold. It should be emphasized that in this model, at low applied fields the composite is isothermal. The instability is a result of composite granularity and because it is extremely narrow, it could lead to breakdown.

Various microscopic models have been proposed to explain this increase in contact resistance; e.g., some suggest-ing that the contact resistance between particles can be modeled by quantum mechanical tunneling currents, which are exponentially dependent on the particle gaps.[7–9] Classical conduction effects can also be important, since the contact resistance between spherical particles in a conducting path aligned with the field depends on the logarithm of the dimensionless gap. Also, real particles are rough, so classical edge singularities occur in the electrical field at the particle surfaces, creating highly gap-sensitive conduction. Regardless of the microscopic details of the conductivity mechanism, the conductivity of these particle composites is a nonlinear network problem that is subject to strong positive feedback and catastrophic failure.

A significant amount of work has been done on networks that exhibit catastrophic failure. This work falls into two classes: Resistor-Short models, which describe dielectric breakdown, and Resistor-Fuse models, which describe both current-limiting devices and fracture of materials (at the scalar level). Resistor-Short models consist of linear resistors that become electrical shorts when a critical voltage drop[10–13] or power dissipation[14,15] is exceeded. Fluctuations can be introduced in a variety of ways, including fluctuations in the threshold values for shorting, and geometrical disorder such as proximity to the percolation threshold. Resistor-Fuse models consist of linear resistors that suddenly become electrical open circuits when a critical voltage is exceeded. These models[16–18] of *hard irreversible fusing* show the sheetlike failure zones characteristic of fracture, and consider the effect of critical voltage fluctuations. The *reversible thermal fusing* model of current-limiting thermistors we present here differs from these earlier studies in that the networks we construct are based on simulated three-dimensional (3D) composite structures, and so have structural disorder mimicking these materials; and the nonlinear resistance is a continuous, reversible function of the instantaneous power dissipation. In the following we describe the nonlinear network model, consider instabilities that occur in series networks, and apply this model to simulated hard sphere composites, including those near the percolation threshold. The simple model we present might encourage the full scale computation of the properties of current limiting thermistors, using realistic structural models, and simultaneously solving for both the heat diffusion and the electric fields in these composite materials.

MODEL

Nonuniform self-heating. A key issue is the conditions under which fast fusing can occur. In other words, under what conditions can we expect large local temperature variations? Real materials have very complex structures, which can only be treated accurately by exhaustive discrete numerical calculations, but some general conclusions can be reached from simple considerations. The carbon black composite is in essence a resistor network, where the resistors connect the line of centers (''bonds'') between neighboring particles. Because the conductivity of carbon black is many orders of magnitude greater than that of the polymer, the resistance values are determined by roughly the logarithm of the dimensionless gap between particles (true for perfectly conducting spheres), as well as the particle roughness tunnel-

ing conductivity, etc. Large variations in these resistance values can be expected,[9] which is a fundamental type of disorder in the equivalent resistor network, and is thought to be a source of the observed nonuniversality in the conductivity divergence near the percolation threshold.[9] A second issue is the geometrical disorder that exists in these networks. Even when each resistance is identical, a voltage applied to contacting parallel planar electrodes will lead to large variations in the currents through each resistor, and thus large variations in the voltage drop and Joule heating. This is especially true near the percolation threshold,[19,20] where there has been significant investigation of the so-called ''hot bond'' problem.[14,15] Because carbon black current limiters are often manufactured near the percolation threshold,[21] we envision sparse, branched current paths, with well isolated hot bonds providing most of the Joule heating. We now need to develop some idea about the nature of fusing in these materials.

The Joule heating in the hot bonds will largely occur in the resistive gaps between particles. Consider the elementary problem of a point source of heat Q in a three-dimensional continuum. If heat is instantaneously delivered at the origin, the distribution of heat in a volume d^3r around $\mathbf{r}$ will be given by the random walk result

$$p(\mathbf{r},t)d^3r = (4\pi Dt)^{-3/2}\exp(-r^2/4Dt)d^3r, \qquad (1)$$

where D is the thermal diffusivity, and the integral of the distribution is normalized to unity. If heat is supplied at the origin at a constant rate $\dot{Q}$, the distribution of heat will be

$$Q(\mathbf{r},t)d^3r = \dot{Q}\int_0^t p(\mathbf{r},t-s)ds\,d^3r. \qquad (2)$$

The temperature rise field will then be given by $\Delta T(\mathbf{r},t) = (1/c_p\rho)Q(\mathbf{r},t)$, where c_p is the constant pressure heat capacity per unit mass and ρ is the density of the material. From Eqs. (1) and (2) the temperature rise is

$$\Delta T(\mathbf{r},t)d^3r = \frac{\dot{Q}}{4\pi c_p\rho Dr}\times\mathrm{erfc}(r/\sqrt{4Dt})d^3r, \qquad (3)$$

where $\mathrm{erfc}(x)$ is the complementary error function. This function decays faster than exponentially, having the limits $\mathrm{erfc}(x\ll1)\approx1$ and $\mathrm{erfc}(x\gg1)\approx0$. Thus the temperature rise field decays as $1/r$ for distances small compared to the diffusion length $\sqrt{4Dt}$ and rapidly approaches zero for larger distances, rather like a screened Coulomb potential. The fact that the stationary state result is Coulombic on length scales $r\ll\sqrt{4Dt}$ is trivial, since the time-independent thermal field is just described by Laplace's equation. The thermal gradient is then equivalent to the electric field, and Gauss's theorem guarantees that the heat flux through a closed spherical surface is independent of it's radius—the definition of steady state.

Now we must apply this result to composites. In terms of the thermal conductivity $\kappa=c_p\rho D$ the temperature rise near the point source will quickly approach $\Delta T(\mathbf{r},t)=\dot{Q}/4\pi\kappa r$, and will not increase beyond this. In the particle gap the heating is uneven, but we can at least expect that heating occurs within a domain that scales as the particle radius a. Because the heat is being generated in a distributed source, the average temperature rise in this region will scale as ΔT $\propto\dot{Q}/\kappa a$. This temperature rise will be large when the heating rate is large and/or the source is of small spatial extent and/or the thermal conductivity is small. This temperature rise will occur very quickly, on the time scale $\tau_1\approx a^2/6D$.

To relate this result to real composites we first stipulate that we are in the regime where $\Delta T\propto\dot{Q}/\kappa a$ is sufficiently large to cause substantial nonlinearities in the contact resistance between particles, presumably by achieving melting of the crystalline domains in the poly(ethylene). Consider the effect of having many active heat sources (hot bonds) distributed in space with an average separation ξ. The temperature rise $\Delta T\propto\dot{Q}/\kappa a$ achieved at any hot bond at time $\tau_1\approx a^2/6D$ will persist until heat finally floods in from the many other active sources, and this will be on a timescale $\tau_2\approx\xi^2/6D$. If $\xi\gg a$ there will be a substantial time where the emergence of a strong temperature dependent contact resistance is transmitted through the composite only electrically, not thermally. In this time domain, it is a good approximation to treat the composite as a network of nonlinear resistors whose contact resistance is a function of temperature, which in turn is only proportional to the rate of heat production, i.e. the instantaneous iv drop across that resistor.

To obtain the transition to uniform heating, one can integrate Eq. (3) over the n heat sources in the thermistor volume V, each of which has a heat production $\dot{Q}$. The spatially averaged temperature rise is then linear in time in this adiabatic approximation

$$\Delta T(t) = \frac{n}{V}\frac{\dot{Q}}{4\pi c_p\rho D}\int\frac{1}{r}\mathrm{erfc}(r/\sqrt{4Dt})d^3r = \frac{\dot{Q}_{\mathrm{tot}}}{c_p M}t. \qquad (4)$$

Here $\dot{Q}_{\mathrm{tot}}=n\dot{Q}$ is the total Joule heating in the composite of mass M.

Estimating the temperature rise in the hot zones between particles is not simple, but it is at least clear that the mean heat rise in the particle gaps will be the overall Joule heating of the composite, divided by the total volume fraction of polymer between the particle gaps. This will probably lead to very large local heating rates, especially in the hot bonds. In real materials there is also a substantial heat of fusion of the poly(ethylene), and this should increase heat localization, making the fast fusing regime more attainable. It is likely that in a real device this regime can be achieved, though it might immediately precipitate breakdown.

To summarize, in the following the composite is treated as a voltage-controlled device and its resistivity increase with applied voltage is determined. As the applied voltage is ramped up, Joule heating produced at the resistive particle contacts raises the temperature locally, causing the temperature to rise in that region, which further increases the contact resistance. As the temperature increases, a steady state situation evolves as shown above, and the gap temperature is determined by the balance of heat production and diffusion. This regime ends when heat from nearby hot bonds diffuses in (times large compared to $\tau_2\approx\xi^2/6D$) which reduces temperature variations in the material and leads to a more uniform thermal field. The following applies only to current limiting behavior on times short compared to τ_2.
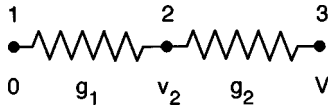
FIG. 1. The series network of two nonlinear conductors used to illustrate the emergence of instabilities. V is the applied potential, and g the conductances.

Thermal fusing model. We model this system abstractly and qualitatively by a network of nonlinear resistors. Each conductor represents the contact resistance between carbon black particles in contact, so the carbon black particles are the nodes of the network. The conductance of each bond is assumed to be of the form

$$g = \frac{g_0}{1+[(i/i_0)(\Delta v/v_0)]^\alpha} = \frac{g_0}{1+[(g/g_0)(\Delta v/v_0)^2]^\alpha}, \quad (5)$$

where $i = g\Delta v$ is the current across the conductor, Δv is the voltage drop, $i\Delta v$ is the Joule heating, and $\alpha > 0$ is an exponent that determines how rapidly the conductance changes with heat production. A few limits of this equation are readily obtained. When $\Delta v/v_0 = \sqrt{2}$ the bond conductance is given by $g/g_0 = 1/2$ for all α. For small $\Delta v/v_0$ the result

$$g/g_0 \cong \frac{1+\alpha(\Delta v/v_0)^{2\alpha}}{1+(1+\alpha)(\Delta v/v_0)^{2\alpha}} \cong 1-(\Delta v/v_0)^{2\alpha}, \quad (6)$$

is obtained, showing that for any fixed value $\alpha > 0$, taking the limit $\Delta v \to 0$ gives $g = g_0$. Finally, for values of $\Delta v/v_0 \gg 1$ the conductance scales like $g \propto \Delta v^{-2\alpha/(1+\alpha)}$. In this paper we restrict our attention to exponent values in the range $\alpha \geq 0.5$, which covers the interesting range of nonlinear network behavior. We apply this nonlinear network model to both 1D and 3D networks.

The unstable nature of networks of these nonlinear elements can be understood by considering just two conductors in series, labeled as in Fig. 1. For simplicity, we set $v_0 = 1$. One node is at ground potential, one is at an applied potential V, and the potential of the central node v_2 is to be determined numerically, by an iterative Laplacian relaxation. To do this, one first guesses the potential of the central node, and then determines the conductances g_1 and g_2 from Eq. (5), with $\Delta v_1 = v_2$ and $\Delta v_2 = V - v_2$. The next approximation to the correct value of the floating potential will then be given by solving the conductance-weighted average of the neighboring potentials, that is,

$$v_2' = \frac{g_1 \times 0 + g_2 \times V}{g_1 + g_2}. \quad (7)$$

The difference $\Delta v_2 = v_2' - v_2$ is therefore the correction to the estimated voltage, and understanding how this difference depends on v_2 for various values of the exponent α and the applied voltage V illustrates the nature of the instabilities involved.

In Fig. 2 we show the stability plot for the case where $\alpha = \frac{1}{2}$. In this case there is only a single stable value of $v_2 = V/2$, and when the estimated value of v_2 is too small, the correction is positive, so that successive iterations will lead to this stable value, regardless of the applied voltage. Likewise, when the estimated value of v_2 is too large, the cor-
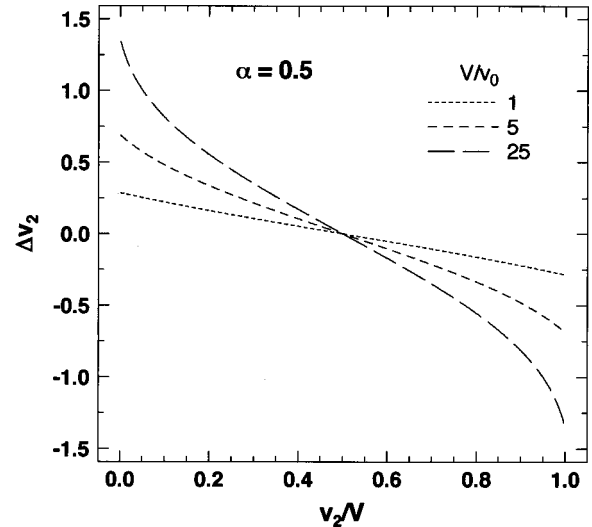

FIG. 2. When the exponent α in Eq. (5) is less than 1.0 (in this case $\alpha = 0.5$) the voltage of the central node is always stable, regardless of the applied potential. Furthermore, Δv_2 increases with the applied potential V.

rection is negative, and successive iterations will again lead to $v_2 = V/2$. When the exponent $\alpha = 2$, this completely stable behavior is altered, Fig. 3. Only for applied voltages less than the threshold value ~ 2.84 is a stable regime now observed, where only the single solution $v_2 = V/2$ found. For larger values of the applied voltage, the solution $v_2 = V/2$ becomes unstable, since the derivative $d\Delta v_2/dv_2$ becomes positive, and two symmetrically disposed stable solutions appear with negative values of $d\Delta v_2/dv_2$. Thus at high applied voltages, an instability occurs where essentially all the voltage drop will be over one conductor of very low conductance $g \propto V^{-2\alpha/(1+\alpha)}$, and the other conductor will have $g \cong 1$. The exponent $\alpha = 1$ marks the boundary of stable and unstable nonlinear network models, Fig. 4. In this case there
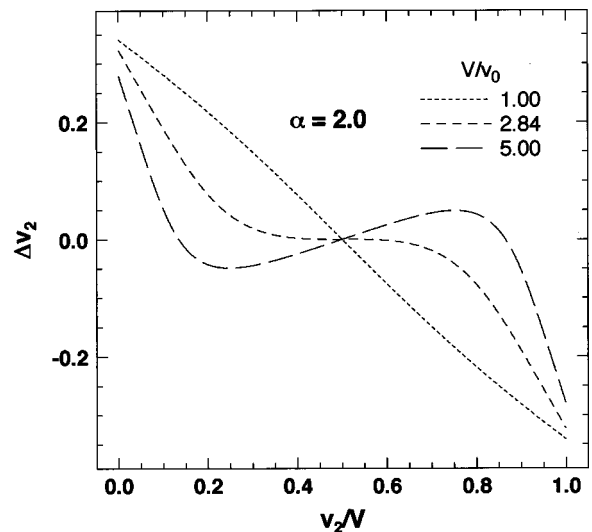

FIG. 3. When the exponent α in Eq. (5) is greater than 1.0 (in this case $\alpha = 2$) an instability develops at the central node as the applied voltage increases. This instability occurs when the derivative $d\Delta v_2/dv_2$ changes sign from negative to positive, which occurs in this case at $V \cong 2.84$.
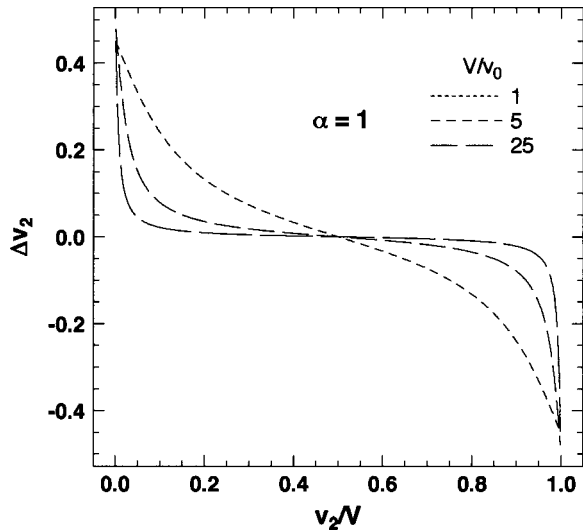
FIG. 4. The case $\alpha = 1$ is at the edge of stability. At high applied voltages the derivative $d\Delta v_2/dv_2$ approaches 0, so that any value of v_2 is essentially a solution. In this case large voltage fluctuations are expected to be observed in the floating potential nodes, and the system is quite sensitive to fluctuations in the conductances g_0 and their crossover voltages v_0. Numerically, this problem is quite difficult to solve, requiring ever increasing numerical accuracy as the applied field increases.

is a single stable solution at $v_2 = V/2$, but at high applied voltages the derivative $d\Delta v_2/dv_2$ vanishes in the vicinity of the solution. Thus voltage fluctuations can be expected to be quite large in a network with $\alpha \cong 1$, and solving numerical problems in this limit with fixed numerical precision limits one to applied voltages beneath some threshold value.

Fluctuations. The model just described lacks fluctuations, and clearly these can be important in real physical systems. Fluctuations can be introduced in the voltage crossover term v_0 or in the scale of the conductance g_0. In some of the following simulations we introduced fluctuations into g_0 to avoid numerical problems associated with defining particles in contact with the electrodes, as discussed below. Introducing these fluctuations has one subtle effect—the $\alpha = 1$ case shows an instability.
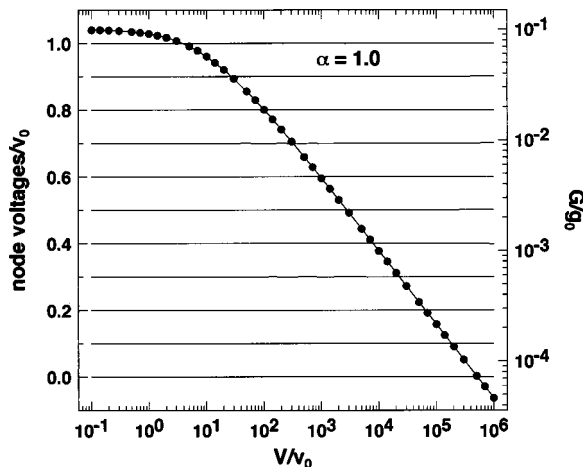

FIG. 5. A series network of 10 conductors solved for the case $\alpha = 1$. The node voltages are stable, and the network conductance is inversely proportional to the applied voltage.
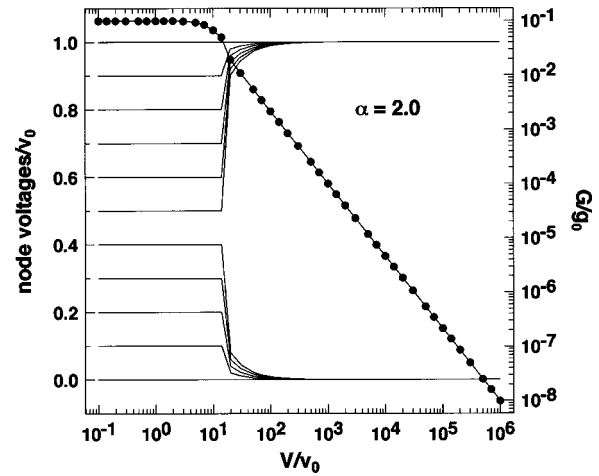

FIG. 6. A series network of 10 conductors solved for the case $\alpha = 2$ illustrates the emergence of a dissipation instability. The network conductance is inversely proportional to the $V^{4/3}$.

RESULTS

Series networks. Numerical solutions to simple 1D series networks are instructive. It is worth pointing out to those that might be interested in pursuing this model that these computations require unusually high numerical accuracy. For example, we found it necessary to solve Eq. (5) for the conductances to full double precision accuracy using a variety of initial guesses and iterative schemes, depending on the value of α. We then used a Laplacian over-relaxation method with local update and an over-correction factor of 1.94 to relax the node voltages.

With the exponent $\alpha = 1$, the results are shown in Fig. 5 for a network of $N = 10$ conductors in series. As the voltage is increased the network remains stable, in that the conductors all have equal potential drops, and thus equal conductances. The network conductance is then trivially $G^{-1} = \Sigma g^{-1}$, so $G = g/N$. Solving Eq. (5) for g gives
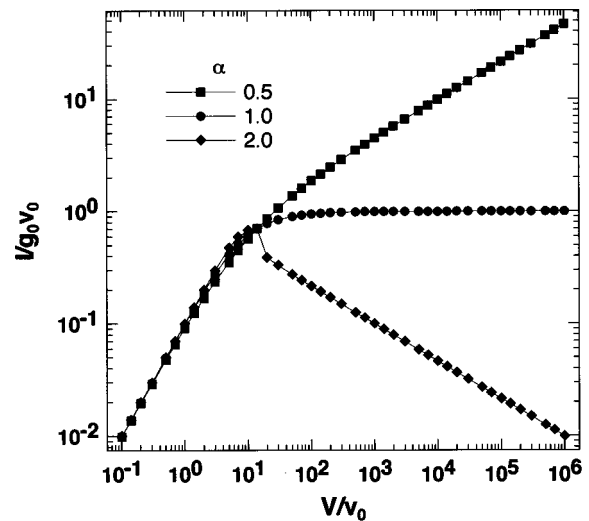

FIG. 7. A comparison between the computed I-V characteristics of stable and unstable network models, in this case series networks of ten conductors, shows that the emergence of dissipation instabilities occurs when the thermal fusing is strong enough to reduce the current with increasing voltage.
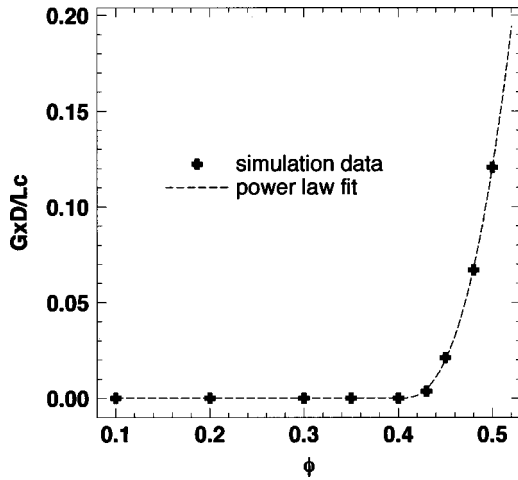
FIG. 8. The conductivity as a function of hard sphere volume fraction ϕ when particles with gaps smaller than 2.5% of the particle diameter D have a contact resistance c. Here L is the size of the simulation volume. The conductivity is zero until the percolation threshold ϕ_c, whereupon it increases roughly quadratically with $\phi - \phi_c$.

$$G = \frac{g_0}{N} \frac{\sqrt{1+4(V/Nv_0)^2}-1}{2(V/Nv_0)^2} \cong g_0 \frac{v_0}{V} \quad \text{for} \quad V \gg Nv_0. \tag{8}$$

Thus in this special case the conductance becomes independent of the network size in the nonlinear regime. In this regime the current is then just given by $I = GV = g_0 v_0$, and is thus independent of the applied voltage. The Joule heating P does increase with applied voltage, however, and is $P = IV = g_0 v_0 V$.

The case where $\alpha = 2$, shown in Fig. 6, is more interesting, and probably much more relevant to real materials. The voltage drops across each of the ten conductors remain equal until the applied voltage reaches a critical value, at which point an instability occurs and very rapidly essentially all of the voltage drop ends up across a single conductor, and the other conductors end up with conductances close to 1. In fact, studies of various system sizes shows that the limit of stability actually occurs at a fixed electric field, which makes good sense physically. For these large voltages this leads to

$$G \cong g_0 \left(\frac{v_0}{V} \right)^{2\alpha/(\alpha+1)} \tag{9}$$

so that the current actually decreases with the applied voltage as

$$I \cong g_0 \frac{v_0^{2\alpha/(\alpha+1)}}{V^{(\alpha-1)/(\alpha+1)}} \tag{10}$$

and the dissipation increases as

$$P \cong g_0 v_0^{2\alpha/(\alpha+1)} V^{2/(\alpha+1)}. \tag{11}$$

Within the context of this power-law Thermal Fusing model, the strongest soft fusing behavior occurs when α is infinite, whereupon $G \sim V^{-2}$, $I \sim V^{-1}$, and $P \sim V^0$. Note that in this limit the power dissipation actually becomes independent of the applied voltage. Numerically computed currents are
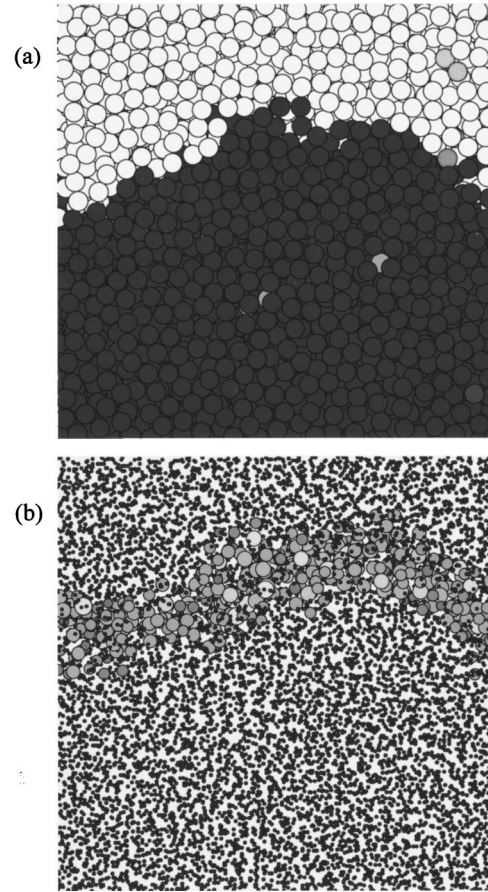

FIG. 9. (a) The node potentials are visualized for a system of 10 000 hard spheres at 55 vol. %, with a large applied voltage and $\alpha = 2$. The ground electrode is at the bottom and the high potential electrode at the top. Ground potential particles are colored blue, and the color then increases with potential from blue to red to yellow to white. Essentially all of the balls are either blue or white, due to the formation of an instability. (b) Thus all the voltage drop occurs over a narrow 2D region, and this is where power dissipation occurs. In this visualization, the particle volume is proportional to the power dissipation of the conductors to which it is a node. Particles that essentially do not dissipate are shown in a reduced size.

shown in Fig. 7 for selected values of α. It is noteworthy that just when the nonlinear behavior is strong enough to actually cause the current to decrease with applied voltage, i.e. $\alpha = 1$, the dissipation instability occurs.

Simulated 3D composites. The structure of carbon black/polymer composites is complex, apparently consisting of dispersed carbon black aggregates that percolate to form a conducting network. The experimentally determined percolation threshold[21] for this system is around $\phi = 17$ vol. %, so it is clear that the particle positions are strongly correlated, given that for random hard spheres in a *continuum* (such as a polymer) the percolation threshold occurs at the random close pack concentration of 64 vol. %. There is some confusion over the proper percolation value for particle composites, and this apparently stems from the Scher and Zallen[22] investigation of the percolation volume fraction for a random mixture of equal-size spheres of type A and B arranged in contact on a periodic lattice. They found that the percolation threshold for either type of sphere is about 15 vol. %, depending somewhat on the lattice type. The Scher-Zallen re-
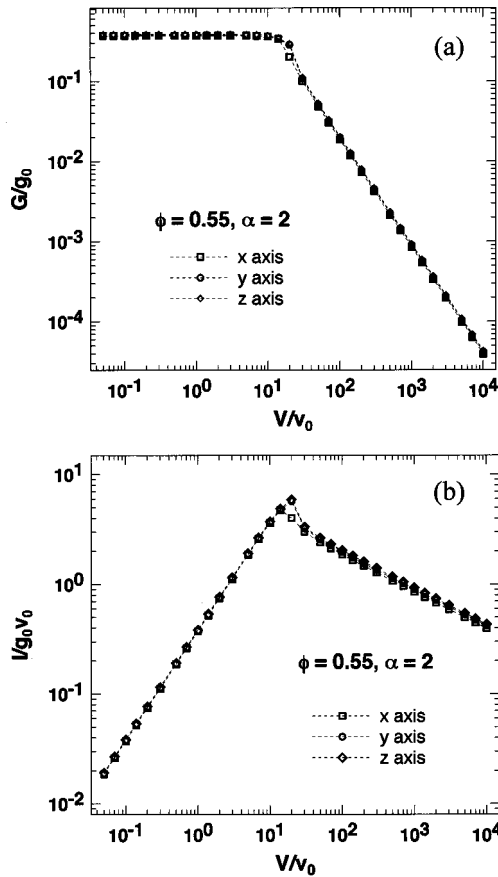
FIG. 10. (a) The conductance of the 3D random network of Fig. 9 is shown, with the field applied along the three orthogonal axes. As expected, this conductance decreases as $V^{4/3}$. (b) The current is shown, which decreases as $V^{1/3}$.
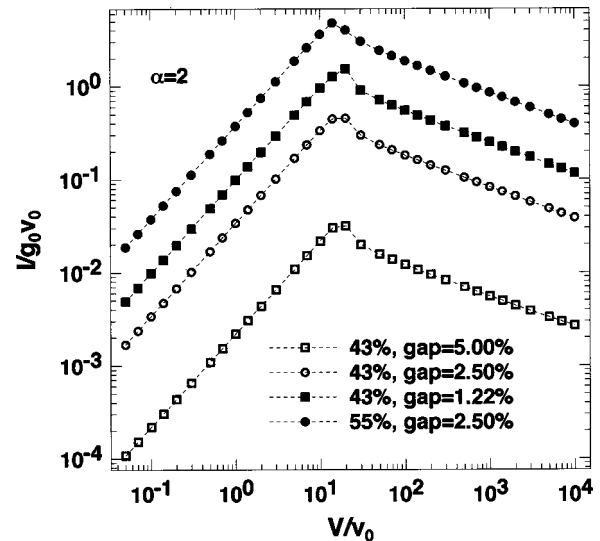

FIG. 11. Results near the percolation threshold show that the voltage where fusing starts is essentially independent of particle concentration, so that the maximum current is proportional to the conductivity.

sult is probably also relevant to random mixtures of two types of hard spheres at the close pack density, thus causing the confusion, but is not applicable to hard spheres in a continuum.

Rather than try to model the detailed structure of these complex correlated materials, we took a simpler approach and generated random hard sphere systems at various concentrations well beneath random close packed. These simulated composites will not easily percolate if one insists that only perfectly contacting spheres have conducting pathways between them. Thus to map these systems onto a conducting network, we simply defined a nonzero threshold for the particle gaps that qualify as conducting paths. Particles closer than this threshold are considered to have a conducting path between them. Choosing this threshold particle gap to be 2.5% of the particle diameter then gives a percolation threshold of around 42 vol. %, and in point of fact, the value we choose is completely arbitrary, being immaterial to all of the issues that follow. With this choice of the particle gap, the dependence of the linear conductivity (fixed conductances) on particle volume fraction is shown in Fig. 8.

To investigate the dissipation instabilities that can occur in these systems we set $\alpha = 2$ and slowly ramped up the applied potential. Results well above the percolation threshold were computed for a system at $\phi = 55$ vol. %. In Fig. 9(a) we show a visualization of the particle voltages for a large applied voltage that is well into the unstable region. A

roughly two-dimensional zone perpendicular to the applied field can be observed over which essentially all the voltage drop occurs. In Fig. 9(b) we visualize the zone of dissipation, and the plate-like nature of this zone becomes more apparent. The dependence of the conductance and current on the applied voltage are shown in Fig. 10.

At this point a word of explanation is in order. We found that with the simple model that did not include conductance fluctuations, the platelike instability always occurred at an electrode. This we attribute to the fact that the particles at an electrode are at fixed potential and create a rough boundary condition that is subtly special. To eliminate this tendency, we introduced small fluctuations into the conductances, which are certainly reasonable from a physical standpoint.

Closer to the percolation threshold, this zone becomes broader, probably increasing as the connectivity correlation length in the material, which diverges at the percolation threshold. The zone of dissipation also decreases to just a few particles, due to the tenuous nature of percolating pathways close to the threshold. For samples near the percolation threshold the currents are shown as functions of the applied voltage in Fig. 11. Proximity to the percolation threshold does not appear to cause the onset of nonlinear behavior to occur at smaller voltages, but this is really a little misleading. Very close to the critical point such an effect should be observed, since the length of a conducting path that traverses the sample will increase. Networks near the percolation threshold do have much smaller maximum currents, and will act as much more sensitive fuses, because these will act as the load at much smaller circuit conductance, due to their lower conductance. The maximum current near the percolation threshold will scale as the conductivity in this model.

DISCUSSION

The principal finding we have made is that in the regime where the fusing behavior is strong enough to generate current limiting behavior, an instability develops wherein dissi-

pation occurs in a platelike zone orthogonal to the applied field. This platelike failure occurs at a fixed field in the sample, essentially independent of the proximity to the percolation threshold. It is in this unstable region where the voltage drop and power dissipation occurs. In real materials, the formation of this platelike zone should have a tremendous impact on the rate of fusing: because Joule heating is essentially confined to this region, the temperature rise should be very fast, causing fusing to occur very quickly. However, the narrowness of this instability will lead to tremendous fields, which could in turn lead to dielectric breakdown.

Does this platelike electric field instability occur in real composite systems? In fact, infrared imaging of carbon black composites during fusing[23] actually shows this platelike electric field instability, and so this model may describe some aspects of the physics of these devices. But this limited success should not lead one to believe that the thermal fusing model is a realistic description of the actual device, since this instability can occur from continuum models as well.[4,5] A more realistic description of these current-limiting thermistors would enable the full prediction of the device dynamics over a wide range of self-heating rates. This is a complex issue involving heat production and thermal diffusion in composites that is beyond the scope of this rudimentary network model, and would doubtlessly require full scale, finite element modeling of the material—a very difficult numerical problem in a system of contacting particles with a large conductivity contrast.

CONCLUSIONS

We have proposed a nonlinear network model for the fusing behavior of carbon black current-limiting thermistors, wherein the conductance of the network elements depends on their Joule heating in a power law fashion at high applied voltages. The underlying motivation for this model is experiments reported by Heaney[2,3] that conclusively show that the conductivity of these composites is a smooth, strong function of the thermal expansion of the material, which increases the contact resistance between carbon black particles. This model is solved for 1D series networks and a dissipation instability is shown to occur when the current through the network actually decreases with increasing applied voltage. In the strong fusing limit of this model, the conductance decreases as the inverse square of the applied voltage at high applied voltages, the current decreases as the inverse voltage, and the Joule heating in the composite is independent of the voltage.

Networks constructed from random hard sphere composites show that in 3D networks this dissipation instability is platelike, and roughly orthogonal to the field. Experimental measurements using thermal imaging[23] confirm the development of the dissipation instability during thermal fusing. The existence of this instability should make these devices fuse much more rapidly than if this instability did not occur, since heating is confined to a small region in the sample. Because the width of this zone should scale as the connectivity correlation length of the material, one would guess that the device dynamics would be sensitive to the particle size, with small particle systems fusing more rapidly. However, an instability of small width will result in tremendous electric field development and subsequent dielectric breakdown, and this might ultimately limit practical applications of these devices to slow fusing situations.

Finally, the field at which the instability occurs is insensitive to the percolation threshold, but the maximum current that can be transmitted through the device should scale as the material conductivity, i.e., should obey a second-order critical point behavior, and so in practical applications these devices should become more sensitive near the percolation threshold.

[1] F. Carmona, Physica A **157**, 461 (1989).
[2] M. B. Heaney, Appl. Phys. Lett. **69**, 2602 (1996).
[3] M. B. Heaney, Physica A **241**, 296 (1997).
[4] R. A. Dougal, IEEE Trans. Power Electron. **11**, 304 (1996).
[5] W. Loser and C. Mattheck, Phys. Status Solidi **18**, 247 (1973).
[6] H. J. Herrmann, D. C. Hong, and H. E. Stanley, J. Phys. A **17**, L261 (1984).
[7] K. Ohe and Y. Naito, Jpn. J. Appl. Phys. **10**, 99 (1971).
[8] F. Carmouna and C. Mouney, J. Mater. Sci. **27**, 1322 (1992).
[9] I. Balberg, Phys. Rev. Lett. **59**, 1305 (1987).
[10] B. Last and D. Thouless, Phys. Rev. Lett. **27**, 1719 (1971).
[11] P. M. Duxbury, P. D. Beale, and P. L. Leath, Phys. Rev. Lett. **57**, 1052 (1986).
[12] L. A. Dissado and P. J. J. Sweeney, Phys. Rev. B **48**, 16 261 (1993).
[13] J. E. Martin, C. P. Tigges, R. A. Anderson, and J. Odinek, Phys. Rev. B **60**, 7127 (1999).
[14] P.-O. Jansson and G. Grimvall, J. Phys. D **18**, 893 (1985).
[15] M. Soderberg, Phys. Rev. B **35**, 352 (1987).
[16] P. M. Duxbury, P. L. Leath, and P. D. Beale, Phys. Rev. B **36**, 367 (1987).
[17] B. Kahng, G. G. Batrouni, S. Redner, L. de Arcangelis, and H. J. Herrmann, Phys. Rev. B **37**, 7625 (1988).
[18] C. Vaneste and D. Sornette, J. Phys. I **2**, 1621 (1992).
[19] S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973).
[20] D. Stauffer and A. A. Aharony, *Introduction to Percolation Theory*, 2nd ed. (Taylor&Francis, Washington, D.C., 1992), p. 52.
[21] M. B. Heaney, Phys. Rev. B **52**, 12 477 (1995).
[22] H. Scher and R. Zallen, J. Chem. Phys. **53**, 3759 (1970).
[23] Lamaignere, F. Carmona, and D. Sornette, Physica A **241**, 328 (1997).