Analytical approximation for chemical potential in organic materials with Gaussian density of states

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Abstract
Charge carrier mobility in disordered organic materials depends on the chemical potential. Chemical potential has an implicit functional dependence on the carrier concentration and the density of states. However, for efficient calculation of mobility in simulation programs it is highly useful to have an explicit and accurate approximation for the chemical potential. In this study, we focus on analytical approximation for the chemical potential in organic materials with Gaussian disorder and provide an accurate expression in both non-degenerate and degenerate regimes.

Charge transport in disordered organic materials is exploited in a wide range of devices, including organic light-emitting diodes (OLEDs) [1], organic field-effect transistors (OFETs) [2] photoreceptors [3] and photovoltaic cells [4]. In disordered organic materials, the carrier mobility is due to thermally assisted tunnelling 'hopping' between localized molecular states [5, 6]. It is known that the carrier mobility depends on the temperature, energetic disorder, and carrier concentration [7, 8]. For efficient device modelling it is useful to have a compact analytical expression for mobility. Coehoorn *et al* [6] provided an analytical expression for mobility in organic materials with Gaussian energetic disorder. However, the authors noted that the expression for mobility is not suitable for practical numerical device modelling because no analytical expression for the chemical potential as a function of carrier concentration and energetic disorder is available which is valid over a wide range of carrier concentrations. The main purpose of this paper is to show that an analytical expression for the chemical potential in organic materials with Gaussian energetic disorder can be obtained from the first principles, with no free parameters. We show that the derived expression for the chemical potential is fairly accurate and the error involved is well below the thermal energy.

Within the Gaussian disorder model, it is assumed that the density of states (DOS) is given by

$$g(E) = \frac{N_\mathrm{t}}{\sqrt{2\pi}\sigma} \exp\left(-\frac{E^2}{2\sigma^2}\right), \tag{1}$$

where σ is the standard deviation of the DOS and is a measure of the energetic disorder while N_t is the total number of hopping sites per unit volume. For a given charge carrier concentration, p, the chemical potential, μ, is related to the density in the following way:

$$\int_{-\infty}^{\infty} \frac{g(E)}{1+\exp\left(\frac{E-\mu}{k_\mathrm{B}T}\right)} \mathrm{d}E = pN_\mathrm{t}, \tag{2}$$

where k_B is Boltzmann's constant and T is the temperature.

In general, for given p and σ, equation (2) is solved iteratively to obtain the chemical potential. However, in the limit of vanishing carrier concentration, an analytical expression for the chemical potential can be easily obtained because in the limit of small p carriers can be considered essentially independent of each other. In this case equation (2) can be solved for μ by replacing the Fermi–Dirac (FD) statistics with the Boltzmann statistics [6]. In this limit, referred to as the Boltzmann approximation (BA), the density

of occupied states (the product of DOS and the FD distribution function, DOOS) is to a very good approximation given by a Gaussian, centred at the energy value $E = -\sigma^2/(k_B T)$ [6]. The corresponding expression for μ is given by

$$\mu = -\frac{\sigma^2}{2k_B T} + k_B T \ln p. \quad (3)$$

The BA limit is applicable to OLEDs, where under typical operating conditions, the concentration is 10^{-4}–10^{-5} carriers per hopping site [9]. On the other hand in OFETs [9] application of high gate voltage can lead to a concentration of 0.01–0.1 carriers per hopping site. At these carrier concentrations, interaction between carriers becomes significant implying that Pauli's exclusion principle must be taken into account. In this high concentration regime, the BA is no longer valid and FD distribution must be used. We show that even in this regime, an analytical solution for μ can be obtained in a simple and intuitive manner. In the following text we identify three regimes referred to as the non-degenerate, degenerate and saturated regime. In each regime we calculate analytically the chemical potential as a function of the carrier concentration.

Our objective is to solve equation (2) for the chemical potential, μ, for given values of carrier concentration, p, energetic disorder, σ, and temperature, T. We evaluate the integral in equation (2) using a saddle point approximation. We assume that the saddle point, E_*, of the integrand is known. Assuming this one gets two coupled algebraic equations for the chemical potential, μ, and the saddle point of the integrand instead of one integral equation for the chemical potential [10]. The first algebraic equation is obtained by imposing the condition that E_* is the saddle point of the integrand in equation (2). On doing so we get the following equation for the chemical potential

$$\mu = E_* + k_B T \ln\left(-\frac{\sigma^2}{E_* k_B T} - 1\right). \quad (4)$$

Saddle point approximation implies that the integrand (equivalently the DOOS) is a Gaussian centred at E_* with a standard deviation σ_*. Namely, equation (2) is approximated by

$$\int_{-\infty}^{\infty} h(E)\,\mathrm{d}E = pN_t, \quad (5)$$

where the expression for the DOOS is

$$h(E) = \frac{N_t \mathrm{e}^{-\frac{E_*^2}{2\sigma^2}}\left(E_* k_B T + \sigma^2\right)}{\sqrt{2\pi}\sigma^3} \exp\left[-\frac{(E - E_*)^2}{2\sigma_*^2}\right], \quad (6)$$

and

$$\sigma_* = \sqrt{\frac{k_B T \sigma^4}{\sigma^2(k_B T - E_*) - E_*^2 k_B T}}. \quad (7)$$

On evaluating equation (5) we obtain the second algebraic equation:

$$\frac{\mathrm{e}^{-\frac{E_*^2}{2\sigma^2}}\left(E_* k_B T + \sigma^2\right)}{\sigma\sqrt{\sigma^2 - E_*^2 - \frac{E_*\sigma^2}{k_B T}}} = p. \quad (8)$$

The two coupled equations equations (4) and (8) can be solved to obtain μ and E_*. We now solve equations (4) and (8) self-consistently in three limiting cases:

(a) Non-degenerate regime. This regime corresponds to the case of vanishing carrier concentration. equation (8) implies that in this regime the saddle point occurs at

$$E_* \simeq -\sigma^2/k_B T. \quad (9)$$

The dependence of E_* on the carrier concentration p is obtained as

$$E_* = -\frac{\sigma^2}{k_B T}\left(1 - p\mathrm{e}^{\sigma^2/2(k_B T)^2}\right). \quad (10)$$

Self-consistency in this regime requires that carrier concentration is low enough such that the condition (9) holds. This implies that in this regime $p \ll p_1$, where

$$p_1 = \mathrm{e}^{-\frac{1}{2}\left(\frac{\sigma}{k_B T}\right)^2}. \quad (11)$$

The chemical potential in this regime is well known and is given by

$$\mu = -\frac{\sigma^2}{2k_B T} + k_B T \ln p. \quad (12)$$

The functional form of μ in the non-degenerate regime is well known in the literature [6, 11, 12]. The non-degenerate regime corresponds to the BA limit. In this regime an increase in carrier concentration leads to an increase in the maximum of DOOS with negligible shift in E_* [6].

(b) Degenerate regime. For $p \gg p_1$ the saddle point, E_*, shifts significantly from $-\sigma^2/k_B T$ and the BA limit is no longer valid. In this regime the carrier concentration is such that saddle point satisfies $-\sigma^2/k_B T \ll E_* \ll -k_B T$, so equation (8) implies

$$E_* = -\frac{\sigma}{\sqrt{2}}\sqrt{W\left[\frac{2}{(\sigma/k_B T)^2 p^4}\right]}, \quad (13)$$

where W is the Lambert W function [13]. Self-consistency in this regime requires $p_1 \ll p \ll p_2$, where

$$p_2 = \mathrm{e}^{-\frac{1}{2}\left(\frac{k_B T}{\sigma}\right)^2}. \quad (14)$$

The chemical potential in this regime is given by

$$\mu = -\frac{\sigma}{\sqrt{2}}\sqrt{W\left[\frac{2}{(\sigma/k_B T)^2}\left(\frac{1}{p}\right)^4\right]} + k_B T \ln\left\{\frac{\sqrt{2}(\sigma/k_B T)}{\sqrt{W\left[\frac{2}{(\sigma/k_B T)^2}\left(\frac{1}{p}\right)^4\right]}} - 1\right\}. \quad (15)$$

This analytical expression for the chemical potential in the degenerate regime is the main result of this paper. Since our focus is on the systems with $\sigma > k_B T$, the second crossover value, p_2, is of the order of one and degenerate regime is valid until almost the full saturation of all the available states. For the sake of completeness we discuss below this saturated regime.

(c) Saturated regime. In this regime the carrier concentration, p, approaches the limiting value of $p_2 \simeq 1$ where almost all the states are occupied and the DOOS is

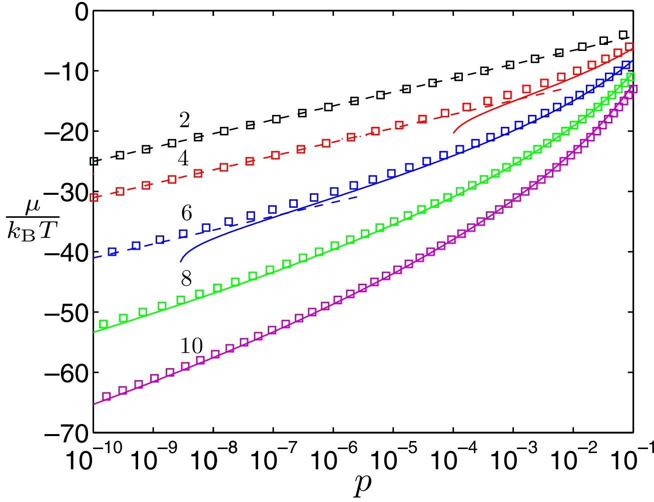

Figure 1. Chemical potential μ versus the normalized carrier concentration p for different values of $\sigma/k_\mathrm{B}T$ (numbers on the plot). Full lines and dashed lines correspond to the non-degenerate, equation (12), and degenerate, equation (15), regime, respectively. Symbols correspond to the numerically calculated chemical potential.

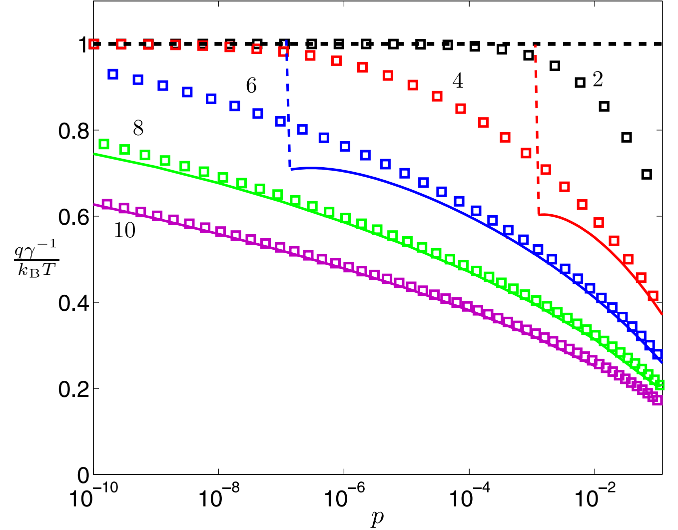

Figure 2. Comparison of analytical result, equation (19) (lines), and the numerical calculation (squares) for different values of $\sigma/k_\mathrm{B}T$ (numbers on the plot). Full lines correspond to the degenerate regime. The horizontal dotted line corresponds to the limit of the non-degenerate regime.

the same as the DOS. In this limit, the saddle point satisfies $0 > E_* \gg -k_\mathrm{B}T$, so equation (8) implies

$$E_* = -\sigma\sqrt{2\ln\frac{1}{p}}. \tag{16}$$

Self-consistency in this regime requires $p > p_2$. The chemical potential in this regime is given by

$$\mu = -\sigma\sqrt{2\ln\frac{1}{p}} + k_\mathrm{B}T\ln\left(\frac{\sigma}{k_\mathrm{B}T\sqrt{2\ln\frac{1}{p}}} - 1\right). \tag{17}$$

This regime is irrelevant for organic devices because even in OFETs, where carrier concentration can be tuned by applying gate voltage, the concentration is typically much smaller than 1 [9].

In figure 1, we plot the chemical potential as obtained above for different values of σ. As predicted by equation (11), with increasing σ, the crossover from the non-degenerate to the degenerate regime occurs at lower concentrations. The crossover from the degenerate to the saturated regime is not shown in the figure. The saturated regime, irrelevant for organic devices, is a narrow regime with divergence of chemical potential at $p = 1$. Our results for the non-degenerate regime are in complete agreement with those reported by Oelrich *et al* [14] for $\sigma = 4k_\mathrm{B}T$. It is also clear from the figure that in the regime of low carrier concentration, the chemical potential is located in the tail of the DOS. The chemical potential moves deeper into the tail of the DOS with increasing width of the DOS. These findings are consistent with those reported recently [15, 16] in which the authors showed that in the non-degenerate regime, with increasing width of the DOS, the carriers become more localized. When charge carriers are highly localized, the mobility can be well described by thermally assisted tunnelling 'hopping' between localized molecular states [5, 6]. On the other hand when carrier density is high ($\geqslant 1\%$), the chemical potential is close to or above the mobility edge [15]. For such carrier concentrations, which can be obtained in single-crystal FETs, charge transport acquires a band-like nature [15, 16]. It is clear from the figure that the analytically obtained chemical potential and the crossover density, equation (11), are in good agreement with the numerical calculations in both non-degenerate and degenerate regimes.

In addition to the mobility of carriers, to model charge transport one needs to calculate the diffusion coefficient. Assuming equilibrium conditions, the diffusion coefficient is determined from the generalized Einstein relation [17] which is given as

$$\gamma = \frac{p}{q}\frac{\partial\mu}{\partial p}, \tag{18}$$

where γ is ratio of diffusion coefficient to the mobility of carriers and q is the elementary charge. Roichman and Tessler [18] showed that in a Gaussian DOS, γ deviates significantly from the low density limit value of $k_\mathrm{B}T/q$. They obtained γ as an implicit function of the chemical potential, μ. Our expression for the chemical potential allows us to obtain an analytical expression for the generalized Einstein relation in each of the regimes as a function of p, σ and T:

$$\gamma = \frac{k_\mathrm{B}T}{q} \times \begin{cases} 1 & p \ll p_1 \\ \dfrac{\frac{\sqrt{2}\sigma}{k_\mathrm{B}T}\left\{2 - W\left[\frac{2}{p^4(\sigma/k_\mathrm{B}T)^2}\right] + \frac{\sqrt{2}\sigma}{k_\mathrm{B}T}\sqrt{W\left[\frac{2}{p^4(\sigma/k_\mathrm{B}T)^2}\right]}\right\}}{\left\{\frac{\sqrt{2}\sigma}{k_\mathrm{B}T} - \sqrt{W\left[\frac{2}{p^4(\sigma/k_\mathrm{B}T)^2}\right]}\right\}\left\{1 + W\left[\frac{2}{p^4(\sigma/k_\mathrm{B}T)^2}\right]\right\}} & p_2 \gg p \gg p_1 \\ \dfrac{1 + \frac{\sqrt{2}\sigma}{k_\mathrm{B}T}\sqrt{\ln\frac{1}{p}} - 2\ln\frac{1}{p}}{2\ln\frac{1}{p} - 2\sqrt{2}\frac{k_\mathrm{B}T}{\sigma}\ln^{3/2}\frac{1}{p}} & p > p_2. \end{cases} \tag{19}$$

In figure 2 we compare our analytical expression for γ, equation (19), with the numerical results (notice that the inverse

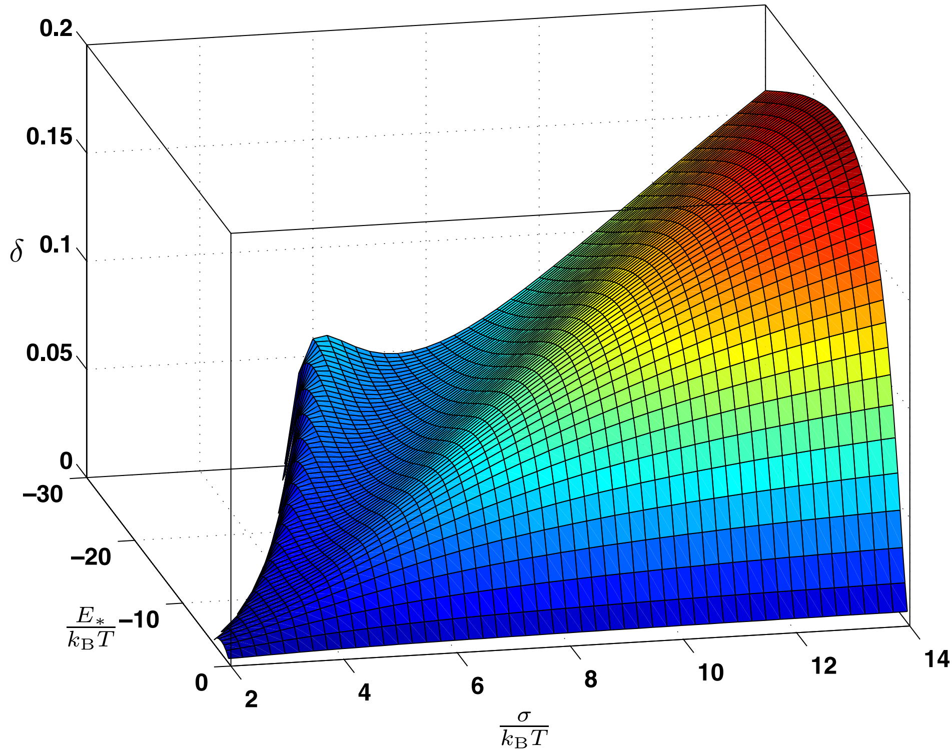

Figure 3. Relative error δ. For the range of σ considered the error does not exceed 20%.

of γ is shown). As expected, fairly good agreement is obtained far from the crossover concentration, p_1.

The results above indicate that the analytical expressions for the chemical potential are fairly accurate. Nevertheless, it is useful to estimate analytically the error in the derived formulae. The main source of the error is the saddle point approximation, equation (6), in evaluating the integral in equation (2). Under the saddle point approximation, the integrand (or equivalently the DOOS) of the integral in equation (2) is a Gaussian centred at E_*. The integrand is well approximated by a Gaussian only in the neighbourhood of E_* (within few standard deviations, σ_*). Away from E_*, the deviation of the integrand from the Gaussian gives rise to the error in evaluation of equation (2). The relative error in saddle point approximation of the integral can be written as

$$\delta = \left| 1 - \frac{\int_{-\infty}^{\infty} h\left(E\right)\,\mathrm{d}E}{\int_{-\infty}^{\infty} \frac{g(E)}{1+\exp\left(\frac{E-\mu}{k_B T}\right)}} \right|. \quad (20)$$

For energies well below the saddle point, $E \ll E_* - 3\sigma_*$, the FD distribution can be approximated as unity whereas well above the saddle point, $E \gg E_* + 3\sigma_*$, it can be approximated by the Boltzmann distribution. Therefore, the error can be estimated as

$$\delta \simeq \left| 1 - \left[\int_{-\infty}^{\infty} h(E)\,\mathrm{d}E \right] \left[\int_{-\infty}^{E_*-3\sigma_*} g(E)\,\mathrm{d}E + \int_{E_*-3\sigma_*}^{E_*+3\sigma_*} h(E)\,\mathrm{d}E + \int_{E_*+3\sigma_*}^{\infty} g(E)\mathrm{e}^{-\frac{E-\mu}{k_B T}}\,\mathrm{d}E \right]^{-1} \right|. \quad (21)$$

The integrals appearing in the above expression can be simplified using an error function. For given values of carrier concentration, p, and energetic disorder, σ, the other parameters E_*, σ_* and μ can be calculated as shown above. In figure 3 we show that for relevant range of σ and p values, the value of δ does not exceed 20%. This implies that the error in the chemical potential is well below than the thermal energy, $k_B T$.

Although we derived the expressions for the chemical potential only in the respective regimes, the algebraic equations equations (4) and (8) can be easily solved numerically to any desired degree of accuracy for any given values of p and σ.

To conclude, in this paper we derive analytical expression for the chemical potential in organic materials with Gaussian disorder. In the most relevant, degenerate regime our result, equation (15), is new and, as we demonstrate, is fairly accurate. We show that over the relevant range of carrier concentration and energetic disorder, the error in calculation is well below the thermal energy. In addition, the existing iterative numerical techniques to calculate chemical potential can use our derived expressions as fairly accurate starting point. This can lead to much more efficient algorithms to calculate chemical potential and therefore the mobility in organic materials with Gaussian disorder.

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References

[1] Friend R H *et al* 1999 *Nature* **397** 121
[2] Drury C J, Mutsaers C M J, Hart C M, Matters M and de Leeuw D M 1998 *Appl. Phys. Lett.* **73** 108

[3] Borsenberger M and Weiss D S 1998 *Organic Photoreceptors for Xeroxgraphy* (New York: Marcel Dekker)

[4] Brabec C J, Sariciftci N S and Hummelen J C 2001 *Adv. Funct. Mater.* **11** 15

[5] Bässler H 1993 *Phys. Status Solidi* b **175** 15

[6] Coehoorn R, Pasveer W F, Bobbert P A and Michels M A J 2005 *Phys. Rev.* B **72** 155206

[7] Pasveer W F, Cottaar J, Tanase C, Coehoorn R, Bobbert P A, Blom P M, de Leeuw D M and Michels M A J 2005 *Phys. Rev. Lett.* **94** 206601

[8] Coropceanu V, Cornil J, da Silva Filho D A, Olivier Y, Silbey R and Brédas J-L 2007 *Chem. Rev.* **107** 926

[9] Tanase C, Meijer E J, Blom P W M and de Leeuw D M 2003 *Phys. Rev. Lett.* **91** 216601

[10] Sheinman M and Kafri Y 2012 *Phys. Biol.* **9** 056006

[11] Baranovskii S D, Zvyagin I P, Cordes H, Yamasaki S and Thomas P 2002 *Phys. Status Solidi* b **230** 281-–7

[12] Baranovskii S, Zvyagin I, Cordes H, Yamasaki S and Thomas P 2002 *J. Non-Cryst. Solids* b **299** 416—19

[13] Abramowitz M and Stegun I A 1964 *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (New York: Dover)

[14] Oelerich J O, Huemmer D, Weseloh M and Baranovskii S D 2010 *Appl. Phys. Lett.* **97** 143302

[15] Perroni C A, Nocera A, Ramaglia V M and Cataudella V 2011 *Phys. Rev. B* **83** 245107

[16] Gargiulo F, Perroni C A, Ramaglia V M and Cataudella V 2011 *Phys. Rev.* B **84** 245204

[17] Ashcroft N W and Mermin N D 1988 *Solid State Phys.* (New York: Holt, Rinehart and Winston)

[18] Roichman Y and Tessler A 2002 *Appl. Phys. Lett.* **80** 1948