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TEMPERATURE-DEPENDENT DIELECTRIC STRENGTH OF A MAXWELL–WAGNER TYPE RELAXATION

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A relationship between the temperature and the dielectric strength of a Maxwell–Wagner (MW) type relaxation was deduced based on the conventional two-layer model for inhomogeneous systems and under the usual assumptions that the conductivity of each layer obeys the thermally activated law and the dielectric constant of each layer is relatively temperature independent. The relation shows that the relaxation peak height in the imaginary part of the complex permittivity for a MW-type relaxation increases with decreasing temperature and saturates at low enough temperature. This behavior was well-proved by both numeral and experimental results and therefore could be regarded as a fingerprint of a MW-type relaxation in most practical cases.

Keywords: Maxwell–Wagner relaxation; criterion.

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1. Introduction

Recently, a number of materials were found to show colossal and flat dielectric constants in a broad temperature range around room temperature.[1–4] This intriguing dielectric behavior is very desirable for device implementation and numerous efforts have been made to understand the underlying physics. However, the explanations of this stunning behavior are often at odds with each other. Some authors attribute it to the intrinsic material properties,[1,5] whereas others tend to believe an extrinsic, MW-type origin resulting from spatial inhomogenity,[6] contact effect,[7] and internal barrier layer capacitor.[8]

MW relaxation is an ancient phenomenon, having been discussed extensively first by Maxwell and later by Wagner in 19th century.[9,10] It is the well-known interfacial polarization caused by inhomogeneity, which usually behaves as a characteristic frequency dispersion kink in the dielectric constant (ε') accompanied by

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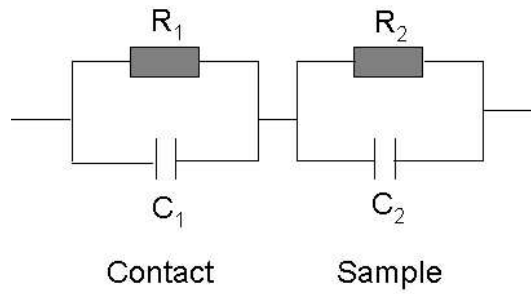

Fig. 1. Equivalent circuit for a two-layer system.

a peak in the corresponding dielectric loss (ε''). This behavior is similar to that caused by dipolar relaxation and therefore raises an important question. How can we confirm a relaxation is a MW-type relaxation, not a dipolar-type relaxation?

To answer this question, a general criterion to identify a MW-type relaxation is imperative. It is well-known that there are four primary mechanisms of polarization in materials: electronic polarization, ionic or atomic polarization, dipolar or orientational polarization, and interfacial polarization. The polarization corresponding to the last mechanism occurs in the lowest frequency range due to the largest inertial mass of space charge compared to the other polarizations. When the measuring frequency increases efficiently (usual about 1 MHz), the interfacial polarization cannot follow the variations of the applied field, then it no longer responds to the field and has no contribution to the polarization. On the other hand, the relaxation time of a MW relaxation is widely confirmed to follow perfectly the Arrhenius law. It could be expected that the relaxation would become much weaker with increasing temperatures as the relaxation would occur at higher frequencies. In this paper, we truly found that the MW relaxation can be characterized by a temperature dependence of dielectric strength. Our results indicate that this characteristic could be considered as a fingerprint of the MW-type relaxation and would be helpful for understanding dielectric responses in the studies of dielectric materials.

2. Results and Discussion

The heterogeneity associated with different contacts (electrodes, interfaces, and grain boundaries) can be modeled by a two-layer model as shown in Fig. 1, which consists of two RC (R = resistance and C = capacitor) circuits in series, one for the contact and the other for the sample.[11] The dielectric properties of the system can be characterized by the conductivities σ_i ($i = 1,\ 2$) (or resistivities ρ_i), permittivities ε_i (unit-free), and thicknesses d_i, with the real (dielectric constant) and imaginary (dielectric loss) parts of the complex permittivity can be written as[12,13]:

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\tau_\varepsilon)^2}\,, \tag{1}$$

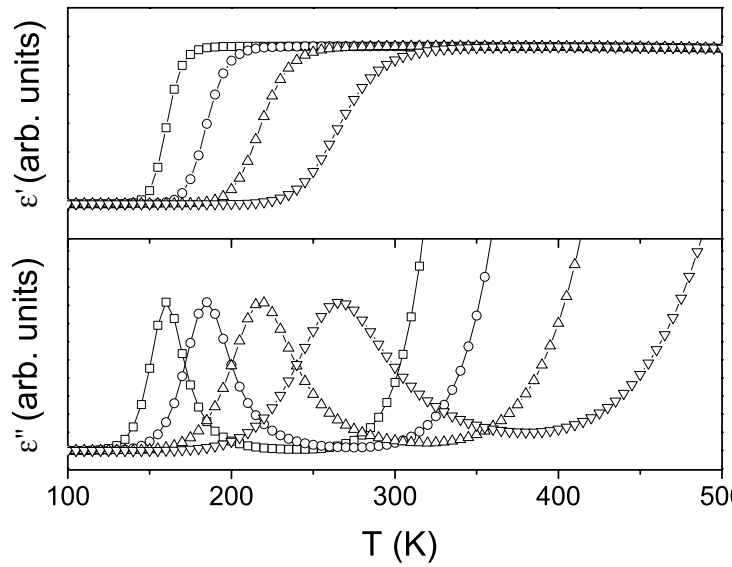

Fig. 2. Dielectric constant and loss as a function of temperature calculated by the model in Fig. 1 with frequencies of 1000, 10 000, 100 000, and 1000 000 Hz (from left to right).

$$\varepsilon''(\omega) = \frac{d\sigma_1\sigma_2}{\omega\varepsilon_0(d_1\sigma_2 + d_2\sigma_1)} + \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau_\varepsilon}{1 + (\omega\tau_\varepsilon)^2}\,, \tag{2}$$

with

$$\varepsilon_s = \varepsilon'(\omega = 0) = \frac{d(d_1\varepsilon_1/\sigma_1^2 + d_2\varepsilon_2/\sigma_2^2)}{(d_1/\sigma_1 + d_2/\sigma_2)^2}\,, \tag{3}$$

$$\varepsilon_\infty = \varepsilon'(\omega \to \infty) = \frac{d}{d_1/\varepsilon_1 + d_2/\varepsilon_2}\,, \tag{4}$$

$$\tau_\varepsilon = \frac{\varepsilon_0(\varepsilon_1 d_2 + \varepsilon_2 d_1)}{\sigma_1 d_2 + \sigma_2 d_1}\,, \tag{5}$$

where $d = d_1 + d_2$, ω and ε_0 are the angular frequency and the permittivity of free space, respectively. It can be seen that the MW relaxation exhibits a Debye-like behavior. For a Debye-like relaxation, three relaxation parameters are most important:

(i) the relaxation time, τ, which dominates the position of the relaxation peak. It is well-known that the relaxation peak appears at the temperature where $\omega\tau = 1$, and τ can be described by the Arrhenius relation, the Vogel–Fulcher relation, or a complicated relaxation-time distribution function.[14]

(ii) The activation energy, E, which dominates the width of the relaxation peak. In the case of a pure Debye relaxation, the width of the peak at half-maximum

is given by $\Delta(\log_{10}\omega\tau) = 1.144$ in the frequency spectrum and $\Delta(T^{-1}) = 2.635k_B/E$ (for Arrhrnius relation) in the temperature spectrum.[15]

(iii) The dielectric relaxation strength, Ω, which dominates the height of the relaxation peak, apparently, $\Omega = (\varepsilon_s - \varepsilon_\infty)/2$.

For a certain MW relaxation process, τ and E are defined. Thus, the parameter Ω should reflect the weakening of a MW relaxation. Actually, since ε_s and ε_∞ depend strongly on the temperature-dependent quantities σ_i and ε_i, thus the dielectric strength is different as the measuring frequency (temperature) is varied. To deduce a specific relation between the strength and the temperature, detailed information about the thermal dependencies of σ_i and ε_i is required. It is usually assumed that the conductivity obeys the thermally activated law, i.e., $\sigma_i = \sigma_{i0}\exp(-E_{ic}/k_BT)$ ($i = 1, 2$. σ_0 is the preexponential term and E_c is the activation energy of the conductivity), while ε_i ($i = 1, 2$) is relatively temperature independent. Under these assumptions, $\varepsilon_\infty =$ constant, and the dielectric strength is therefore dominated by ε_s. In the case of $\sigma_1 \ll \sigma_2$ (and vice versa), the term $(\sigma_1/\sigma_2)^2$ can be neglected, then one immediately obtains from Eq. (3) the dielectric strength of a MW relaxation, which can be written as

$$\begin{aligned}\Omega \propto \varepsilon_s &\propto \frac{(d_1/d)\varepsilon_1}{[(d_1/d) + (d_2/d)(\sigma_1/\sigma_2)]^2} \\ &\propto \frac{(d_1/d)\varepsilon_1}{(d_1/d)^2 + 2(d_2d_1\sigma_{10}/d^2\sigma_{20})\exp[-(E_{1c} - E_{2c})/k_BT]} \\ &= \frac{L}{M + N\exp(-H/k_BT)}\,, \end{aligned} \tag{6}$$

where $L = (d_1/d)\varepsilon_1$, $M = (d_1/d)^2$, $N = 2d_2d_1\sigma_{10}/d^2\sigma_{20}$, and $H = E_{1c} - E_{2c}$.

In the other case of $\sigma_1 \sim \sigma_2$, ε_s is nearly temperature-independent, which corresponds to $H \sim 0$ in Eq. (6). Therefore, Eq. (6) gives an expression for the temperature dependence of the dielectric strength in either case. Since L, M, N, and H are constants (or nearly constants), Eq. (6) indicates that the peak height of a MW relaxation increases with decreasing temperature and saturates at low enough temperature.

To test the validity of Eq. (6), a numerical result is shown in Fig. 2 to simulate the dielectric behaviors of the two-layer system with proper values of $\sigma_{10} = 0.341$ S cm^{-1}, $E_{1c} = 0.24$ eV, $\varepsilon_1 = 20$, $\sigma_{20} = 0.196$ S cm^{-1}, $E_{2c} = 0.54$ eV, $\varepsilon_2 = 10$, and $d_2/d = 0.1$. It is seen that $\varepsilon'(T)$ exhibits the typical features of materials exhibiting colossal dielectric response. That is, with decreasing temperature, $\varepsilon'(T)$ shows a step-like decrease from a higher dielectric plateau to a lower one, accompanied by a peak in $\varepsilon''(T)$ with the peak position shifting to higher temperatures as the modeling frequency increases. This peak is caused by the relaxation term [the second term in Eq. (2)]. At the same time, a nearly exponential increasing background resulting from the conductivity term [the first term in Eq. (2)] is also distinguishable especially in curves obtained with lower modeling frequencies.

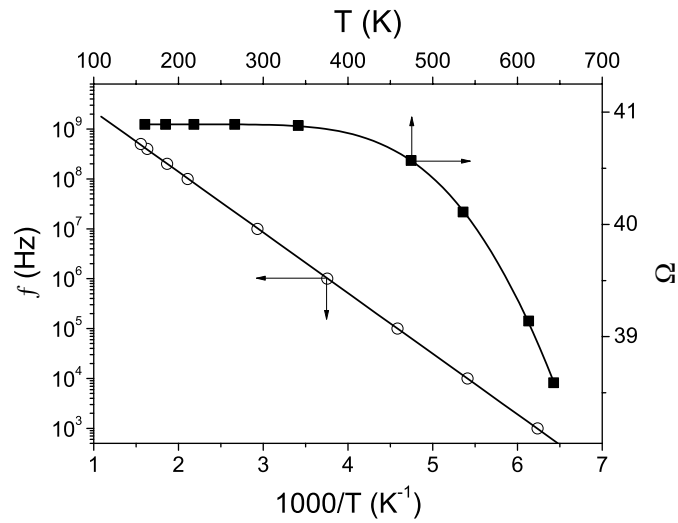

Fig. 3. Plot of the peak position extracted from Fig. 2 as a function of the reciprocal temperature. The straight line is the result of a linear fit according to Arrhenius relation; and plot of the peak height as a function of temperature. The solid line is the least-squares fitting result based on Eq. (6).

By subtracting the backgrounds, the extracted dielectric peak heights shown as closed squares in Fig. 3 fall perfectly on the solid line of the fitting result based on Eq. (6). Besides, the temperature dependence of the peak position (open circles) follows quite well the Arrhenius law as seen from the figure.

We herein show the comparison between model calculations and experimental results to further prove the validity of Eq. (6). The key point of the application of Eq. (6) is the deduction of the background, which is related to the conductivity, and in most practical cases, exponentially increases with increasing temperature.

Figure 4 illustrates an experimental sample from the results we have,[16] in which the MW relaxation is caused by the surface-layer effect in $CaCu_3Ti_4O_{12}$. By subtracting the backgrounds, a notable decay of the net relaxation peaks with increasing temperature can be clearly seen. The peak heights (closed squares) are satisfactorily described by the decreasing line obtained from the least-squares fitting based on Eq. (6).

Figure 5 presents the experimental sample from Refs. 17 and 18, therein MW relaxations were reported in $Bi_{2/3}Cu_3Ti_4O_{12}$ and $(1-x)SrTiO_{3-x}SrMg_{1/3}Nb_{2/3}O_3$ with $x = 0.03$, respectively. Again excellent agreement can be seen between the experimental data (open and closed squares) and the calculated results (solid lines).

It is worth noting that the loss tangent, $\tan\delta$ ($\tan\delta = \varepsilon''/\varepsilon'$), is usually used to express the dielectric dissipation. A pertinent question is whether the deduced relation also holds in the case of loss tangent. In this case, the relaxation term is given by $(\varepsilon_s - \varepsilon_\infty)\omega\tau_\delta/[\sqrt{\varepsilon_s\varepsilon_\infty}(1 + (\omega\tau_\delta)^2)]$, where $\tau_\delta = \sqrt{\varepsilon_\infty/\varepsilon_s}\tau_\varepsilon$. It takes the

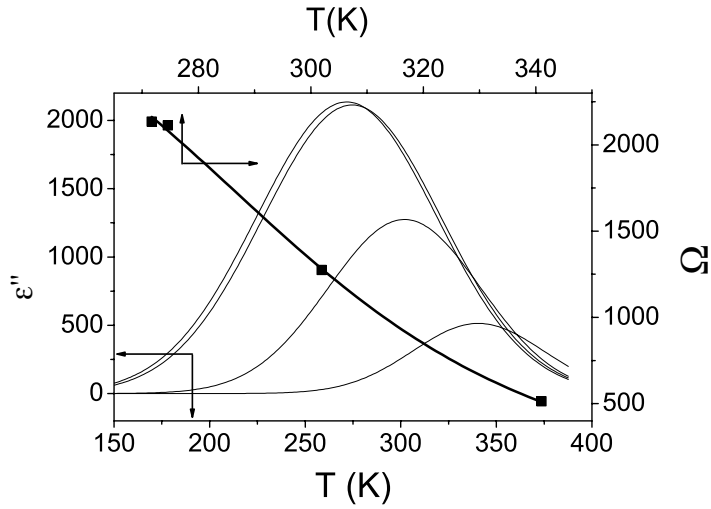

Fig. 4. Comparison of the extracted relaxation peaks from $CaCu_3Ti_4O_{12}$ (Ref. 16) with the measuring frequencies of 100, 120, 1000, and 10 000 Hz (from left to right); and the temperature dependence of the peak height. The closed squares are experimental results, while the solid line is the least-squares fitting result based on Eq. (6).

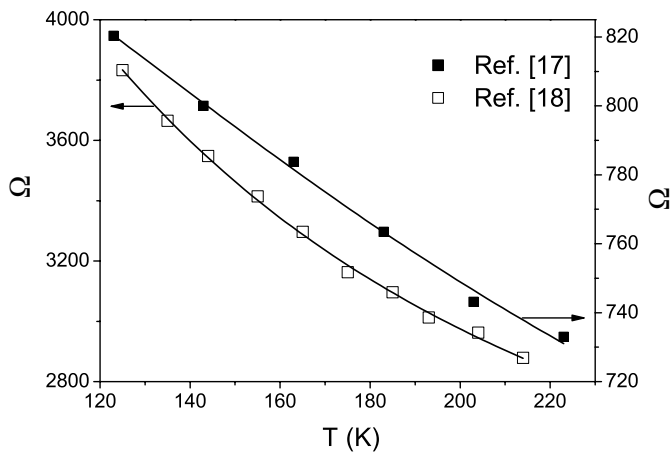

Fig. 5. The temperature dependence of the peak height obtained from Refs. 17 and 18 ($x = 0.03$). The open and closed squares are experimental results, the solid lines are the least-squares fitting results based on Eq. (6).

same form as that of $\varepsilon''(\omega)$. Hence, $\tan\delta$ registers a peak at $\omega\tau_\delta = 1$ with the maximum value $\Omega_\delta = (\varepsilon_s - \varepsilon_\infty)/2\sqrt{\varepsilon_s\varepsilon_\infty}$. Conventionally, $\varepsilon_s \gg \varepsilon_\infty$, this allows us to rewrite the peak height of $\tan\delta$ as

$$\Omega_\delta \propto \sqrt{\varepsilon_s}\,. \tag{7}$$

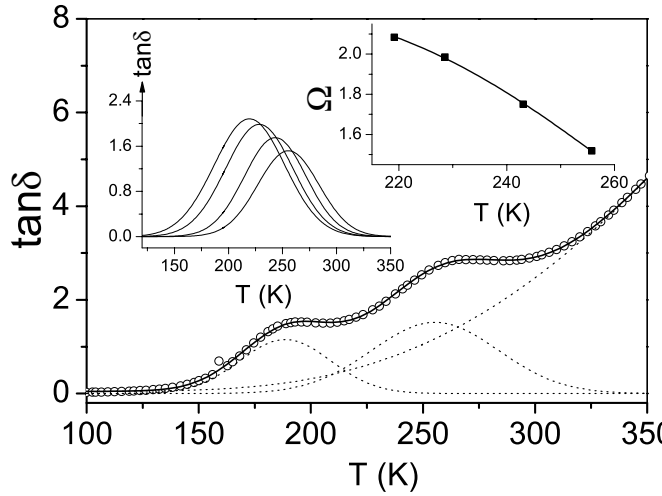

Fig. 6. Temperature dependence of $\tan\delta$ for $TbMnO_3$ ceramics (open symbols) measured at 100 kHz. The solid curve through the data points is the least-squares fitting result. The dashed curves are the resultant fitting peaks and background. The left inset shows the comparison of the extracted high-temperature relaxation peaks with the measuring frequencies of 100, 120, 1000, and 10 000 Hz (from left to right). The right inset displays the temperature dependence of the peak height. The solid line is the least-squares fitting result based on Eq. (6).

By substituting Eq. (6) into Eq. (7) and on condition that $(N/M)\exp(-H/k_BT) \ll 1$, Eq. (7) can be simplified to the same form as Eq. (6) by neglecting the second and higher-order terms. This fact indicates that the peak height of $\tan\delta$ in certain cases varies with temperature in the same manner as $\varepsilon''(T)$ does. A justifying examination was performed on $TbMnO_3$ ceramics. The sample possessing two dielectric relaxations with the high-temperature relaxation was clarified to be a MW-type relaxation originating from the internal barrier layer capacitor effect.[19] The value of $(N/M)\exp(-E/k_BT)$ in this sample was found to be 0.00411 at 200 K, which perfectly meets the above condition. Figure 6 plots the experimental data (open circles) at 100 kHz and the fitting result (solid line). The resultant fitting peaks and background were indicated by dashed lines. The extracted high-temperature relaxation peaks at different measuring frequencies were pictured in the left inset for comparison. It is clearly seen that the peak height decreases distinctly as the peak position shifts to higher temperatures with increasing frequencies. The temperature-dependent peak height of $\tan\delta$ can be accurately described by Eq. (6) as clearly evidenced in the right inset of the figure. However, the peak height of $\tan\delta$ in most cases is more complicated than that of ε'' and a simple explicit relation between the temperature and the peak height as described by Eq. (6) cannot be achieved.

Finally, it is worth stressing that, although both dipolar relaxation and MW relaxation follow the similar relaxation equations as described by Eqs. (1) and (2),

their T-dependent relaxation strengths are quite different. In the case of free dipolar system, i.e., the dipoles are considered without any interaction, the reorientation dipolar polarization under an applied electric field is expressed by a Langevin function and the T-dependent relaxation strength takes the form $\Omega_{\mathrm{D}} \propto \varepsilon'(\omega = 0) \propto 1/T$. In the case of dipolar relaxation associated with hopping localized change carriers, the static dielectric constant is proportional to the thermally activated carriers.[20] One has the relation $\Omega_{\mathrm{C}} \propto \exp(-A/k_B T)$, where A is the activation energy. Thus, analysis of the relationship between Ω and T does distinguish the two types of relaxation. This suggests that the temperature-dependent dielectric strength, i.e., Eq. (6), might be considered as a criterion of the MW-type relaxation in most practical cases.

3. Conclusion

In conclusion, under the usual assumptions that the conductivity of each layer follows the thermally-activated behavior and the dielectric constant of each layer is nearly temperature-independent, we show that the MW relaxation of a two-layer system can be characterized by a simple explicit relation between the temperature and the peak height of. This relation works well in describing the experimental data and in these cases, the T-dependent dielectric strength could be taken as a criterion for a MW mechanism.

Acknowledgments

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References

1. M. A. Subramanian, D. Li, N. Duan, B. A. Reisner and A. W. Sleight, *J. Solid State Chem.* **151** (2000) 323.
2. J. Wu, C. W. Nan, Y. Lin and Y. Deng, *Phys. Rev. Lett.* **89** (2002) 217601.
3. I. P. Raevski, S. A. Prosandeev, A. S. Bogatin, M. A. Malitakaya and L. Jastrabik, *J. Appl. Phys.* **93** (2003) 4130.
4. B. Renner, P. Lunkenheimer, M. Schetter, A. Loidl, A. Reller and S. G. Ebbinghaus, *J. Appl. Phys.* **96** (2004) 4400.
5. C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto and A. P. Ramirez, *Science* **293** (2001) 673.
6. M. H. Cohen, J. B. Neaton, L. X. He and D. Vanderbilt, *J. Appl. Phys.* **94** (2003) 3299.
7. P. Lunkenheimer, R. Fichtl, S. G. Ebbinghaus and A. Loidl, *Phys. Rev. B* **70** (2004) 172102.
8. D. C. Sinclair, T. B. Adams, F. D. Morrison and A. R. West, *Appl. Phys. Lett.* **80** (2002) 2153.
9. J. C. Maxwell, *Electricity and Magnetism*, Vol. 1 (Clarendon Press, Oxford, 1892).

10. K. W. Wagner, *Die Isolierstoffe der Elektrotechnik*, ed. H. Schering (Springer-Verlag, Berlin, 1924).
11. G. Catalan, *Appl. Phys. Lett.* **88** (2006) 102902.
12. D. O'Neill, R. M. Bowman and J. M. Gregg, *Appl. Phys. Lett.* **77** (2000) 1520.
13. A. F. Gibson, F. A. Kröger and R. E. Burgess, *Progress in Semiconductors*, Vol. 4 (Heywood & Co. Ltd., London, 1960).
14. P. Debye, *Polar Molecules* (The Chemical Catalog Company, Inc., New York, 1929).
15. A. S. Nowick and B. S. Berry, *An Elastic Relaxation in Crystalline Solids* (Academic Press, New York and London, 1972).
16. C. C. Wang and L. W. Zhang, *Appl. Phys. Lett.* **88** (2006) 042906.
17. J. Liu, C.-G. Duan, W.-G. Yin, W. N. Mei, R. W. Smith and J. R. Hardy, *Phys. Rev. B* **70** (2004) 144106.
18. V. V. Lemanov, A. V. Sotnikov, E. P. Smirnova and M. Weihnacht, *Phys. Solid State* **44** (2002) 2039.
19. C. C. Wang, Y. M. Cui and L. W. Zhang, *Appl. Phys. Lett.* **90** (2007) 012904.
20. I. G. Austin and N. F. Mott, *Adv. Phys.* **18** (1969) 41.