

Charge Density and Film Morphology dependence of Charge Mobility in
Polymer Field Effect Transistors

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The electronic transport in organic semiconducting polymers have been studied extensively in the past decades^[1-9]. Among the physical pictures suggested the most widely accepted one is that of hopping-transport in a disordered-system having a Gaussian density of states (DOS), developed by Baessler and co-workers^[1, 3]. However, despite the success of this physical-model in describing phenomena related to organic light-emitting diodes it is rarely used to describe charge-transport in organic field effect transistors (FETs). This may be partially due to the lack of theoretical predictions as to the effect of the charge density on the mobility and diffusivity. Recently, the disorder picture has been extended to the high carrier density regime^[10]. It has been shown that the density of the charge carriers affects both the ratio between the mobility and diffusivity (Einstein relation)^[10] and the mobility value^[11, 12]. One of the predictions made by the model developed by Roichman&Tessler^[10] is that the important parameter is the charge density relative to the electronic density of states. In this paper we present experimental investigation of the effect of the charge density as well as the film morphology on the charge carrier mobility in MEH-PPV^[13] polymer field-effect transistors (FET) and make a qualitative comparison with theoretical predictions.

The advantage of studying MEH-PPV is that it has been extensively studied and is widely available. Within the context of exciton and interchain-exciton generation it has been shown that the use of poor solvents with MEH-PPV tends to affect the film morphology^[14-16] as well as interchain interactions. A possible implication for the charge transport was given as an indirect evidence of mobility

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enhancement in an LED device configuration^[15]. In the context of charge transport it has also been suggested by Rakhmanova&Conwell^[2] that in the polymer film there are regions that are better ordered and hence exhibit a narrower (Gaussian) density of states. This morphological effect was shown to affect the field dependence of the mobility. In this work we chose to control the solubility parameter by varying the polymer molecular weight rather than the solvent. In this manner we arrive at a systematic set of film morphologies and for each case we study the charge concentration effect on the charge-mobility.

Figure 1 shows the photoluminescence (PL) spectra of three molecular weights of MEH-PPV (Mw=100k, 1M, 2.8M) spin cast from toluene. The figure shows a pronounced red shift as the molecular weight increases. In past solubility studies of MEH-PPV^[14, 15] this has been assigned to the formation of aggregates. The PL spectrum of the high MW polymer in THF is also shown and it confirms that the spectral shift is indeed solvent (solubility) related. To farther check if the spectral shifts are also associated with morphological changes we measured the three polymers (span from toluene) in a scanning atomic force microscope^[17] operating in the phase mode. Figure 2 shows the data collected for MEH-PPV films prepared in the same manner as in Figure 1. The morphological differences between the different films are expressed in the different film – AFM tip interactions. The film of the low molecular weight polymer (Mw=100k) appears as a rather homogeneous, non-sticky, solid film that induces only minor phase shifts to the tip resonant vibration. Only very few isolated spots appear to have stronger film – AFM tip interactions that cause a larger phase shift. In contrast, the film of the high molecular weight polymer (Mw=2.8M) appears as a viscoelastic sticky medium with isolated solid islands. The film of the intermediate molecular weight polymer (Mw=1M) seems to be composed of a mixture of the two phases, showing both solid and viscoelastic domains. A strong correlation is found between the phase shift and height of the different domains. Similar observations were reported for MEH-PPV cast from different solvents using the less informative contact topography method^[15].

The above polymers were used to prepare field effect transistors in the bottom contact configuration^[18]. The channel length was varied between 2 and 32 μm and the width was fixed at 6000 μm ($C_{\text{OX}}\approx 43\text{nFcm}^{-1}$). Extra care was given to remove any residual effects resulting from the device structure^[18, 19] that may interfere with the

device material analysis. Figure 3 shows the drain-source current as a function of gate bias ($V_{GS} < 0$) for a given drain-source bias of $-2V$. First we examine the threshold voltage (V_T) which is an indication of defects occurring at the polymer/oxide interface due to either the polymer or the oxide. As the polymer is undoped a large contribution to the threshold voltage may arise only from charged defects in the oxide/polymer^[20]. We find that the current onset is effectively $V_T=0$ indicating that both the oxide and the polymer are relatively free of charged defects. Further indication for the good material and device properties is given by the high on/off ratio which is close to 10^5 (a high number for MEH-PPV). As a general rule we found that the reliability of the material parameters degrades in devices that exhibit threshold voltage above $4V$ and that such high threshold values are generally due to imperfect device processing procedures.

Results as in Figure 3 can be used to determine the field effect mobility using the known formula for the linear regime ($|V_G| > |V_{DS}| = 2V$)^[21]

$$I_{DS} = K\mu \left([V_{GS} - V_T] V_{DS} - \frac{V_{DS}^2}{2} \right) \quad (1)$$

Using formula (1) with $V_T=0$ we calculated the field effect mobility as a function of gate bias. As the mobility is charge density (gate bias) dependent^[22] we can use a constant mobility value across the channel only for $V_{GS} \gg V_{DS}$ or when formula (1) reduces to $I_{DS} = K\mu ([V_{GS} - V_T] V_{DS})$. Based on the above we consider the low voltage (very low mobility) values to be of less significance and hence we largely plot the results on a linear scale.

Figure 4 shows the mobility value as extracted for the different MWs PPV spin coated from toluene to $\sim 100nm$ thick film. We note a clear trend in the mobility as the MW is increased from $100K$ to $2.8M$. A common feature is that the slope has a maximum value at an intermediate gate bias value (S shape). For the sake of completeness we show in the inset to Figure 4 the same data but on a semi-log scale. We note that for about an order of magnitude in $(V_{GS} - V_T)$ we find up to two orders of magnitude change in the mobility values.

In order to shed light on the physical mechanisms governing the gate-bias dependence of the mobility we use the same physical picture often used for polymer light-emitting diodes^[2, 3]^[23], namely a disordered material having a Gaussian density of states of a given width σ . The calculation is the same as presented in^[11] and is used

here only for the low electric field limit which is applicable to the operating conditions of the FETs used in this paper ($|E_{DS}|=2V/2\mu\text{m}=10^4\text{Vcm}^{-1}$). In short, to calculate the mobility we assume that the charge carriers hop between localized states according to “Miller-Abrahams” rate ^[24] and that the charge carriers’ population is in quasi-equilibrium (fig. 2). The potential drop between the sites is due to the applied electrical field ($\mathbf{R}_{ij}\cdot\mathbf{E}$). The occupation probability of the state at energy ε_i at a certain site is determined by Fermi-Dirac distribution $f(\varepsilon_i)$. The total current is the integration on the contribution from the hops from state i to state j , according to the following expression:

$$\bar{J}_{ij} = v_{ij} (R_{ij}, \varepsilon_i, \varepsilon_j) g(\varepsilon_i) f(\varepsilon_i, \varepsilon_F) g(\varepsilon_j) [1 - f(\varepsilon_j, \varepsilon_F)] R_{ij} \cdot \hat{E}$$

Where v_{ij} is the Miller-Abrahams hopping rate and $g(\varepsilon)$ is the DOS. From the total current one can then deduce the mobility as $\mu = \frac{J}{qPE}$.

Since there is a range of parameters one can use for the width σ and a combination of widths we limit ourselves, here, to the methodology and parameters employed by Rakhmanova&Conwell^[2] who used Monte-Carlo simulations to shed light on the field dependence of the mobility in MEH-PPV films. Namely, the MEH-PPV films are assumed to be composed of two phases characterized by a different DOS widths of 8kT and 12kT. This notion is also supported by the AFM images shown in Figure 2. Figure 5 presents the calculation using the same material parameters as in reference ^[2]. It shows the charge density dependence of the mobility for a material having a mixture of regions with $\sigma=8\text{kT}$ and $\sigma=12\text{kT}$. The dashed lines are for a homogeneous sample of $\sigma=8\text{kT}$ (top line) and $\sigma=12\text{kT}$ (lower dashed line). The solid lines are for an inhomogeneous samples having 80% of $\sigma=8\text{kT}$ and 20% of $\sigma=12\text{kT}$ (upper line) or 20% of $\sigma=8\text{kT}$ and 80% of $\sigma=12\text{kT}$ (lower line). The comparison of Figure 4 and Figure 5 suggests that the inhomogeneous nature of the MEH-PPV film must be accounted for also in the modeling of the density dependence of the mobility in these films since only then an S shape of the mobility curve is predicted by the theory. This point is strengthened by the comparison of the calculation presented on semilog scale (Figure 6) to the experimental ones (inset to Figure 4). The effect of mixing two different Gaussian widths is also essential to make the mobility vary by up to two orders of magnitude across an order of magnitude change in the charge density.

To summarize, we have presented a systematic study of the effect of the MW of MEH-PPV on the transport properties in field effect transistors. We found that a critical effect is that of the morphology and film inhomogeneity as a function of the molecular weight. The dependence of the film morphology on the molecular weight is found to be largely due to the effect of the reduced solubility. We found that the presence of inhomogeneity not only affects the field dependence of the mobility^[2] but also the charge density dependence of it. By employing a recently developed extension^[11] to the disorder model we could qualitatively reproduce the experimental data thus suggesting that the disorder model can be used to describe not only LEDs but also FETs. Namely, the density dependence does not require extrinsic traps to be introduced into the physical picture. Finally, in this paper we do not try to directly reproduce the experimental results but mainly reproduce its functional form. The data presented in Figure 2 clearly shows that assuming only two phases in the films is just an approximation (though much better than the single phase picture). We believe that as more material information becomes available (as the density of states) exact modeling and data fitting may become a valid task. In that case one would also need to take into account the change in the Einstein coefficient at high densities (by a factor of $\eta^{[10]}$) which tend to enhance the channel width

$$\left(L_D = \sqrt{\frac{kT\epsilon\epsilon_0}{q^2} \cdot \frac{\eta}{p}} = \frac{1}{pq} \sqrt{kT\epsilon\epsilon_0 \cdot \eta p} \right) \text{ and hence reduce the charge density at the}$$

$$\text{channel} \left(p = \frac{1}{\eta} [(V_{GS} - V_T) C_{ox}]^2 \frac{1}{q \frac{kT}{q} \epsilon\epsilon_0} \right).$$

Experimental: P⁺⁺ silicon substrates were used as the Gate contact. High quality silicon oxide layer (~100nm) was thermally grown to form the gate dielectric. Ti/Gold was thermally evaporated and patterned to form inter-digitated source and drain contacts. Care was taken not to expose the dielectric layer to any contamination during the processing procedure. The polymers were spin-coated from toluene in an inert glove box. All films were annealed under dry vacuum at 90c within the glove box.

MEH-PPV having molecular weights ranging from 100,000 to 2,800,000 were synthesized at American Dyes Source Inc. in grams quantities and were used as prepared. Molecular weight was determined via gel permeation chromatography (GPC) on a Waters Breeze system using polystyrenes as standards.

Topography and phase AFM images were recorded on a DI3100 (Veeco) atomic force microscope. Scans were performed using RTESP7 silicon tips (Veeco) in the tapping mode, scan rate=2Hz (tip velocity=39.4 $\mu\text{m/s}^{-1}$).

Figure Captions

Figure 1. Photoluminescence spectra of MEH-PPV films spin cast from toluene. (a) MW=100,000, (b) MW=1,000,000, (c) MW=2,800,000. Note the red shift in the PL spectra as a function of molecular weight indicating enhanced aggregation (density). The dashed line in (c) is for a film cast from THF.

Figure 2. A $10\mu\text{m}\times 10\mu\text{m}$ scan of the three MEH-PPV polymers (spin from toluene). The data presented was collected in the phase mode.

Figure 3. Source/drain current measured as a function of negative gate voltage. The drain source voltage was -2V . At about 0.5V the drain/source current exceeds the parasitic charging currents. The channel length is $L=2\mu\text{m}$ and its width is $W=6000\mu\text{m}$ and the polymer used was MEH-PPV (MW=2.8M).

Figure 4. Mobility as a function of gate voltage for two MWs of MEH-PPV. The difference between them is almost a constant factor of 3.3.

Figure 5. Calculation of the density dependent mobility for several density of states functions.

Figure 6. The same calculation as in Figure 5 but on a semilog scale.

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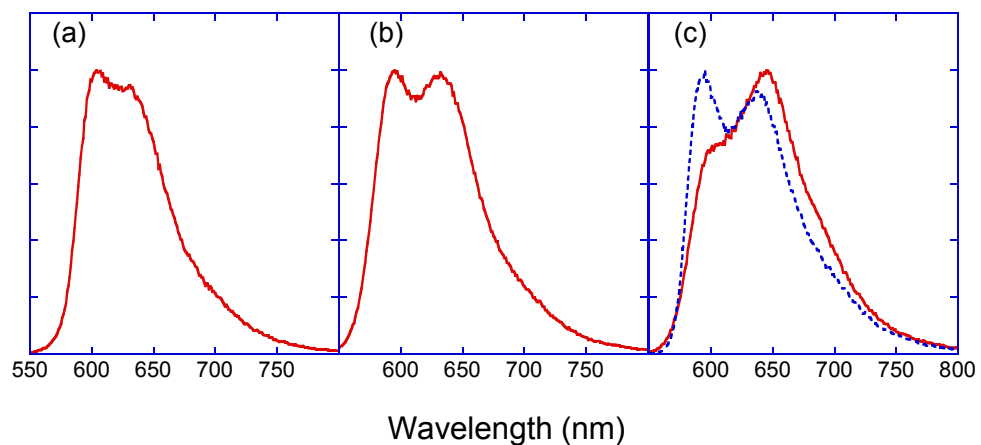


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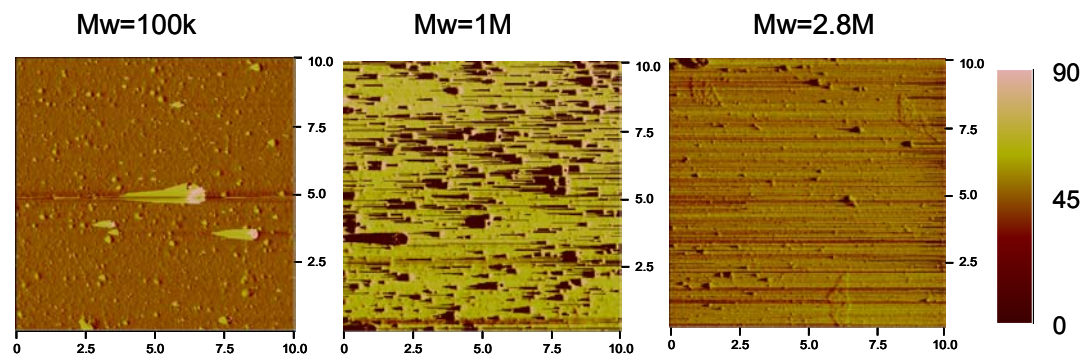


Figure 2. A 10 μm x10 μm scan of the three MEH-PPV polymers (spin from toluene). The data presented was collected in the phase mode.

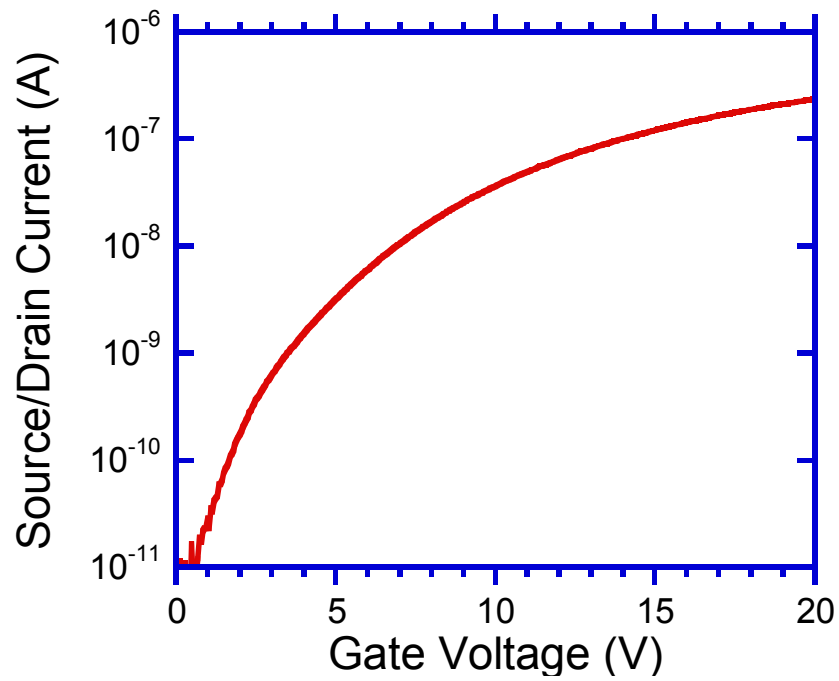


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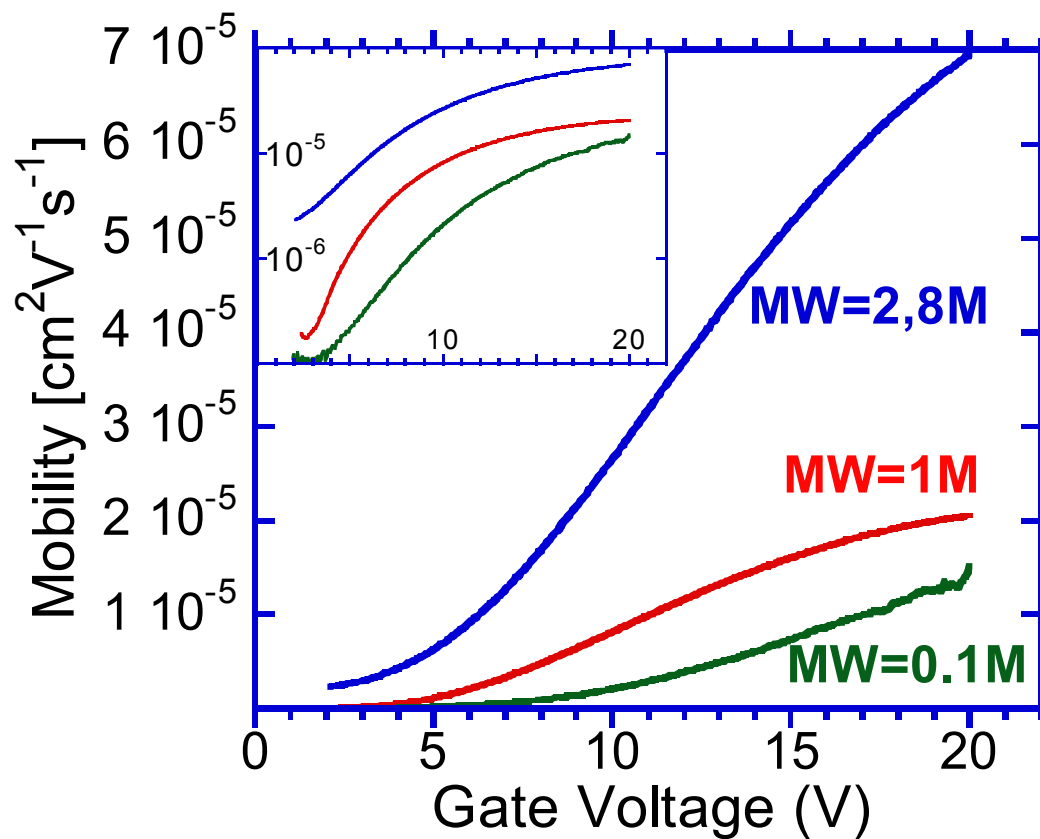


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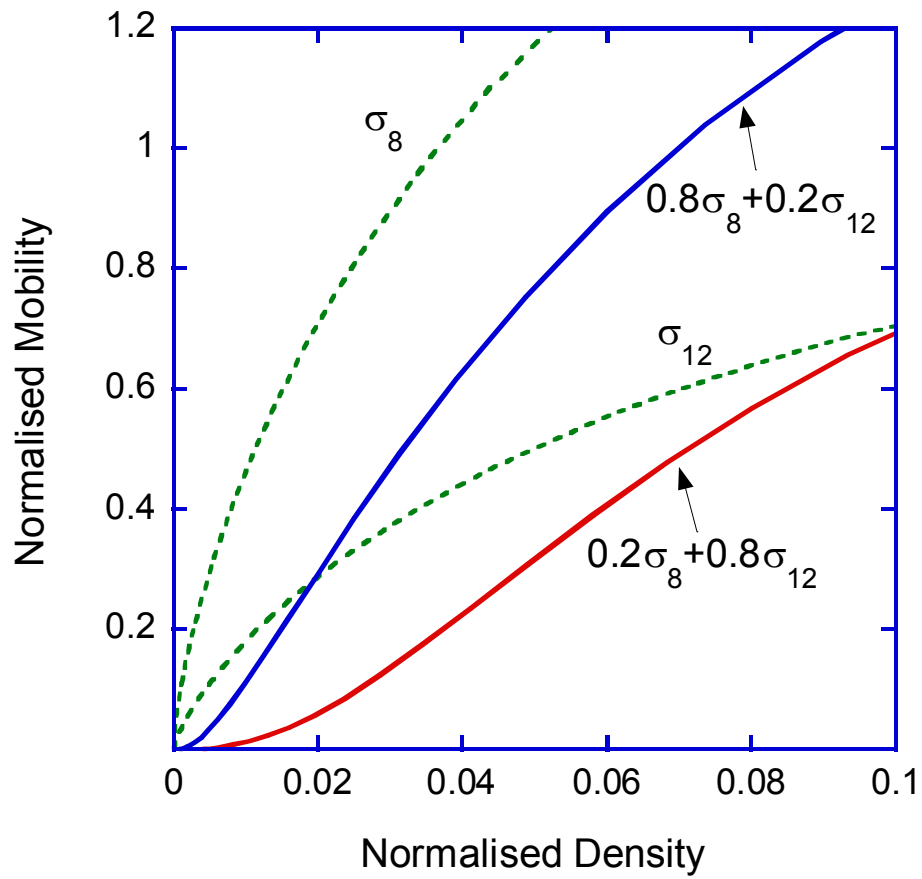


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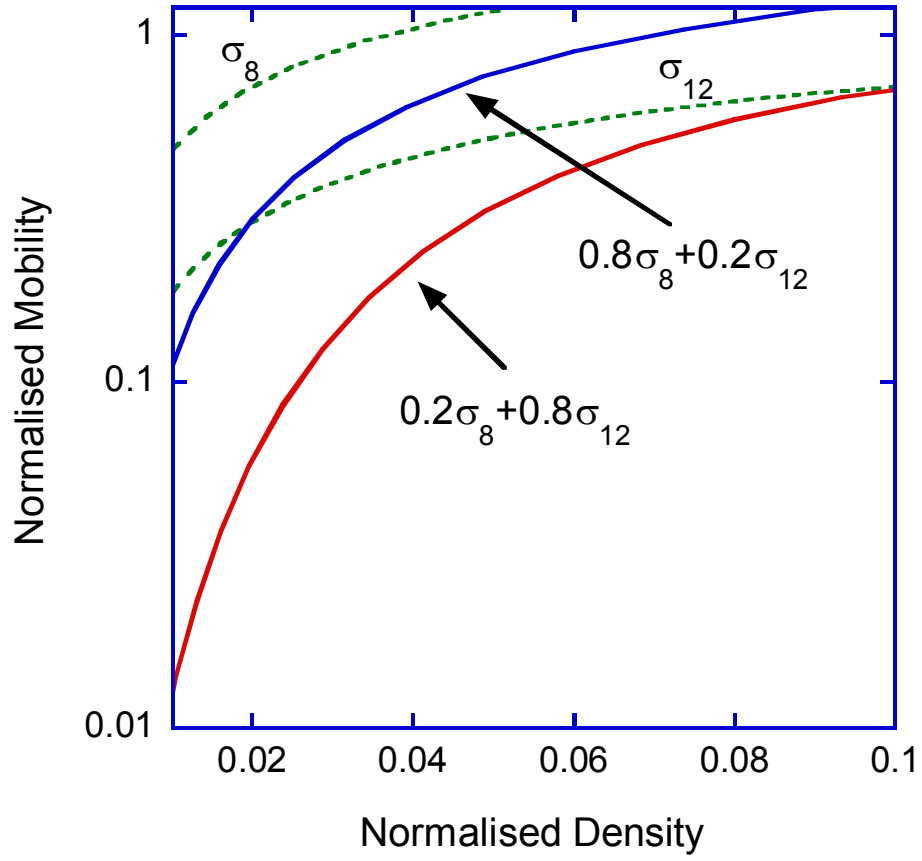


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