Distribution of the electrostatic potential in a lattice of randomly oriented dipoles

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The distribution of the electrostatic potential in a three-dimensional cubic lattice whose sites are occupied by randomly oriented dipoles of an arbitrary number of kinds has been calculated. It has been shown that the far tail of the distribution is highly sensitive to impurities of dipoles with large dipole moments.

1. INTRODUCTION

In recent years considerable efforts have been aimed at developing a theory for the transport of charge carriers in disordered organic hosts, in which the influence of disorder is systematically taken into account from the onset and largely determines the transport characteristics of the host polymer. To prevent any possible misunderstandings we note at once that we shall not consider any of the various polyconjugated systems such as doped polyacetylene. Here we have in mind host polymers which by themselves have insulator properties and acquire short-lived conductivity when charge carriers are injected into them, usually under the action of a laser pulse or an electric discharge. A typical example of such hosts is provided by molecularly doped polymers, i.e., polystyrene or polycarbonate, where the role of the dopant (transport centers) is usually played by various nitrogen-bearing compounds. A detailed review of the theoretical results for the Gaussian model of a disordered medium, which has been developed most thoroughly, and a detailed comparison with experiment can be found in Refs. 1 and 2.

According to the main postulate of the model, transport occurs as a result of the hopping of carriers between localized states of transport centers with an assumed Gaussian density of states:

$$\rho(E)=(2\pi\sigma^2)^{-1/2}\exp\left(-\frac{E^2}{2\sigma^2}\right). \qquad (1)$$

The results, which were obtained mainly with the aid of computer simulations, show that in such a model the dependence of the nondispersive carrier mobility μ on the electric field F and the temperature T has the form

$$\mu=\mu_0\exp\left\{-\left(\frac{2\sigma}{3T}\right)^2+C\left[\left(\frac{\sigma}{T}\right)^2-\Sigma^2\right]\left(\frac{eFr}{2T}\right)^{1/2}\right\}, \qquad (2)$$

where r is the mean distance between transport centers, Σ is a parameter which characterizes the positional disorder, and $C\simeq 1$ is an empirical constant.[1] Practically all the qualitative characteristics in expression (2), especially the non-Arrhenius temperature dependence, are direct consequences of the Gaussian form of the density of states. The problem of determining the real form of the density of states in disordered organic hosts is clearly of paramount importance for substantiating the permissibility of applying the Gaussian model to the description of the transport of charge carriers in real systems.

The most important carriers for nondispersive (equilibrium) transport have energies near the equilibrium value[1,3]

$$E_{eq}=\lim_{T\to\infty}\langle E(t)\rangle=\frac{\int_{-\infty}^{+\infty}dE\,E\rho(E)\exp(-E/T)}{\int_{-\infty}^{+\infty}dE\,\rho(E)\exp(-E/T)}=-\sigma^2/T. \qquad (3)$$

A comparison of (2) with the experimental data revealed that, as a rule, $\sigma/T\simeq 4-6$ (Refs. 4–7). Therefore, in a typical case the far tail of distribution (1) determines the characteristics of nondispersive transport, i.e., the Gaussian form of the density of states in the vicinity of its maximum is totally inadequate for a self-consistent description of nondispersive transport in the framework of the Gaussian model. A stronger condition, viz., maintenance of the Gaussian form of the density of states far from the maximum, must be satisfied. An approximately Gaussian form of the density of states can be more or less guaranteed by the central limit theorem in the vicinity of the maximum, but the far tail of the distribution is usually formed by rare fluctuations of the environment. Then the central limit theorem is not applicable, and we must directly calculate the density of states for a sufficiently realistic model of an organic host.

The most important causes of fluctuations of the carrier energy at different transport centers include fluctuations of the electrostatic potential φ caused by the random distribution of the surrounding dipoles. Another cause is van der Waals interactions; however, in organic hosts it is practically impossible to intentionally alter their contribution to the density of states over any broad range, while this is easily accomplished for the dipole component by introducing inert polar dopants (or polar transport components) into the host polymer. It is perfectly possible that a significant portion of the dependence of μ on the transport center concentration is due specifically to the variation of the electrostatic energy of the carriers $e\varphi$.

In a recent study, Dieckmann *et al.*[8] used the Monte Carlo method to investigate the distribution of the potential in a cubic lattice whose sites are occupied by randomly oriented dipoles. It was concluded on the basis of the results obtained that the distribution of the potential has a Gaussian form at large dipole concentrations and that its form approximates a Lorentzian distribution at small concentrations $c\leqslant 0.1$. It is generally known that the determination of the

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asymptotic behavior of any physical quantity in a computer experiment is a complex problem owing to the influence of large fluctuations on the parameter being determined. Nevertheless, the distribution of φ in a lattice filled by independent dipoles can be calculated analytically.

2. PRINCIPAL EQUATIONS

Let $P(\varphi)$ be the density distribution of φ at the initial lattice site. Then

$$P(\varphi)=\left\langle \delta\left(\varphi-\sum_n \varphi_n\right)\right\rangle$$

$$=\frac{1}{2\pi}\int_{-\infty}^{\infty} dy \exp(iy\varphi)\prod_n \int dp_n W(p_n)$$

$$\times\int_0^{\pi} d\vartheta_n N(\vartheta_n)\exp(-iy\varphi_n). \tag{4}$$

Here the angle brackets denote statistical averaging; the index n runs through all the lattice sites except the initial site; φ_n is the contribution of a point dipole at site n to the total potential φ at the initial site

$$\varphi_n=-\frac{\mathbf{p}_n\mathbf{r}_n}{\varepsilon r_n^3}=-\frac{p_n}{\varepsilon r_n^2}\cos\vartheta_n, \tag{5}$$

where ε is the dielectric constant of the medium, $\mathbf{r}_n$ is the radius vector of the nth site, $N(\vartheta)$ is the probability density for the polar angle ϑ, and $W(p)$ is the probability density of the dipole moment p. For dipoles with completely random orientations we write

$$N(\vartheta)=\frac{1}{2}\sin\vartheta, \tag{6}$$

and for a lattice with m kinds of dipoles and a concentration of the lth kind equal to c_l the function $W(p)$ has the form

$$W(p)=\sum_{l=1}^{m} c_l\delta(p-p_l), \quad \sum_{l=1}^{m} c_l=1. \tag{7}$$

The choice of (7) implies that each lattice site is occupied by one (and only one) dipole of any kind. Only the very special case of $m=2$ and $p_2=0$ was considered in Ref. 8. Another difference from Ref. 8 is that dipoles of finite size were considered there, but this difference is not significant for the most interesting case of small concentrations.

Integrating with respect to p_n and ϑ_n in (4), we obtain

$$P(\varphi)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dy \exp[iy\varphi+S(y)], \tag{8}$$

$$S(y)=\sum_n \ln\left(\sum_{l=1}^{m} c_l\frac{\sin(yz_{ln})}{yz_{ln}}\right), \quad z_{ln}=\frac{ep_l}{\varepsilon r_n^2}.$$

This expression is the main result of the present work. We shall henceforth restrict ourselves to the case of greatest practical importance, $m=2$ and $p_2>0$, in which $c_1=c$ and $c_2=1-c$, and we shall measure the potential in units of $\varphi_0=ep_1/\varepsilon a^2$ (a is the lattice constant) and the dipole moment in units of p_1 (to be specific, let $p_2<p_1$). In this case, for a three-dimensional cubic lattice

$$S(y)=\sum_n \ln\left(c\frac{\sin(y/\rho_n^2)}{y/\rho_n^2}+(1-c)\frac{\sin(yp/\rho_n^2)}{yp/\rho_n^2}\right), \tag{9}$$

where $p=p_2/p_1$ is the dimensionless dipole moment of the second component and $\rho_n^2=i^2+j^2+k^2$. The indices i, j, and k are arbitrary integers with the exception of $i=j=k=0$.

3. CALCULATION OF THE DISTRIBUTION OF THE POTENTIAL

To compare our results with the results in Ref. 8, we first calculate the function $P(\varphi)$ for $m=2$ and $p=0$ when

$$S(y)=\sum_n \ln\left(c\frac{\sin(y/\rho_n^2)}{y/\rho_n^2}+1-c\right).$$

If $c\simeq 1$, the main contribution to integral (8) is made by the range of small values of y, where

$$S(y)=-A_2y^2-A_4y^4+O(y^6), \tag{10}$$

$$A_2=\frac{c}{6}B_4, \quad A_4=\frac{c}{24}\left(\frac{c}{3}-\frac{1}{5}\right)B_8, \quad B_m=\sum_n \frac{1}{\rho_n^m},$$

$$B_4=16{,}46\ldots, \quad B_8=6{,}95\ldots .$$

Therefore,

$$P(\varphi)=\frac{1}{\sqrt{\pi\Delta^2}}^{-1/2}\exp(-\varphi^2/\Delta^2), \quad \Delta^2(c)=\frac{2}{3}cB_4, \tag{11}$$

and the second term in expansion (10) makes only a small correction. At the opposite limit $c\ll 1$ the expression whose logarithm is taken is a smooth function of n; therefore, the summation can be replaced by integration with respect to ρ after preliminary expansion of the logarithm in a series with respect to c. This gives

$$S(y)\approx-4\pi c\int_0^{\infty} d\rho\rho^2\left(1-\frac{\sin(y/\rho^2)}{y/\rho^2}\right)=-4\pi Qcy^{3/2}, \tag{12}$$

$$Q=\int_0^{\infty} d\rho\rho^2(1-\rho^2\sin(1/\rho^2))=0.334\ldots,$$

and

$$P(\varphi)=\frac{1}{\varphi_c}F\left(\frac{\varphi}{\varphi_c}\right), \quad F(x)=\frac{1}{\pi}\int_0^{\infty} dy\cos(xy)$$

$$\times\exp(-y^{3/2}), \tag{13}$$

$$\varphi_c=(4\pi Qc)^{2/3}.$$

It can be shown by the saddle-point method that at $x\gg 1$

$$F(x)=(9\pi/32)^{1/2}x^{-5/2}, \tag{14}$$

and the general form of $F(x)$ is shown in Fig. 1. Thus, at small values of c the distribution $P(\varphi)$ does not tend to a

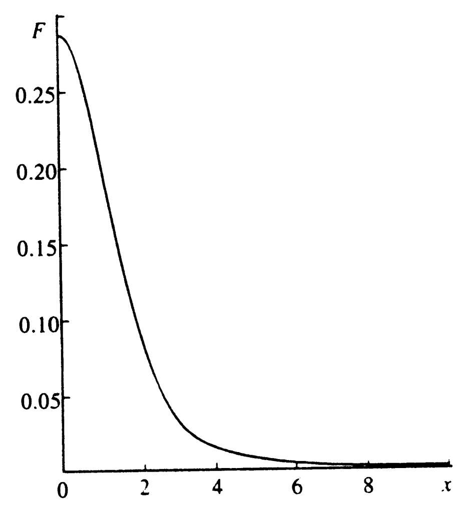

FIG. 1. $F(x)$ from Eq. (13).

Lorentzian distribution, although the difference is not excessively great. Using numerical integration, we obtain

$$\Gamma=1.44\varphi_c, \tag{15}$$

where Γ is the half-width of $P(\varphi)$ at half-maximum.

Let us now consider the case $p>0$. In both limiting cases $c\to1$ and $c\to0$, $P(\varphi)$ has a Gaussian form (with different values for Δ). When $p\ll1$, it is natural to expect the existence of a relatively broad concentration range in which the central portion of the distribution approximates (13). The fact that it actually exists can be seen in Fig. 2. It is the concentration range in which the half-width of $P(\varphi)$ approximates (15). The position of the transition region from distribution (13) to a narrow Gaussian distribution with the parameter $p\Delta$, which describes the fluctuations of the potential in a host polymer consisting nearly entirely of the second component, can be evaluated from the relation $p\Delta\approx\varphi_c$, whence $c\propto p^{3/2}$. Thus, if $p\ll1$, distribution $P(\varphi)$ does, in fact, approximate asymptote (13) for $p^{3/2}\ll c\ll1$. If $p\geqslant0.1$, $P(\varphi)$ does not differ significantly from a Gaussian function at any value of c, and Δ is given by the expression

$$\Delta_p^2=\frac{2}{3}B_4[c+p^2(1-c)] \tag{16}$$

(see also Fig. 2).

FIG. 2. Dependence of the half-width of the distribution $P(\varphi)$ on the concentration c of the component with a larger dipole moment for various values of the dipole moment p of the second component (which are indicated on the respective curves). Broken line—results for Gaussian approximation (16) when $p=0.1$.

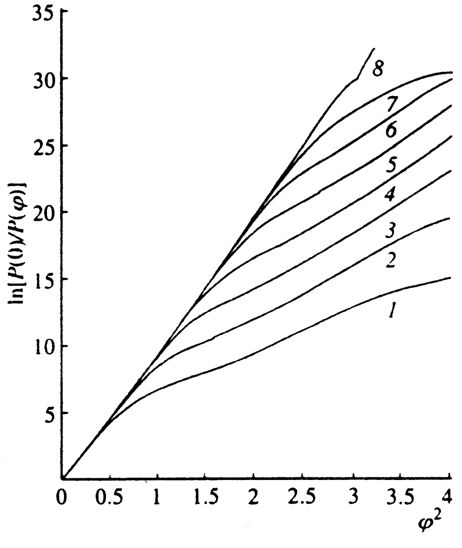

FIG. 3. Deviation of $P(\varphi)$ from the Gaussian form for small values of the concentration c of the component with the larger dipole moment [numerical calculation of integral (8) with $S(y)$ from (9)]. The dipole moment of the second component $p=0.1$, and the concentration c equals 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8}, 10^{-9}, and 0 for curves 1–8, respectively.

A very important result was obtained in the limit $p\ll1$, $c\ll1$ for the far tail of distribution (8). Expanding (9) in a series in c and p, we obtain

$$S(y)=\sum_n\left[\ln\left(\frac{\sin(yp/\rho_n^2)}{yp/\rho_n^2}\right)+c\left(p\,\frac{\sin(y/\rho_n^2)}{\sin(yp/\rho_n^2)}-1\right)\right]$$

$$+O(c^2)\approx-\frac{1}{6}B_4p^2y^2-4\pi Qcy^{3/2} \tag{17}$$

for significant values of y, i.e., $P(\varphi)$ has the form

$$P(\varphi)=\int_{-\infty}^{\infty}d\varphi' P_1(\varphi')P_2(\varphi-\varphi'), \tag{18}$$

with the Gaussian function $P_1(\varphi)$ [expression (11)] and $P_2(\varphi)$, which is given by expression (13). Convolution integral (18) describes a Gaussian distribution in the vicinity of the maximum, and a power-law asymptote (14) along the tail (see Fig. 3). The position of the transition region φ_t can be evaluated from the relation

$$\sqrt{\frac{9\pi}{32}}\,\frac{\varphi_c^{3/2}}{\varphi_t^{5/2}}\simeq\frac{1}{\sqrt{\pi\Delta_p^2}}\exp(-\varphi_t^2/\Delta_p^2). \tag{19}$$

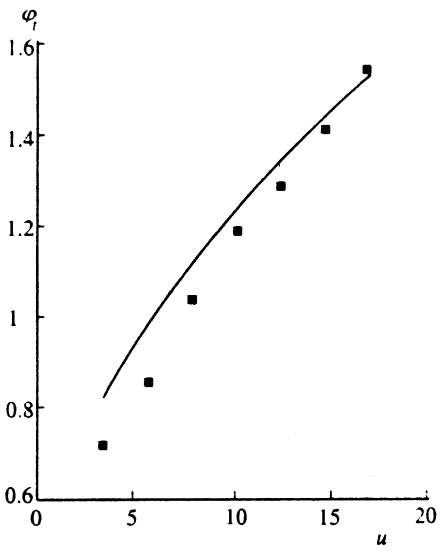

FIG. 4. Position of the transition region φ_t determined from Fig. 3 (points) and calculated from Eq. (19) (solid line).

Asymptotic solution (19) has the form

$$\varphi_t=\Delta_p\sqrt{u}\left(1+\frac{5\ln u}{8u-10}+o\left(\frac{\ln u}{u}\right)\right),\quad u\gg 1, \qquad (20)$$

$$u=\ln\left[\left(\frac{2}{3}B_4\right)^{3/4}\frac{\sqrt{2p^3}}{3\pi^2 Qc}\right]=\ln\left(\frac{0.86p^{3/2}}{c}\right).$$

As can be seen in Fig. 4, solution (20) is fairly accurate for modest values of u [the main sources of disparity between the values of φ_t calculated from (20) and the values obtained from Fig. 3 are the approximate character of Eq. (19) itself and the indefiniteness of the determination of the transition region from Fig. 3]. We note that for the data in Fig. 4 $e\varphi_t$ varies from 3.5σ to 6.5σ as c varies from 10^{-3} to 10^{-9}. Thus, the far tail of distribution (8) is extremely sensitive to very small concentrations of impurities with large dipole moments.[1)] Equilibrium energy (3) for distribution (18) does not exist at all due to the divergence of the integral at the lower limit. This result, however, is not of great significance, since power function (14) does not extend fairly far for real values of p [see footnote 1)], and $P(\varphi)$ decreases considerably more rapidly at large values of φ (see also Fig. 3).

Finally, we note that our main results remain unchanged after the spatial disorder of real organic hosts is taken into account. In fact, the most important results are associated with the region of small concentrations, in which the specific configuration of the lattice sites is unimportant. This situation is also illustrated by the exact solution for a model with a completely random distribution of dipoles when only their mean density is fixed. This solution, which is closely related to Holtsmark's result for a completely disordered electrostatic system,[9] coincides exactly with expression (13). It is not surprising that in this case we are always working at small concentrations, since there is no length scale differing from $c^{-1/3}$ in the problem.

The main restriction on our treatment, as in Ref. 8, is the complete neglect of the relative orientation of neighboring dipoles caused by their interaction (the high-temperature limit). Systematic consideration of this interaction is a complicated problem warranting a separate treatment.

4. CONCLUSION

We showed that the model of an organic host consisting of randomly oriented dipoles that was proposed in Ref. 8 demonstrates the high sensitivity of the far tail of the density of states to small concentrations of impurities with large dipole moments. No other independent contributions to the form of the density of states (e.g., the van der Waals contribution) alter this assertion provided they do not decay more slowly than $E^{-5/2}$. Thus, the universal applicability of the Gaussian model[1] to the description of the nondispersive transport of charge carriers in disordered organic hosts is open to some serious objections. For example, this model is hardly applicable to the description of transport in a nonpolar host polymer such as polystyrene [the dipole moment of a polymer chain subunit is 0.36 D (Ref. 10)] when there is a small concentration of transport components with larger dipole moments [3.16 D (Ref. 11) or 4.34 D (Ref. 12)].

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[1)] In a strict sense, when $p=0.1$, the difference between the dipole moments of the components is still not large enough for power distribution (14) to actually appear in a region of any significant width, as is clear from Fig. 3 (when $p=0.01$, this region can already be reliably demarcated). Nevertheless, even when $p=0.1$, the position of the transition region for the distribution calculated from Eq. (17) coincides almost exactly with the data in Fig. 3, and Eq. (19) is, therefore, approximately applicable.

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