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Scaling Theory Applied Far Infrared Absorption by Metal-Insulator Composite Materials

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ABSTRACT

Dynamic scaling theory is used to obtain expressions for the far infrared absorption coefficient  $\alpha$  of metal-insulator granular composite materials near the dc percolation threshold  $p_c$  in the quasistatic limit. Anomalous frequency dependence is predicted near  $p_c$  for 50 Å radius Au particles. The frequency dependence of  $\alpha$  obtained from an analysis of published data on Au blacks is inconsistent with the scaling theory for Drude Au particles in the three dimensional limit, and the theoretical estimate of the magnitude of  $\alpha$  at  $\omega = 100 \text{ cm}^{-1}$  is a factor of seven too large.

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The anomalous enhancement of the measured far infrared absorption coefficient of granular metal-insulator composite materials of low metallic content with respect to theoretical predictions has attracted interest for over a decade<sup>1-7</sup>. After clustering was convincingly associated with enhanced absorption experimentally<sup>4-6</sup>, theoretical models<sup>8-10</sup> have focused on mechanisms based on clusters of particles. Some of the proposed mechanisms<sup>8,9</sup> treat tenuous clusters and/or clusters with metallic volume fractions very close to the dc percolation threshold  $p_c$ .

Effective medium theories for metal-insulator composite materials fail in the region of composition near  $p_c$ . The scaling theory of percolation<sup>11</sup>, based on the universality of behavior near  $p_c$ , has been generalized to treat the frequency-dependent complex effective dielectric function<sup>12-14</sup>. Recently, Niklasson and Granqvist<sup>15</sup> (NG) argued that scaling theory applies to the mid- and far-infrared absorption coefficient extracted from data on evaporated Au blacks<sup>16-18</sup>.

In this paper, we apply dynamic scaling theory to obtain expressions for the far infrared absorption coefficient  $\alpha$  of a granular metal-insulator composite material for  $p$  near  $p_c$ . We predict anomalous frequency dependence very close to  $p_c$ . We examine the possibility of observing the predicted effects experimentally in the far infrared for 50 Å radius Drude Au particles in a perfect insulator. It is important to verify that the quasistatic approximation is valid. Finally, we reexamine Niklasson and Granqvist's<sup>15</sup> analysis of the data of Harris *et al.*<sup>16-18</sup> and find that our expression is inconsistent in frequency dependence if the sample is in the three-dimensional (3D) limit. Also, the predicted magnitude of  $\alpha$  exceeds the measured value by a factor of seven. We conclude that further experimental work on well-characterized samples, such as cermet films, is required to test the scaling theory.

Consider small metallic particles with complex dielectric function  $\epsilon_m(\omega)$  imbedded in a nonabsorbing host with dielectric constant  $\epsilon_D$ . If  $|p - p_c| \equiv |\Delta p| \ll 1$  and  $|\epsilon_D/\epsilon_m| \ll 1$ , the singular part of the effective complex dielectric function  $\bar{\epsilon}(\omega; p)$  can be written in the scaling form<sup>13,19</sup>

$$\bar{\epsilon}/\epsilon_m = |\Delta p|^t F_{\pm} \left( \frac{\epsilon_D}{\epsilon_m} |\Delta p|^{-s-t} \right), \quad (1)$$

where the subscripts + and - refer to  $p > p_c$  and  $p < p_c$ , respectively. Define  $z \equiv (\epsilon_D/\epsilon_m) |\Delta p|^{-s-t}$ . Following Bergman and Stroud<sup>13</sup>, for  $|z| \ll 1$ ,  $F_{\pm}(z)$  can be expanded to obtain

$$\bar{\epsilon} = B - \epsilon_D |\Delta p|^{-s} + C - (\epsilon_D^2/\epsilon_m) |\Delta p|^{-t-2s} + \dots \quad (2)$$

for  $p < p_c$  and

$$\bar{\epsilon} = A_+ \epsilon_m |\Delta p|^t + B_+ \epsilon_D |\Delta p|^{-s} + \dots \quad (3)$$

for  $p > p_c$ . The coefficients  $A_+$ ,  $B_{\pm}$ , and  $C_-$  are presumed real since the theory should apply when  $\epsilon_m$  and  $\epsilon_D$  are real. Very close to  $p_c$ ,  $|z| \gg 1$ . Since  $\bar{\epsilon}(\omega; p)$  is independent of  $p$  to lowest order,

$$\bar{\epsilon} = \epsilon_D^{t/(s+t)} \epsilon_m^{s/(s+t)} + \dots \quad (4)$$

The absorption coefficient  $\alpha(\omega; p)$  is defined by

$$\alpha = 2 (\omega/c) \text{Im}\{\sqrt{\bar{\epsilon}}\}, \quad (5)$$

where  $c$  is the speed of light. Define  $\bar{\epsilon} \equiv \bar{\epsilon}_R + i\bar{\epsilon}_I$ . Let  $\epsilon_m(\omega)$  be described by the Drude model, which applies to many metals in the far infrared. If  $\omega\tau \ll 1$ ,  $\epsilon_m \simeq i\omega_p^2\tau/\omega$ , where  $\tau$  is the relaxation time and  $\omega_p$  the plasma frequency. For  $|z| \ll 1$  with  $p < p_c$ ,  $\bar{\epsilon}_I \ll |\bar{\epsilon}_R|$  since  $\bar{\epsilon}_R \sim z$  and  $\bar{\epsilon}_I \sim z^2$ . Then  $\alpha \simeq (\omega/c) \bar{\epsilon}_I / \sqrt{\bar{\epsilon}_R}$ , so

$$\alpha = -\frac{C-}{\sqrt{B-}} \frac{\epsilon_D^{3/2}}{\omega_p^2 \tau c} \omega^2 |\Delta p|^{-(t+\frac{3}{2}s)} + \dots \quad (6)$$

Note that  $C- < 0$ . We obtain the same quadratic frequency dependence as is predicted for a Drude metal by effective medium theories in the dilute limit, but with an interesting dependence on  $p$ . For  $|z| \ll 1$  with  $p > p_c$ ,  $\bar{\epsilon}_I \gg |\bar{\epsilon}_R|$ , since  $\bar{\epsilon}_I \sim O(1)$  and  $\bar{\epsilon}_R \sim z$ . Thus,  $\alpha \simeq \sqrt{2} (\omega/c) \sqrt{\bar{\epsilon}_I}$  and

$$\alpha = \sqrt{2A+} \tau \frac{\omega_p}{c} \omega^{1/2} |\Delta p|^{t/2} + \dots \quad (7)$$

For  $p > p_c$ , the sample is conducting, so it is not surprising that we obtain the  $\omega^{1/2}$  dependence of the Hagen-Rubens relation, plus a power law  $p$ -dependence. For  $|z| \gg 1$ , very close to  $p_c$ , Eq. 5 leads to

$$\alpha = \frac{2}{c} \sin\left(\frac{\pi}{4} \frac{s}{s+t}\right) \left(\omega_p^2 \tau\right)^{\frac{s}{2(s+t)}} \epsilon_D^{\frac{t}{2(s+t)}} \omega^{\frac{s+2t}{2(s+t)}} + \dots \quad (8)$$

To lowest order,  $\alpha$  is independent of  $p$ , but shows anomalous frequency dependence. Equations 6–8 are valid if the singular part of  $\bar{\epsilon}$  is the dominant contribution.

To examine whether the predicted effects are observable in the far infrared, we consider  $a=50$  Å radius Drude Au particles supported in vacuum ( $\epsilon_D=1$ ). For Drude Au, the plasma frequency<sup>20</sup> is  $\bar{\omega}_p = 7.27 \times 10^4 \text{ cm}^{-1}$  ( $\bar{\omega} \equiv \omega/2\pi c$  is the frequency in wavenumbers.). For very small particles, the carrier scattering is dominated by the surface of the particle<sup>21</sup>, so we make the approximation  $\tau \simeq a/v_F$ , where  $v_F$  is the Fermi velocity. Thus,  $1/(2\pi c \tau) = 1490 \text{ cm}^{-1}$  ( $\lambda_\tau = 6.73 \text{ } \mu\text{m}$ ).  $\omega \tau \ll 1$  is reasonably obeyed for  $\bar{\omega} < 100 \text{ cm}^{-1}$ . At  $\bar{\omega} = 100 \text{ cm}^{-1}$ ,  $|\epsilon_D/\epsilon_m| = 2.82 \times 10^{-5} \ll 1$ , as required.

The quasistatic approximation, which underlies this scaling theory, applies if  $k\xi \ll 1$ , where  $k = 2\pi/\lambda = 2\pi\bar{\omega}$  ( $k$  is the wavevector,  $\lambda$  the wavelength) and  $\xi$  is the correlation length from percolation theory<sup>22</sup>. Clearly  $\xi \gg \lambda$  sufficiently close to  $p_c$ , so it is important to verify that one can achieve the

conditions required to observe anomalous absorption within the bounds imposed by the quasistatic limit. From percolation theory<sup>22</sup>,  $\xi \simeq a |\Delta p|^{-\nu}$ . We have introduced the particle radius  $a$  as a length scale for numerical estimates. In the quasistatic limit,  $\tilde{\omega} \ll (2\pi\xi)^{-1} = |\Delta p|^\nu / (2\pi a) \equiv \tilde{\omega}_1$ . The crossover frequency  $\omega^*$  for anomalous frequency dependence is obtained by setting  $|z|=1$ . The result is

$$\omega^* = \frac{\omega_p^2 \tau}{\epsilon_D} |\Delta p|^{t+s}. \quad (9)$$

$\omega^* \ll \omega \ll \omega_1$  is required for anomalous frequency dependence. Eqs. 6 and 7 apply when  $\omega \ll \omega^*$ . More restrictive bounds on the region of anomalous frequency dependence are obtained by considering the wavelength inside a cluster of size  $\xi$ ,  $\lambda_c \equiv \lambda/n_c$ , where  $n_c = \text{Re}\{\sqrt{\epsilon_c}\}$  and  $\epsilon_c$  is the dielectric function of the cluster. Although, the quasistatic approximation is easily satisfied for an isolated Au particle, if we assume that the cluster is a Au sphere, we obtain the very strong requirement  $\omega \ll \omega_2$ , where

$$\omega_2 \equiv \frac{2}{\tau} \left( \frac{c}{a\omega_p} \right)^2 |\Delta p|^{2\nu}. \quad (10)$$

It is more plausible to approximate the dielectric function of the cluster by the effective dielectric function at  $p_c$  (Eq. 4). The bound becomes  $\omega \ll \omega_3$ , where

$$\omega_3 = \left[ (a/c) \cos\left(\frac{\pi}{4} \frac{s}{s+t}\right) \right]^{-\frac{2(s+t)}{s+2t}} \epsilon_D^{-\frac{t}{s+2t}} (\omega_p^2 \tau)^{-\frac{s}{s+2t}} |\Delta p|^{\frac{2\nu(s+t)}{s+2t}}. \quad (11)$$

Figure 1 shows the various regions of behavior near  $p_c$  for 50 Å radius Drude Au particles for both 3D and 2D. Following NG, for 3D we use<sup>23</sup>  $s=0.75$  and<sup>24</sup>  $t=1.94$ . Also<sup>25</sup>,  $\nu=0.88$ . For 2D we use<sup>23</sup>  $s=t=1.3$  and<sup>26</sup>  $\nu=4/3$ . We conclude that the possibility of observing anomalous frequency dependence in the far infrared is good in the 3D limit, but uncertain in 2D. The control required of  $p$  ( $\sim 0.1-1\%$ ) is achievable.

Niklasson and Granqvist<sup>15</sup> analyzed old data of Harris *et al.*<sup>16-18</sup> on evaporated Au blacks and concluded that anomalous absorption as predicted by scaling theory is observed for certain samples in the mid- to far-infrared. The Au blacks are tenuous ( $p \sim 0.002$ ). Since the particles are self-supporting the conducting materials must be close to  $p_c$ . The particles are  $\sim 100 \text{ \AA}$  in diameter. The thicknesses of the two samples of interest are 19 and 27  $\mu\text{m}$ .

NG used the approximation

$$\sqrt{\epsilon} = \sqrt{1 + \frac{4\pi i}{\omega} \bar{\sigma}} \simeq 1 + \frac{2\pi i}{\omega} \bar{\sigma} \quad (12)$$

to obtain

$$\alpha = \frac{4\pi}{c} \text{Re}\{\bar{\sigma}(\omega; p)\}, \quad (13)$$

where  $\bar{\sigma}(\omega; p)$  is the effective conductivity. Scaling theory predicts<sup>12</sup>  $\bar{\sigma} \sim \omega^{t/(t+s)}$  in the anomalous region. Using the values  $s=0.75$  and  $t=1.94$  for 3D, NG calculated the exponent 0.72, which agrees well with the exponents 0.703 and 0.717 obtained by converting the transmission and reflection data of Harris *et al.* to an absorption coefficient.

Harris and Beasley<sup>27</sup> state that the approximation given by Equation 12 does not apply if  $\lambda > 15 \text{ \AA}$ . For 50  $\text{\AA}$  radius Drude Au particles in the anomalous region,  $|4\pi\bar{\sigma}/\omega| \simeq |\epsilon| \simeq 19$  and 188 at  $\bar{\omega} = 100 \text{ cm}^{-1}$  for 3D and 2D, respectively. However, based on NG's Figure 1,  $|4\pi\bar{\sigma}/\omega| \simeq 0.3$  at  $\bar{\omega} = 100 \text{ cm}^{-1}$ . Thus, the data of Harris, *et al.*, as analyzed by NG, appear to be consistent with the use of Equation 12. We conclude that there is an inconsistency between the prediction based on the Drude model, which accounts for the FIR properties of bulk Au, and the data in NG's Figure 1.

The correct expression for the frequency dependence of  $\alpha$  for Drude Au particles is given by Eq. 8. Using the same values of  $s$  and  $t$  used by NG, we obtain exponents of 0.86 and 3/4 for 3D and 2D,

respectively. Neither exponent provides as excellent a fit to the data as does 0.72, but the 2D exponent is closer. A transition from 3D to 2D percolation behavior<sup>28-29</sup> is expected as  $p_c$  is approached. Using  $\xi \sim a\Delta p^{-\nu} \sim L$ , where  $L$  is the thickness of the sample, the transition is estimated to take place at  $\Delta p \sim 1 \times 10^{-4}$  for  $L = 19 \mu\text{m}$ . It is unlikely that the gold black deposits are so close to  $p_c$ . Also, the spectral region covered by the data does not fall within the bounds  $\omega^* < \omega < \omega_3$  for 2D. We conclude that the scaling theory applied to Drude Au particles is not able to explain the anomalous frequency dependence obtained by NG's analysis of the data of Harris *et al.*

Equation 8 provides an estimate for the magnitude of  $\alpha$  very close to  $p_c$ . For 3D,  $\alpha(\tilde{\omega} = 100 \text{ cm}^{-1}) = 1.2 \times 10^3 \text{ cm}^{-1}$ , which exceeds the measured value obtained from NG's Figure 1 by a factor of seven.

It is well-known that eddy current losses (magnetic dipole absorption) contribute to the far infrared absorption by isolated metal particles<sup>1,30-31</sup> and clusters<sup>8,32</sup>. The question of whether eddy current losses diverge at  $p_c$  has been addressed for both normal metal-insulator and superconducting composite materials. Both numerical work<sup>33-34</sup> and a scaling theory<sup>35</sup> predict divergent response at  $p_c$ . However, a recent treatment<sup>36</sup> that takes mutual inductance into account does not show divergent behavior.

The scaling theory applied in this paper lead to a homogeneous effective dielectric function. A scaling theory for the limit  $k\xi \gg 1$  based on geometrical arguments<sup>37</sup> has been successfully applied to cermet films in the mid- and far-infrared<sup>38-42</sup>. These ideas have recently been developed more fully by Yagil, *et al.*<sup>43</sup> Rather than using the wavelength, they introduce a new length scale  $L(\omega)$ , the distance a carrier diffuses on a cluster during the period of the electromagnetic wave given by the theory of anomalous diffusion<sup>44</sup>.  $L(\omega)$  decreases with increasing frequency. For this theory, an effective medium treatment is not valid if  $L(\omega) \ll \xi$ , and the optical properties of the sample must be calculated by summing over cells of size  $L(\omega)$ . According to Yagil, *et al.*<sup>43</sup>,  $L(\omega) = B\xi_o(\lambda/\xi_o)^{1/(2+\theta)}$ , where  $\xi = \xi_o|p - p_c|^{-\nu}$ ,  $\lambda$  is the wavelength,  $B$  is a dimensionless constant of order unity, and  $\theta = 1.5$  in

three dimensions<sup>44</sup>. If we set  $L(\omega)=\xi$  with  $\xi_0=a=50 \text{ \AA}$  and  $B=1$ , we obtain the crossover frequency  $\tilde{\omega}_c = \frac{1}{a}|p-p_c|^{\nu(2+\theta)} = (2.0 \times 10^4 \text{ cm}^{-1})|\Delta p|^{3.1}$ . According to this estimate, a description based on finite-size scaling is required to calculate the far infrared properties of  $50 \text{ \AA}$  radius Au particles near  $p_c$ .

We conclude that dynamic scaling theory predicts interesting frequency and composition dependence for the far infrared absorption coefficient of granular metal-insulator composite materials. Experiments on cermet films and other composite materials in the far infrared with composition near  $p_c$  would further test the applicability of scaling theories.

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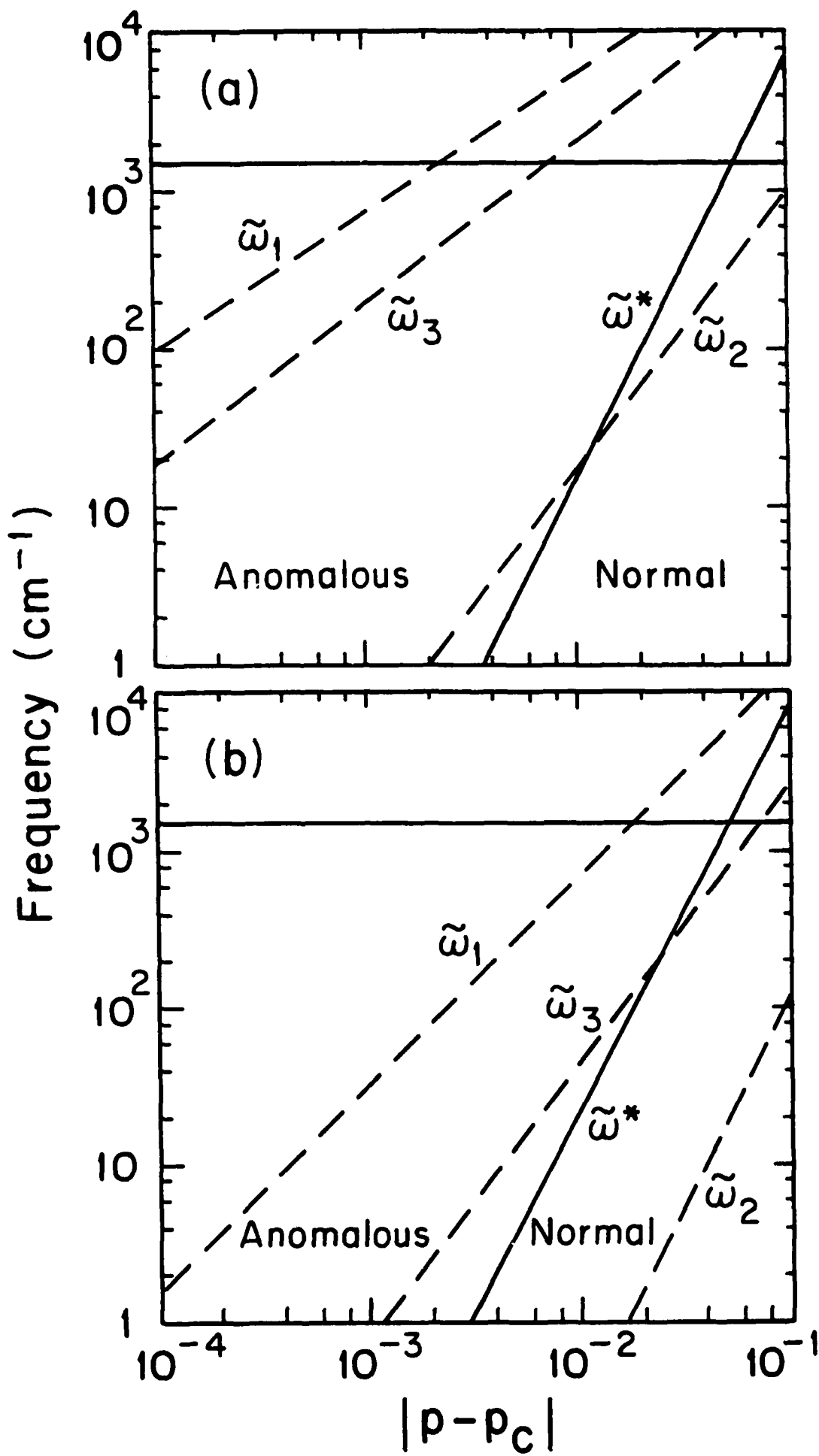
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# FIGURE CAPTION

Regions of behavior of the far infrared absorption coefficient of unsupported 50 Å radius Au particles near  $p_c$  predicted by dynamic scaling theory. The horizontal line indicates  $\omega\tau=1$ . The other solid line separates the region of anomalous frequency dependence ( $\omega \gg \omega^*$ ) very near  $p_c$  from the region of "normal" frequency dependence ( $\omega \ll \omega^*$ ). The three dashed lines are estimates of the limit of the region of applicability of the quasistatic approximation, as discussed in the text. a) 3D b) 2D.



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