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Thermal fusing model of conducting particle composites

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Abstract: Composites of carbon black particles in polyethylene are known to exhibit an unusually rapid increase in resistivity as the applied field is increased, making this material useful in automatically resettable fuses. In this application the composite is in series with the circuit it is protecting: at low applied voltages this 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 conductors. Each conductor has a conductance that depends on its instantaneous Joule heating. It is shown that in the fusing regime, where the current through the composite decreases with increasing voltage, an plate-like dissipation instability develops normal to the applied field. Experimental evidence of this phenomena is described.

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DISCLAIMER

Introduction

The electrical conductivity of composites of conducting carbon-black particles in a solid insulating polymeric matrix has been a subject of recent interest, due to the applications of this material to automatically resettable fuses and self-regulating heating elements. The 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 conduct current. The contact resistance of these particles is sensitively dependent on the gap between particles, and when the temperature of the composite is increased, the polymer expands, separating the particles slightly, and greatly increasing the resistivity of the composite. Heaney [1,2] has conducted careful experiments of this temperature dependence and has found a very abrupt increase in the resistance at 133°C, which he has demonstrated is related to the sudden specific volume increase that accompanies melting of the partially crystalline polymer matrix. In fact, when the resistance is plotted against the thickness of the sample, a smooth, superexponential dependence of the resistivity is found.

To understand Heaney's data, various microscopic models have been proposed, e.g. some suggesting that the contact resistance between particles can be modeled by quantum mechanical tunneling currents, which are exponentially dependent on the particle gaps [3]. Likewise, one could model the system classically, since the contact resistance between spherical particles in a percolative conducting path depends inversely on the gap between them. However, because the particles are rough, classical edge singularities occur in the electrical field at the particle surfaces, so the situation is

probably quite complex. These models have not taken into account the strong feedback that can occur in network models that can fail catastrophically. Resistor-Short models, where a resistor becomes a short when a critical voltage drop is exceeded, have been shown to give a reasonable account of the dielectric breakdown behavior in materials, especially when fluctuations are admitted into the model [4-6]. Likewise, Resistor-Fuse models, where a resistor becomes a fuse when a critical current is exceeded, have been shown to give a reasonable description of the mechanical fracture of materials [6]. Resistor-Short models show catastrophic behavior (strong positive feedback) when the device is voltage driven, whereas Resistor-Fuse models show catastrophic, hard fusing behavior when the device is current driven. We believe an approach of this type describes some of the complex physics of conducting-particle composites, which exhibit a sort of progressive *soft fusing*.

Rather than consider a specific microscopic model of this phenomena, we simply start with the point of view that the temperature dependence of the contact resistance is large. We then suggest a simple, generic nonlinear network model and show that this leads to a 2-dimensional heat dissipation instability when the voltage applied to this device is quickly ramped up. These instabilities occur in the regime where the resistivity increases quickly enough with applied voltage to limit the current through the device, and thus appear to be an inextricable aspect of soft fusing. In the following we describe the non-linear network model, consider instabilities that occur in series networks, and apply this model to simulated hard sphere composites.

Theory

A tremendous amount of work has been done on electrical network models, most of which has focused on the conductivity singularity that exists at the percolation threshold, [7-8] but some of which has focused on various types of catastrophic behavior mentioned above. Here we propose a primitive nonlinear network model of "soft" fusing. The physical basis of this model is the aforementioned experiments of Heaney, [1,2] which show a strong increase of the resistivity of the composite with temperature. In these experiments the sample was heated uniformly in an oven, and a small voltage was applied to measure the resistance. In the model we propose, the strong temperature dependence of the resistivity plays a central role, but it is the applied voltage alone that heats the sample.

When a carbon black composite is used as a resettable fuse, it is electrically in series with the circuit it is protecting. Under normal operating conditions, the resistance of the circuit is greater than that of the fuse, so the voltage drop across the fuse is small. However, should a short occur, the resistance of the fuse will become much greater than the remaining electrical path to ground and the voltage drop will occur across the composite. Thus we treat the composite as a voltage controlled device and consider how its resistivity increases with applied voltage. If the applied voltage is ramped up, then the Joule heating produced at the resistive contact between two carbon black particles will raise 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 will evolve, and the local temperature will be determined by the balance of heat production and diffusion, provided the applied voltage is quasi-static on the timescale

required to reach steady state. On the other hand, if the applied voltage is increased very rapidly, the situation is quite complex, with the local temperature determined by the time integral of the Joule heating.

Thermal Fusing Model. We model this system qualitatively by a network of nonlinear conductors. 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 we will write as

$$g = \frac{g_0}{1 + c(i\Delta v)^{\alpha}} = \frac{g_0}{1 + \left[(g/g_0)(\Delta v / v_0)^2 \right]^{\alpha}} \qquad (1)$$

where i is the current across the conductor, Δv is the voltage drop, $i\Delta v$ is the Joule heating, and α is an exponent that determines how rapidly the conductance changes with heat production. At low values of Δv the conductance of a bond is just the constant g_o, whereas at high values of Δv the conductance scales like $g \propto \Delta v^{\frac{-2\alpha}{1+\alpha}}$.

The unstable nature of networks of these non-linear elements can be understood by considering just two conductors in series, labeled as in Figure 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. 1, 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

$$v_2' = \frac{g_1 \times 0 + g_2 \times V}{g_1 + g_2} \qquad (2)$$

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 Figure 2 we show the stability plot for the case where α = 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 correction is negative, and successive iterations will again lead to v_2 = V/2. When the exponent α = 2, this completely stable behavior is altered, Figure 3. Only for applied voltages less than ~2.84 is a stable regime now observed, where only the single solution v_2 = V/2 is 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 $g \propto V^{\frac{-2\alpha}{1+\alpha}}$, and the other conductor will have $g \cong 1$. The exponent α = 1 marks the boundary of stable and unstable nonlinear network models, Figure 4. In this case there 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.

Results

Series networks. Numerical solutions to simple 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. 1 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 Figure 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 $G^{-1} = \sum g^{-1}$, so $G = g/N$. Solving Eq. 1 for g gives the result

$$G = \frac{g_0}{N} \frac{\sqrt{1 + 4\left(\mathrm{V}/N\mathrm{v}_0\right)^2} - 1}{2\left(\mathrm{V}/N\mathrm{v}_0\right)^2} \cong g_0 \frac{\mathrm{v}_0}{\mathrm{V}} \quad for \quad \mathrm{V} >> N\mathrm{v}_0 \qquad (3)$$

Thus in this special case the conductance becomes independent of the network size in the non-linear regime. In this regime the current is then just given by $I = G\mathrm{V} = g_0\mathrm{v}_0$, and is thus independent of the applied voltage. The Joule heating P does increase with applied voltage, however, and is $\mathrm{P} = \mathrm{IV} = g_0\mathrm{v}_0\mathrm{V}$.

The case where $\alpha = 2$, shown in Figure 6, is more interesting, and probably much more relevant to real materials. The voltage drops across each of the 10 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

$$G \cong g_0 \left(\frac{\mathrm{v}_0}{\mathrm{V}}\right)^{\frac{2\alpha}{\alpha+1}} \qquad (4)$$

so that the current actually decreases with the applied voltage as

$$I \cong g_0 \frac{\mathrm{v}_0^{\frac{2\alpha}{\alpha+1}}}{\mathrm{V}^{\frac{\alpha-1}{\alpha+1}}} \qquad (5)$$

and the dissipation increases as

$$P \equiv g_0 V_0^{\frac{2\alpha}{\alpha+1}} V^{\frac{2}{\alpha+1}}. \qquad (6)$$

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 shown in Figure 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. α=1, the dissipation instability occurs.

Simulated composites. The structure of carbon black/polymer composites is complex, apparently consisting of large carbon black aggregates that percolate to form a conducting network. The experimentally determined percolation threshold [9,10] for this system is ca. $\phi = 17$ vol. %, so it is clear that the particle positions are strongly correlated, given that in a random *hard sphere* system the percolation threshold occurs at the random close pack concentration of 64 vol. %.

Rather than try to model the 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 systems will not percolate if one insists that only perfectly contacting spheres have conducting pathways between them, so 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 ca. 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 Figure 8.

To investigate the dissipation instabilities that can occur in these systems we set α = 2 and slowly ramped up the applied potential. Results well above the percolation threshold were computed for a system at ϕ = 55 vol. %. In Figure 9a 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 Figure 9b 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 Figures 10a&b.

At this point a word of explanation is in order. We found that with the simple model that did not include conductance fluctuations, the plate-like 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 the currents are shown as functions of the applied voltage in Figure 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 cause the current to decrease with increasing voltage, an instability develops wherein dissipation occurs in a plate-like zone orthogonal to the applied field. This plate-like 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 dissipation occurs. In real materials the formation of this plate-like 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.

Does this plate-like instability occur in real composite systems? In fact, infrared imaging of carbon black composites during fusing actually show this plate-like

instability, and so this model describes some aspects of the physics of these devices. But this limited success, should not be lead one to believe that this Thermal Fusing model is a realistic description of the actual device. A more realistic description of automatically resettable fuses should enable the prediction of the device dynamics, and this is a complex issue involving heat production and thermal diffusion that is beyond the scope of this model, and would probably require full scale, finite element modeling of the material.

Conclusions

We have proposed a non-linear network model for the fusing behavior of carbon black/polymer composites, 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 [1-2] 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 1-D 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 3-D networks this dissipation instability is plate-like, and roughly orthogonal to the field.

Experimental measurements using thermal imaging confirm the development of the dissipation instability during fusing behavior. 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.

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.

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Figure Captions

1. The series network of two nonlinear conductors used to illustrate the emergence of instabilities. V is the applied potential, and g the conductances.
2. When the exponent α in Eq. 1 is less than 1.0 (in this case α=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.
3. When the exponent α in Eq. 1 is greater than 1.0 (in this case α=2) an instability develops at the central node as the applied voltage increases. This instability occurs when the derivative dv_2/dV changes sign from negative to positive, which occurs in this case at V≅2.84.
4. The case α=1 is at the edge of stability. At high applied voltages the derivative $d\Delta v_2 / dv_2$ approaches 0, so that essentially any value of v_2 is essentially a solution. In this case large voltage fluctuations can be 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.
5. A series network of 10 conductors solved for the case α=1. The node voltages are stable, and the network conductance is inversely proportional to the applied voltage.
6. A series network of 10 conductors solved for the case α=2 illustrates the emergence of a dissipation instability. The network conductance is inversely proportional to the $V^{4/3}$.

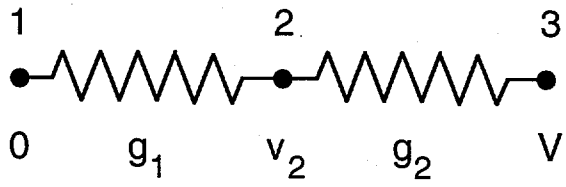
7. A comparison between the computed I-V characteristics of stable and unstable network models, in this case series networks of 10 conductors, shows that the emergence of dissipation instabilities occurs when the thermal fusing is strong enough to reduce the current with increasing voltage.

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 ϕ-ϕ_c.

9. a) The node potentials are visualized for a system of 10,000 hard spheres at 55 vol. %, with a large applied voltage and α=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 2-D 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.

10. a) The conductance of the 3-D random network of Figure 9 is shown, with the field applied along the 3 orthogonal axes. As expected, this conductance decreases as $V^{4/3}$.
    b) The current is shown, which decreases as $V^{1/3}$.

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.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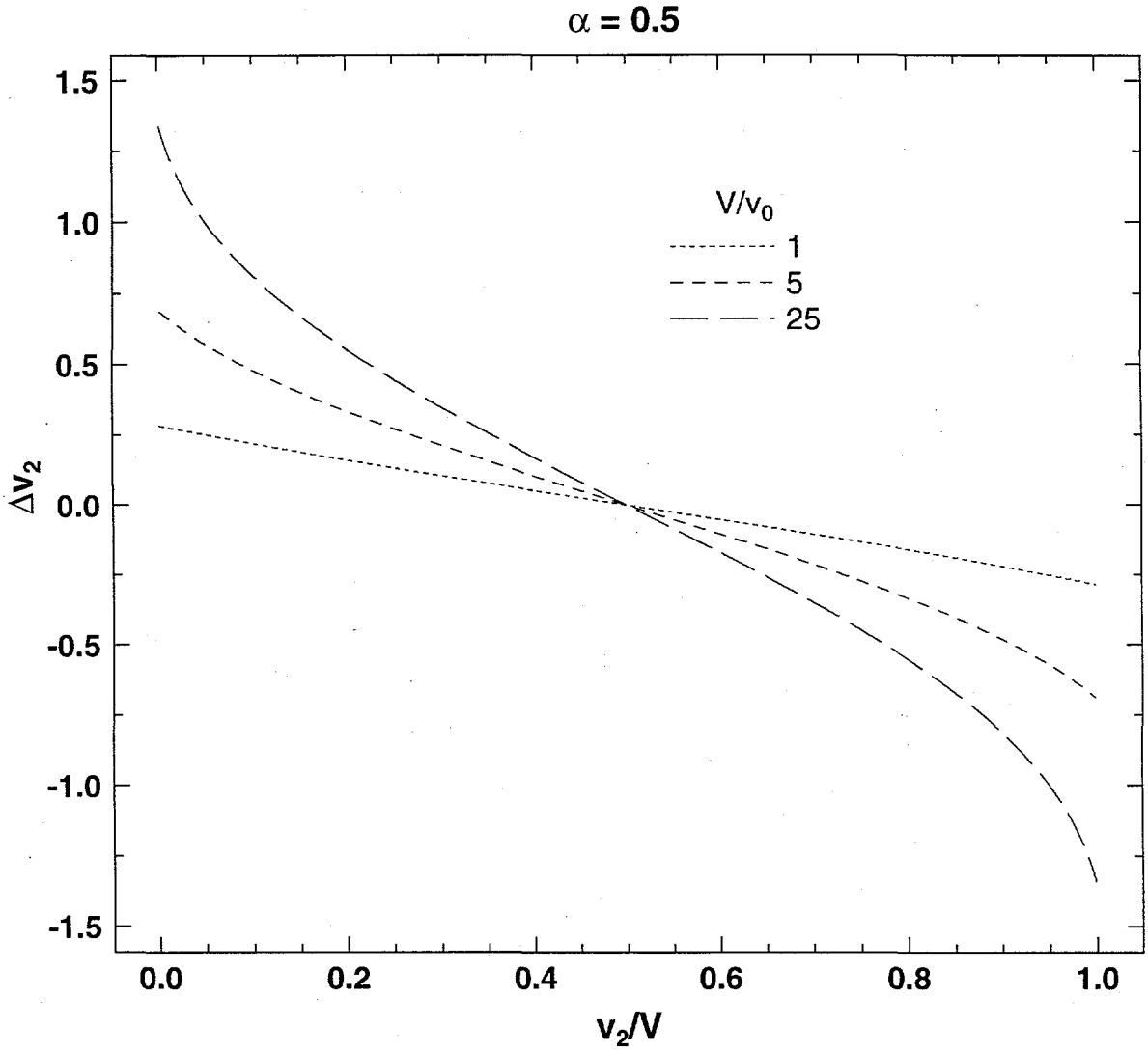
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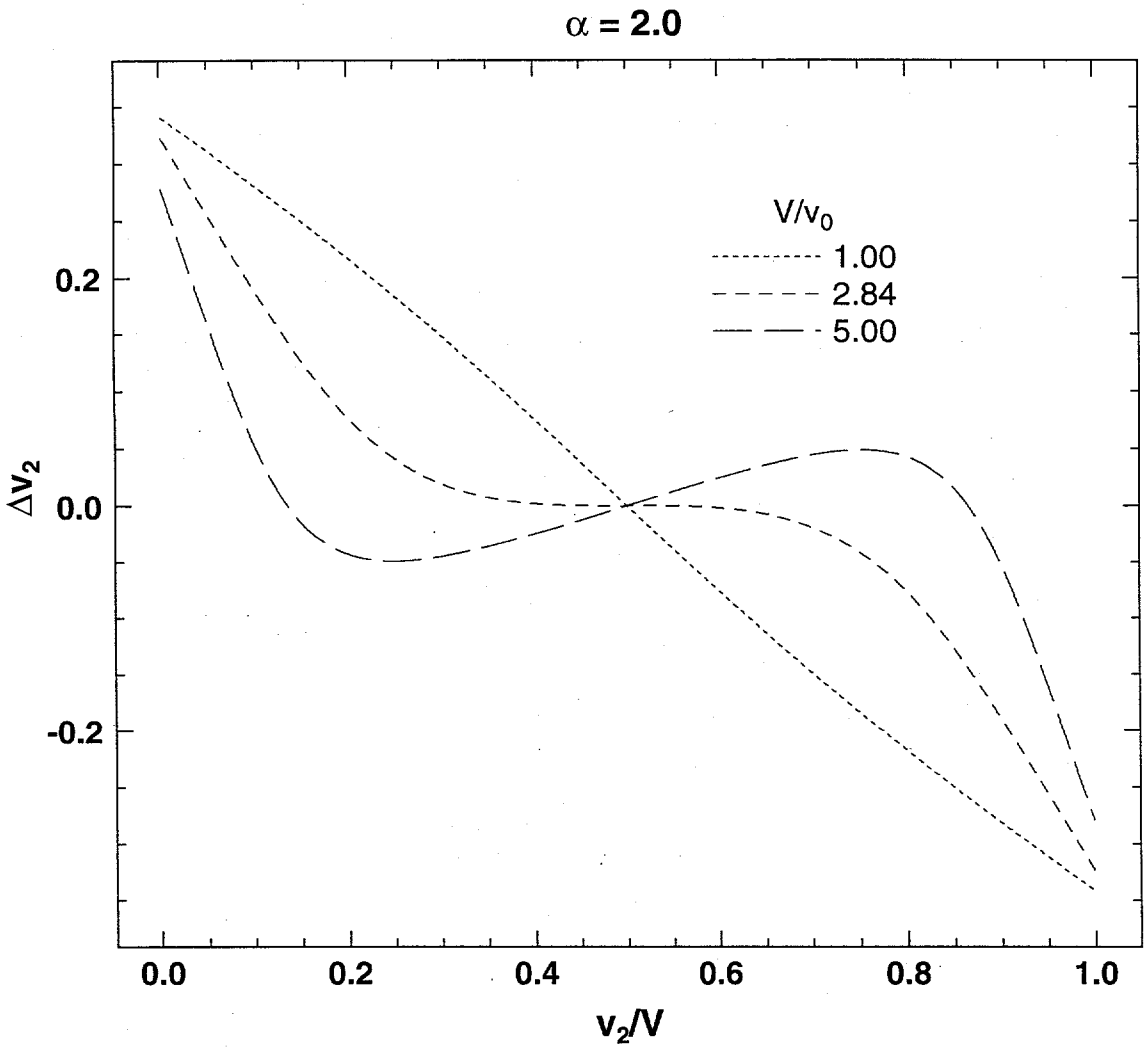
v2/V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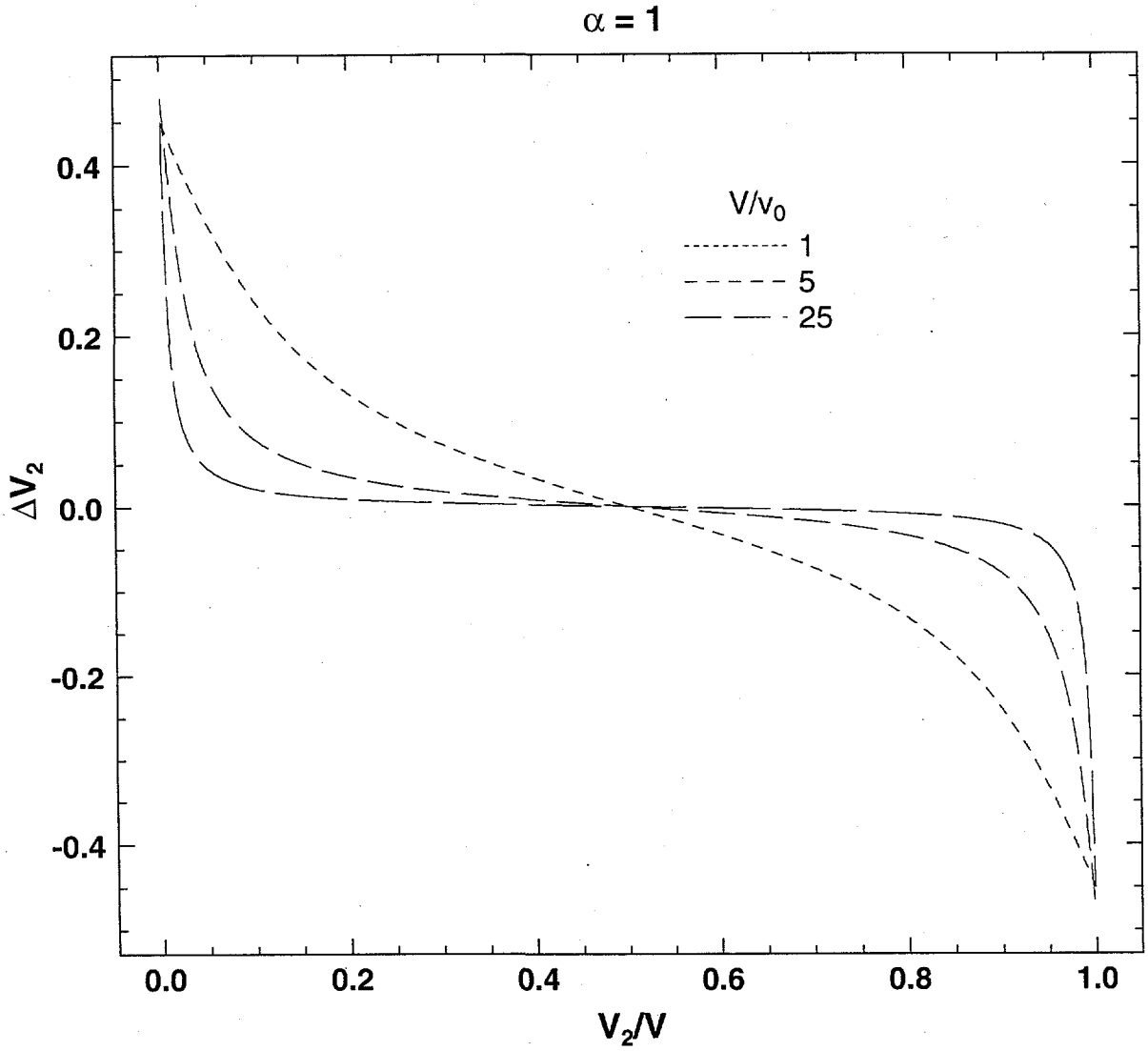
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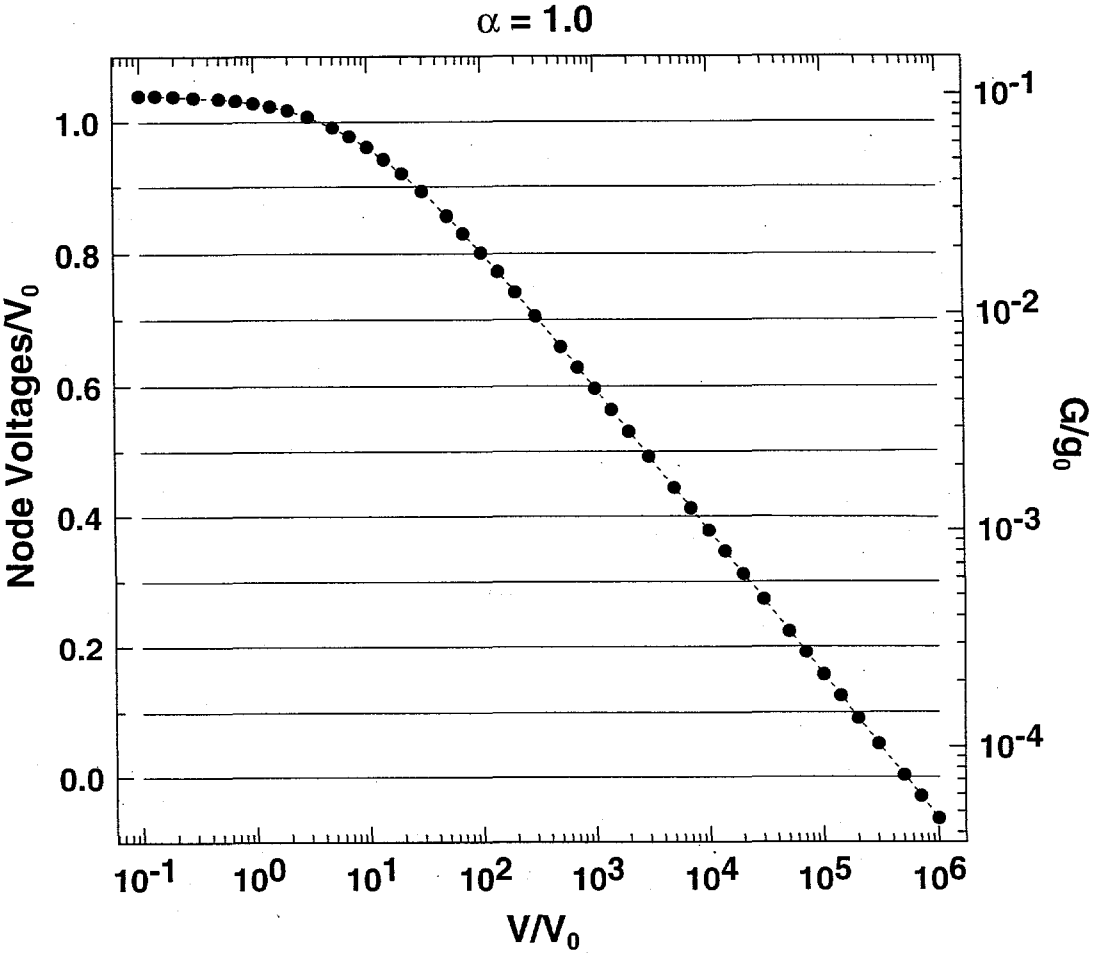
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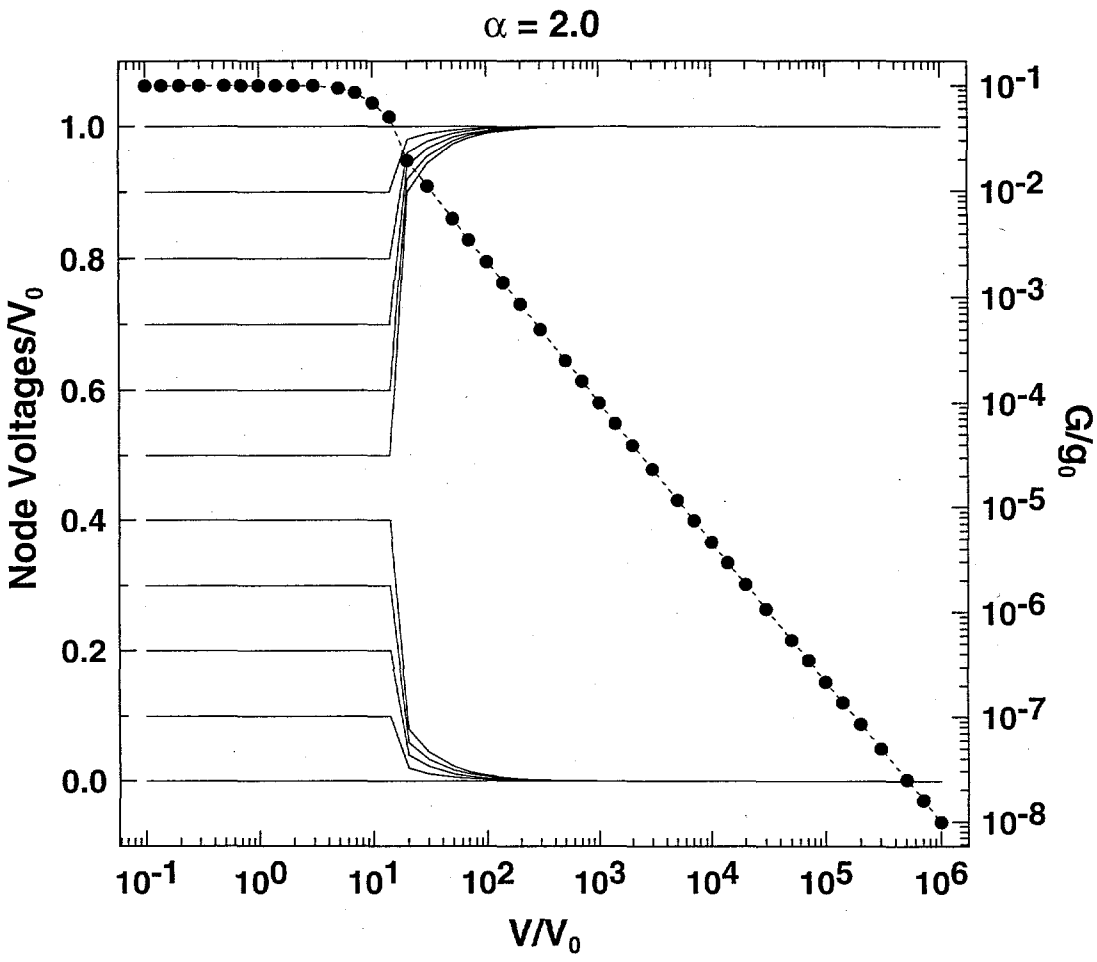
V/V0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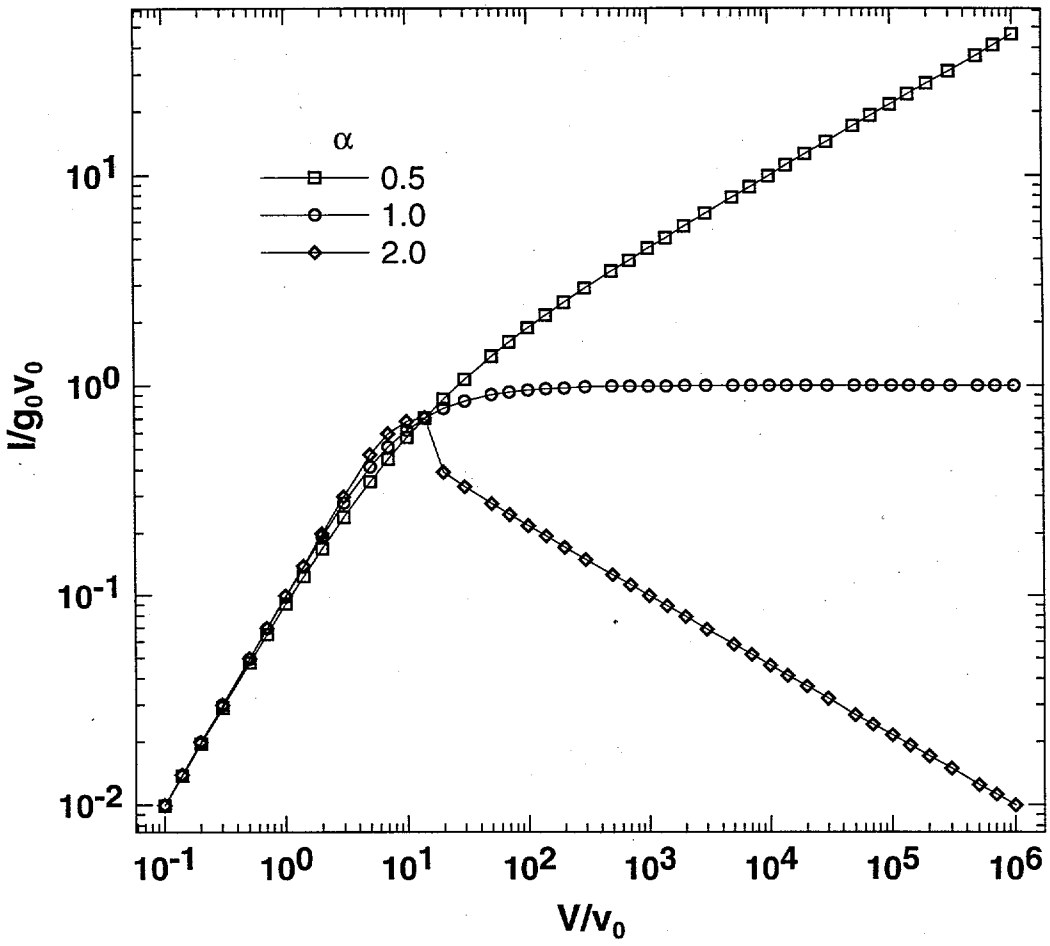
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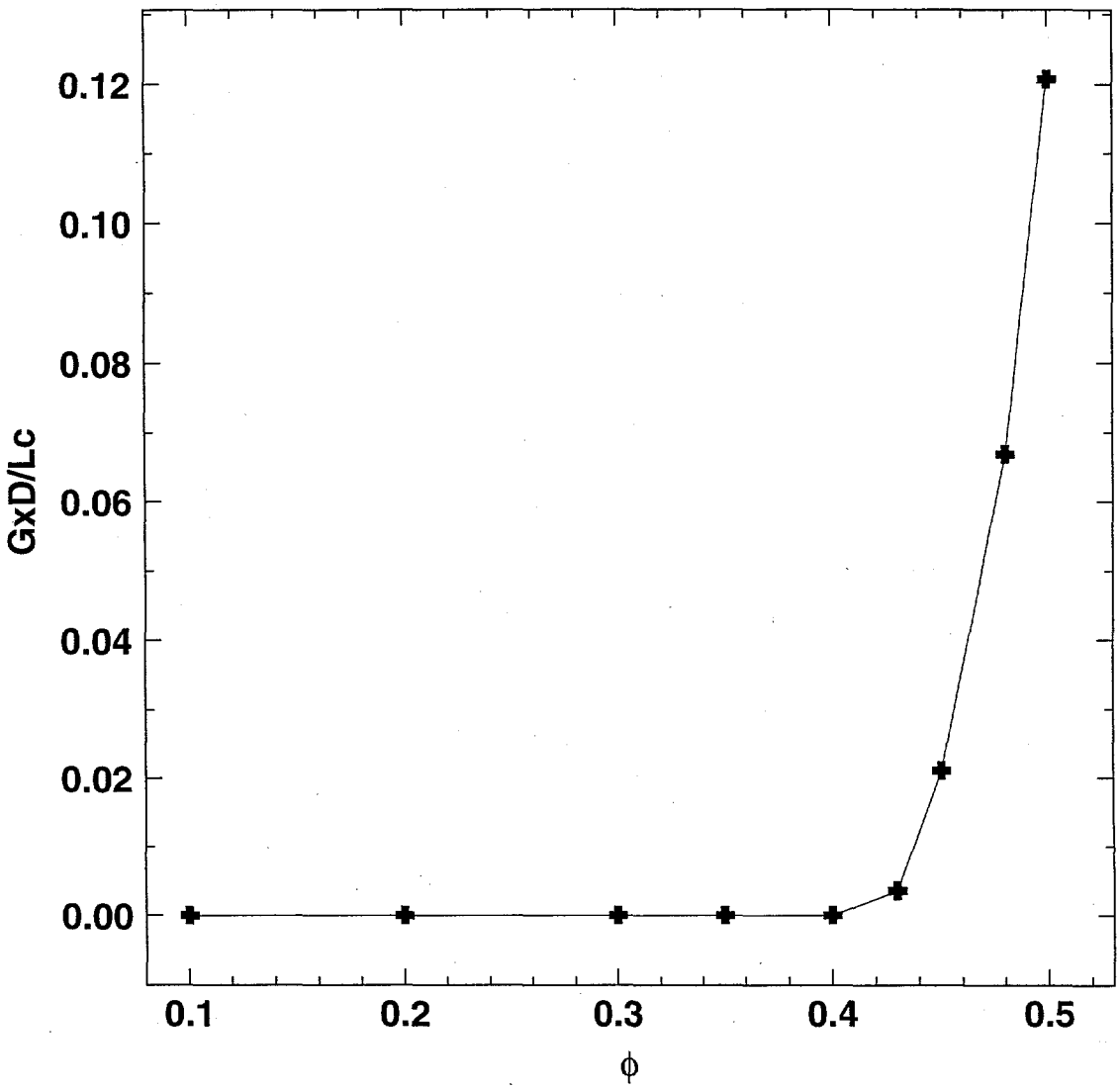
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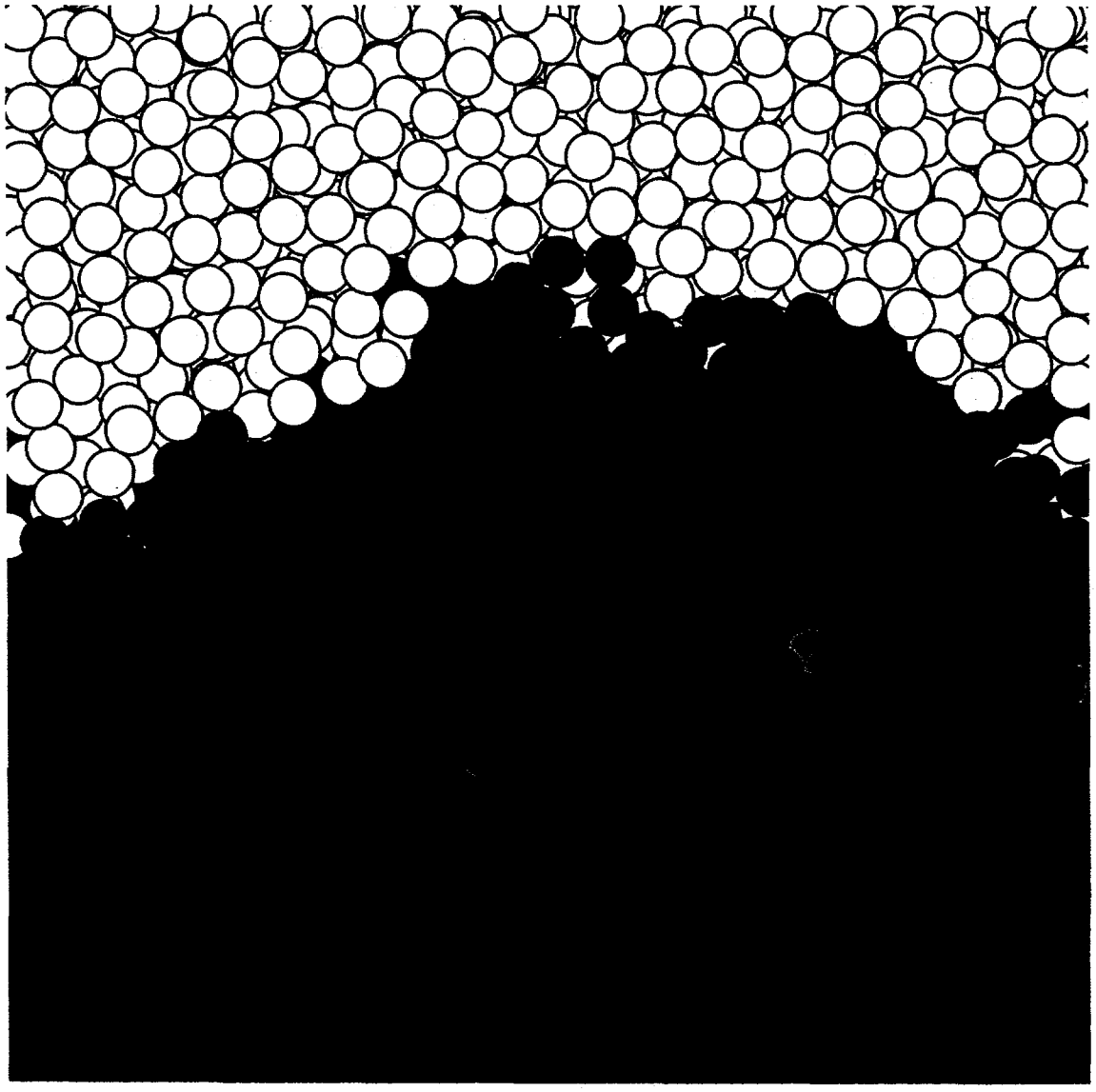

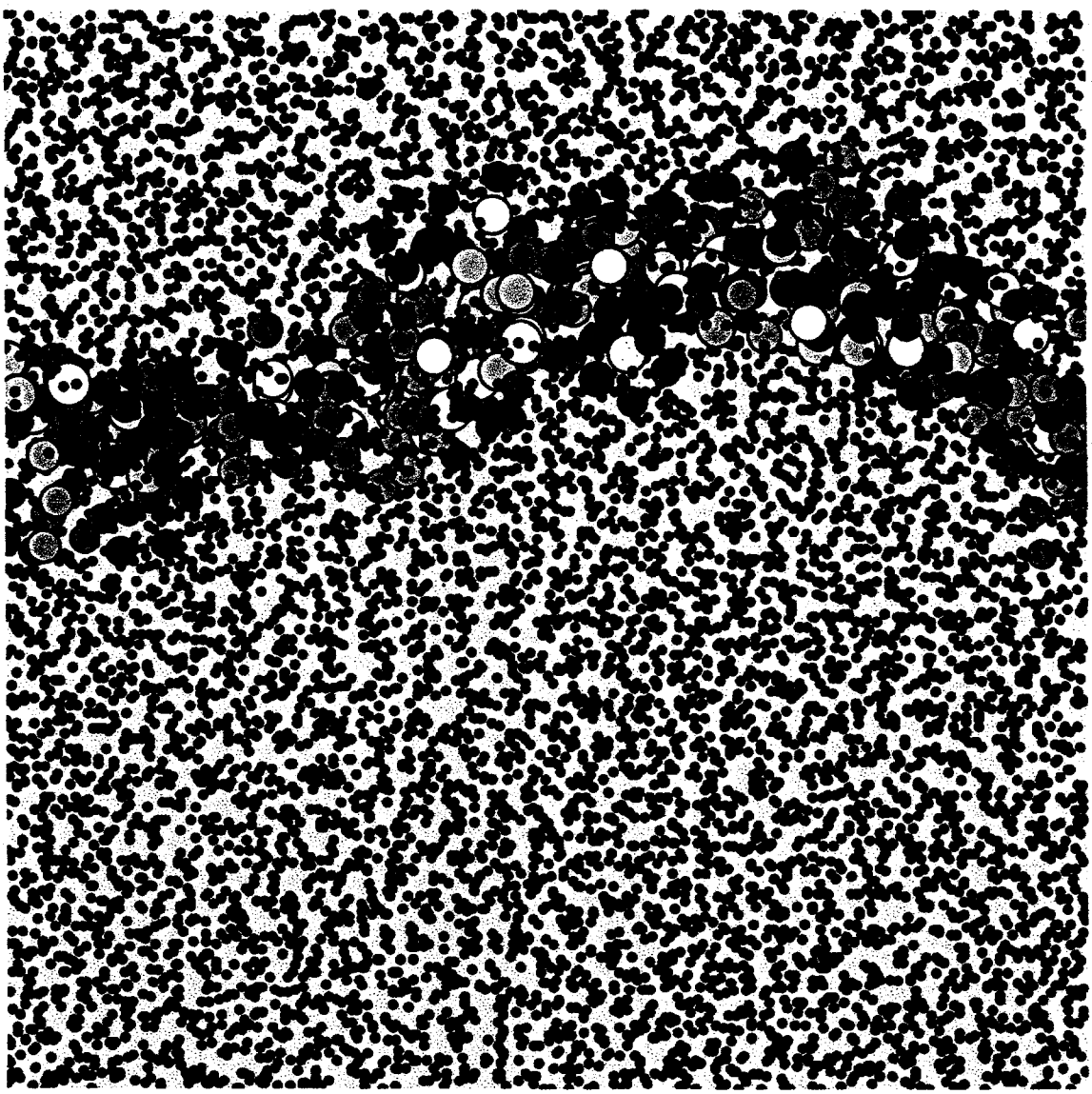

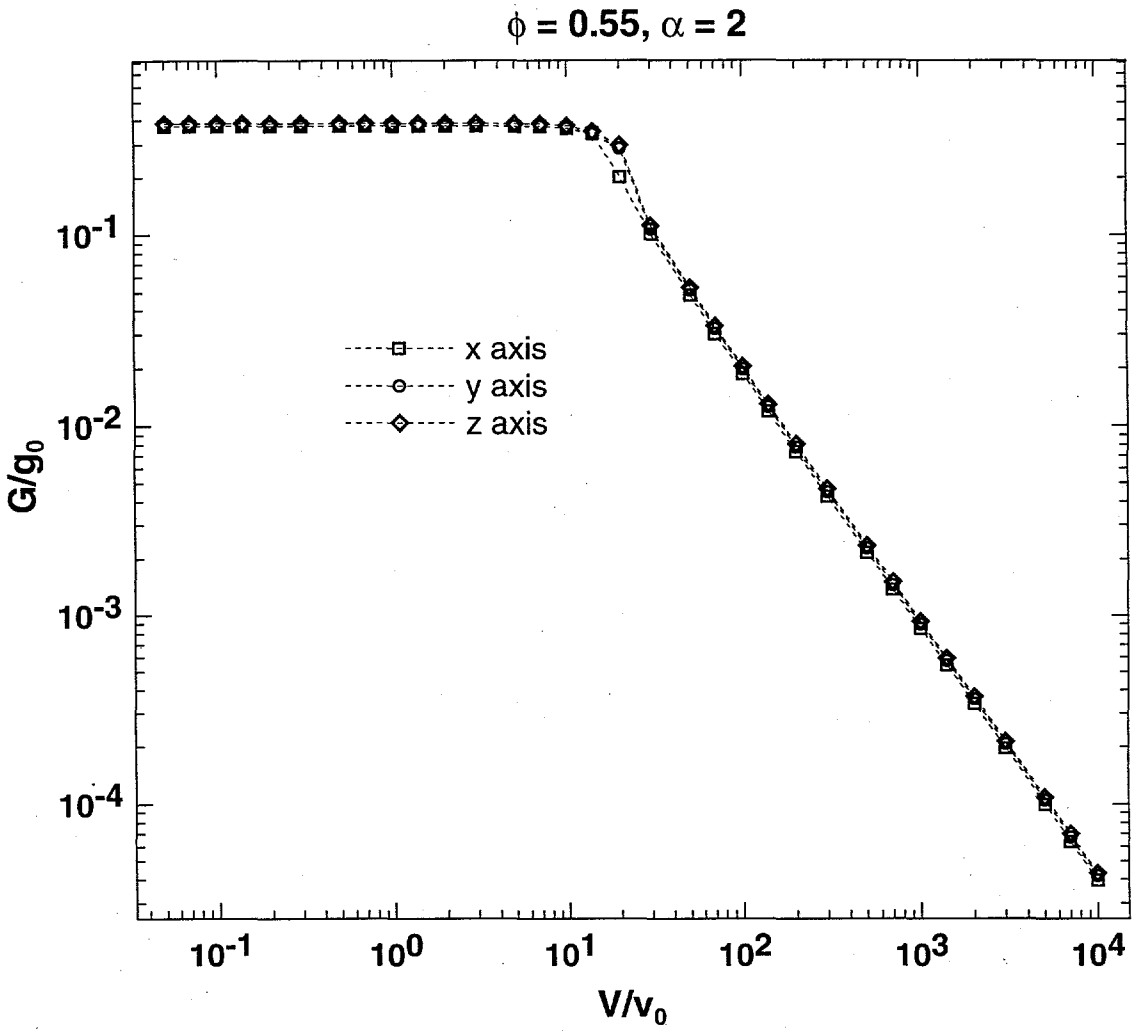
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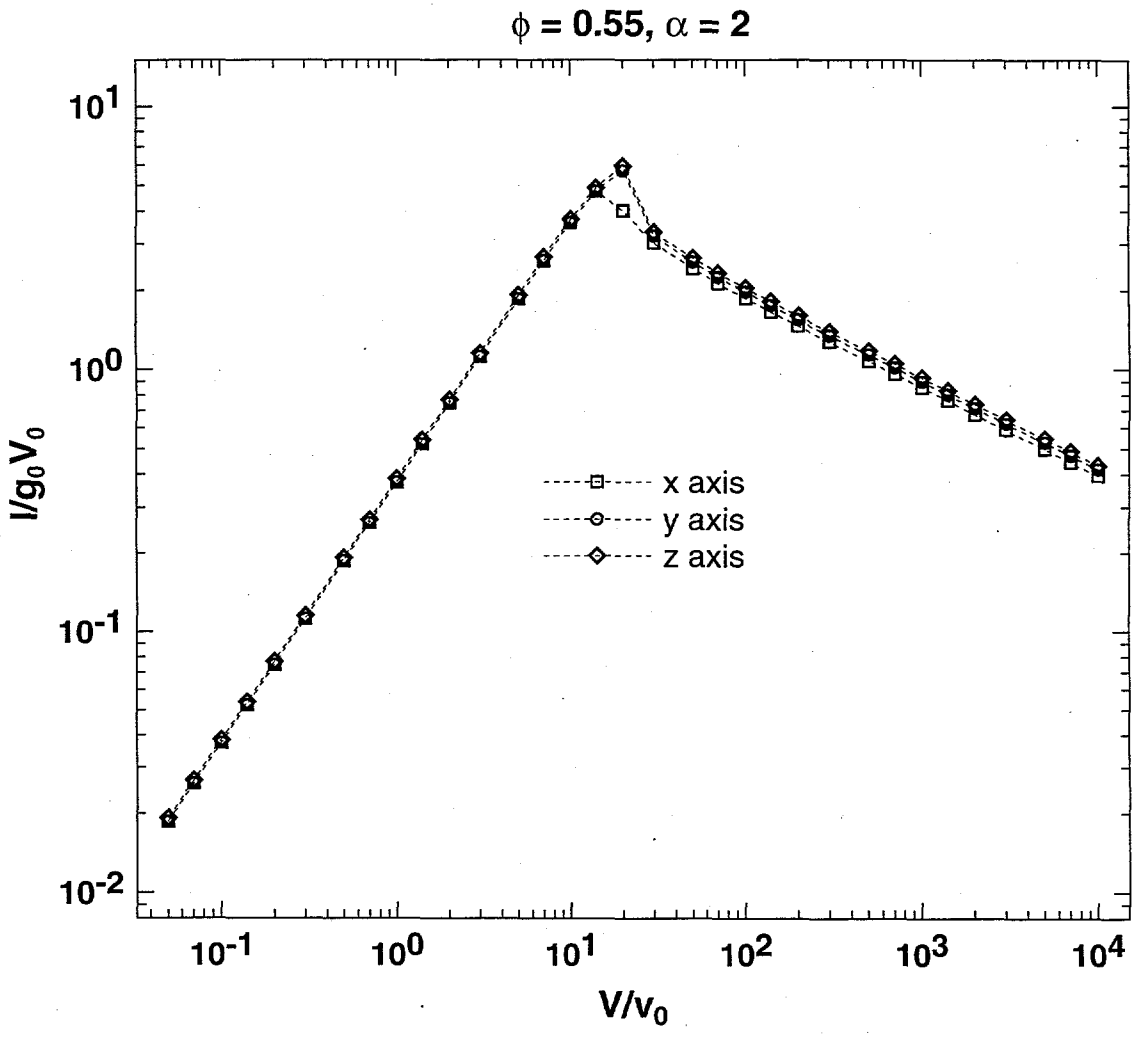
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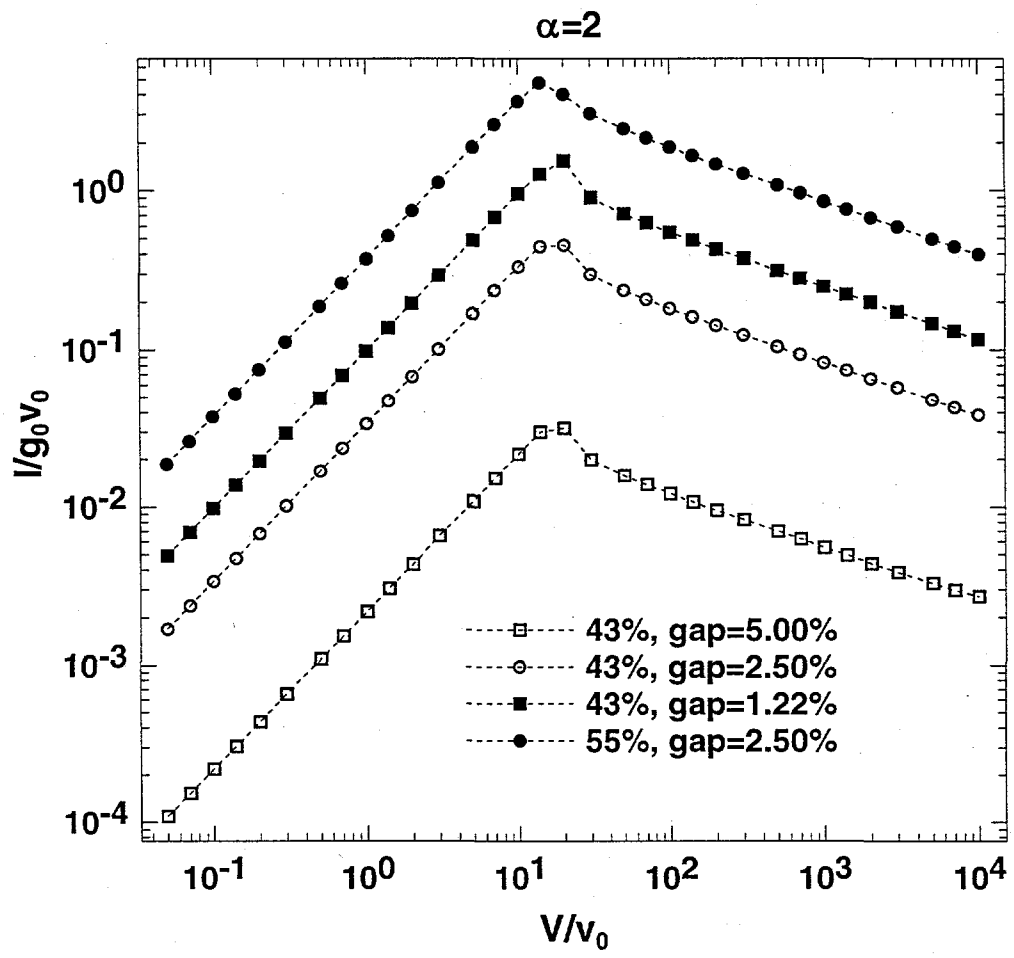
10^4
V/v_0


α=2
10^0
10^-1
10^-2
10^-3
10^-4
I/g0v0
10^-1
10^0
10^1
10^2
10^3
10^4
V/v0
43%, gap=5.00%
43%, gap=2.50%
43%, gap=1.22%
55%, gap=2.50%