

Derivation of the open-circuit voltage of organic solar cells

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Organic photovoltaic cells have improved in efficiency from 1% two decades ago to over 10% today. Continued improvement necessitates a theoretical understanding of the factors determining efficiency. Organic photovoltaic efficiency can be parameterized in terms of open-circuit voltage, short-circuit current, and fill factor. Here we present a theory that explains the dependencies of open-circuit voltage on semiconductor energy levels, light intensity, solar cell and light-source temperatures, charge-carrier recombination, and external fluorescence efficiency. The present theory also explains why recombination at the donor-acceptor heterointerface is a dominant process in heterojunction-based cells. Furthermore, the Carnot efficiency appears, highlighting the connection to basic thermodynamics. The theory presented here is consistent with and builds on the experimental and theoretical observations already in the literature. Crucially, the present theory can be straightforwardly derived in a line-by-line fashion using standard tools from statistical physics.

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I. INTRODUCTION

Organic photovoltaics (OPV) are an active field of study, driven by the promise of cheap materials and manufacturing, and encouraged by recent improvements in power conversion efficiency η [1–5]. OPV are built from carbon-based semiconductors, which typically have conjugated bonds permitting electron mobilities and highest-occupied molecular orbital–lowest-unoccupied molecular orbital (HOMO-LUMO) gaps appropriate for solar cells. In OPV, excited electrons form bound electron-hole pairs (excitons), with binding energies typically hundreds of meV [6–8]; this is to be contrasted with the inorganic case, with binding energies on the order of tens of meV. Consequently, early OPV suffered from poor efficiencies $\eta < 1\%$ [9]. Interest in OPV increased dramatically with the demonstration of $\eta \approx 1\%$ efficient cells based on donor-acceptor heterojunctions, with excitons split via electron transfer at the heterointerface [9,10]. Additional significant OPV developments have included bulk heterojunctions (BHJ) [11], tandem cells [12–15], and a continuous improvement in donor and acceptor materials [1–5]; modern OPV cells combining all these improvements achieve efficiencies $\eta > 10\%$ [15].

Continued improvement necessitates understanding the physical mechanisms determining solar cell efficiency, in order to identify loss mechanisms and circumvent losses where possible. Along these lines, it is helpful to factor the efficiency $\eta = V_{oc} J_{sc} FF / \Psi$ into the product of open-circuit voltage V_{oc} , short circuit current density J_{sc} , and fill factor FF , as a fraction of the incident intensity Ψ . Each of V_{oc} , J_{sc} , and FF tend to vary differently as functions of experimental variables, permitting the larger problem of photovoltaic efficiency to be split into factors influencing these parameters. The origins of V_{oc} , J_{sc} , FF , and ultimately η have been studied extensively in the context of inorganic, homojunction-based photovoltaic (PV) cells [16–21]. Heterojunction-based OPV cells share some basic operating principles with their inorganic counterparts.

Nevertheless, the introduction of distinct donor and acceptor materials and the dominant role played by separating excitons at the donor-acceptor heterointerface necessitates a dedicated theoretical treatment of OPV performance.

In the present paper we focus our attention on the open-circuit voltage V_{oc} of organic solar cells. As model systems we consider OPV cells based on donor-acceptor heterojunctions, as the vast majority of modern OPV cells fall into this category [1–5]. To date, significant experimental evidence has been collected resulting in a long list of factors influencing V_{oc} [1–5]. Theories have been presented describing the dependence of V_{oc} on different factors including the energy gap $\Delta E_{DA} = E_A^{\text{LUMO}} - E_D^{\text{HOMO}}$ between the acceptor LUMO and donor HOMO [22–26], the light intensity Ψ [23–28], external fluorescence efficiency η_{ext}^R [29,30], and charge-carrier concentrations [23–28,31]. The theory of Cheyns *et al.* is noteworthy in that it treats band bending and can be used to study the impact of the contacts on V_{oc} [23], which is typically neglected. Concomitant with its effect on V_{oc} , the fact that ΔE_{DA} is smaller than the donor and acceptor band gaps reduces the theoretical efficiency limit for OPV cells to 22–27% [32–34] (or 10–12% if other losses are considered [22]), to be compared to the 33% Shockley-Queisser limit for inorganic cells [16,21].

Despite significant progress, additional theoretical developments are necessary to understand V_{oc} within a consistent theoretical framework. Furthermore, current expressions for V_{oc} include terms that are either phenomenological, difficult to measure experimentally, or difficult to predict *a priori* such as intrinsic carrier concentrations, carrier concentrations under illumination, Langevin recombination constants, and coefficients relating intensity to carrier concentration. What is lacking in the literature is a simple analytic theory rigorously explaining the factors determining V_{oc} consistently and within one model, in terms of readily measurable experimental variables. Here we address this issue by deriving V_{oc} in terms of ΔE_{DA} , intensity Ψ , temperatures of the cell T_c and light source T_s , ambient index of refraction n_r , external fluorescence efficiency η_{ext}^R , and absorption coefficients c_j , the effect of the last of these being on the order of kT_c . The effects of recombination R , charge-carrier concentrations n and p ,

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as well as exciton and bound polaron-pair concentrations ρ_D and ρ_{DA} are included here, but eliminated in terms of the above variables using a detailed balance argument. The theory presented here gives $V_{oc} = 0$ in the dark; this simple requirement is not obviously met by theories in the literature. In addition, the Carnot efficiency $1 - T_c/T_s$ appears in our theory, consistent with the expectation from thermodynamics. Furthermore, we derive within our model the reason why recombination at the donor-acceptor interface is a dominant process for BHJ-based cells, as identified experimentally [35].

II. DERIVATION OF V_{oc} BASED ON DETAILED BALANCE AND MASS ACTION

Let G and R denote generation and recombination fluxes of electron-hole pairs, respectively, with dimensions of number of electron-hole pairs per unit time per unit area. Included in G and R are the generation and recombination of excitons, bound polaron-pairs, polarons, and free charge carriers. Electron-hole pair generation and recombination can coincide with photon absorption (G_{ext}) and emission (R_{ext}), respectively, or with nonradiative processes. To account for the nonradiative processes, we define the external fluorescence efficiencies $\eta_{ext}^G = G_{ext}/G$ and $\eta_{ext}^R = R_{ext}/R$, where G_{ext} is the flux of electron-hole pairs generated due to incident light, and R_{ext} is the flux of electron-hole recombination resulting in light being emitted from the face of the cell.

Photoabsorption $G_{ext} = \sum_j G_j$ and photoemission $R_{ext} = \sum_j R_j$ can occur via multiple pathways j . For brevity, we limit the radiative processes considered to the generation and recombination of the following: excitons in the donor material, denoted by $j = D$, bound polaron-pairs spanning the heterointerface ($j = DA$), and charge carriers (polarons) in the acceptor material ($j = A$). $j = D$ is the dominant generation process in polymer-fullerene OPV cells [1,2], while $j = DA$ is thought to be the dominant recombination term in such cells under illumination [35]. Fullerene acceptor materials neither absorb nor emit strongly; we include $j = A$ for demonstration purposes to present one of each excitonic, geminate (bound polaron-pair), and charge-carrier (polaron) recombination and generation processes. Additional pathways, e.g., exciton generation or recombination in the acceptor material, can be included in exactly the same fashion.

Suppose that $R_D = \alpha_D \rho_D$ is first order in the exciton concentration ρ_D in the donor material, while $R_{DA} = \alpha_{DA} \rho_{DA}$ and $R_A = \alpha_A n_A p_A$ are first order in the bound polaron-pair concentration ρ_{DA} at the donor-acceptor heterointerface, and the electron n_A and hole p_A polaron concentrations in the acceptor material, respectively; here the various α_j are rate constants. Suppose further that ρ_D , ρ_{DA} , n_A , and p_A obey the law of mass action:

$$\rho_D = \rho_D^{(eq)} \exp(\beta_c \Delta\mu_D), \quad (1)$$

$$\rho_{DA} = \rho_{DA}^{(eq)} \exp(\beta_c \Delta\mu_{DA}), \quad (2)$$

$$n_A p_A = n_A^{(eq)} p_A^{(eq)} \exp(\beta_c \Delta\mu_A), \quad (3)$$

where $\rho_D^{(eq)}$, $\rho_{DA}^{(eq)}$, $n_A^{(eq)}$, and $p_A^{(eq)}$ are the values that ρ_D , ρ_{DA} , n_A , and p_A take in equilibrium. Here $\Delta\mu_{DA}$ is the quasi-Fermi-level splitting between electrons in the acceptor LUMO and

holes in the donor HOMO; $\Delta\mu_D$ and $\Delta\mu_A$ are the quasi-Fermi-level splittings in the donor and acceptor materials, respectively. The rapid exchange of electrons between the donor and acceptor LUMOs and holes between the donor and acceptor HOMOs implies a common quasi-Fermi-level splitting throughout the active layer $\Delta\mu_D = \Delta\mu_{DA} = \Delta\mu_A = \Delta\mu$.

At open circuit, $G = R$ in order for the system to be at steady state. Together with the above first-order rate laws, law of mass action, and common quasi-Fermi-level splitting, this gives

$$\Delta\mu = kT_c \ln \left[\left(\frac{\eta_{ext}^R}{\eta_{ext}^G} \right) \left(\frac{G_D + G_{DA} + G_A}{R_D^{(eq)} + R_{DA}^{(eq)} + R_A^{(eq)}} \right) \right], \quad (4)$$

where the $R_j^{(eq)} = R_j(\Delta\mu = 0)$ are the recombination fluxes in equilibrium. Detailed balance implies $R_j^{(eq)} = G_j^{(eq)}$, where the $G_j^{(eq)}$ are defined as the generation fluxes G_j in equilibrium. Furthermore, given a one-to-one correspondence between photoabsorption and photoexcitation, we have $G_j = \Xi_j$, where Ξ_j is the number of photons per unit area per unit time absorbed in process j , such that

$$\Delta\mu = kT_c \ln \left[\left(\frac{\eta_{ext}^R}{\eta_{ext}^G} \right) \left(\frac{\Xi_D + \Xi_{DA} + \Xi_A}{\Xi_D^{(eq)} + \Xi_{DA}^{(eq)} + \Xi_A^{(eq)}} \right) \right]. \quad (5)$$

The photoabsorption fluxes can be described by

$$\Xi_j = \int_{E=0}^{\infty} \int_{\Omega} a_j(E, \theta) b(E) dE d\Omega, \quad (6)$$

where E is the photon energy, Ω is solid angle; $b(E)$ is the spectral radiance of the incident light with dimensions number of photons per unit area, time, energy, and solid angle; and $a_j(E, \theta)$ is the dimensionless spectral absorptivity, defined as the fraction of incident photons with energy E and angle-of-incidence θ that are absorbed in process j .

Suppose the incoming radiation is black-body radiation at temperature T , such that

$$b(E) = \frac{2n_r}{h^3 c^2} \left(\frac{E^2}{e^{\beta E} - 1} \right), \quad (7)$$

where n_r is the ambient refractive index, h is Planck's constant, c is the speed of light in vacuum, and $\beta = 1/kT$ with k being Boltzmann's constant. In thermal equilibrium with the environment, the cell receives black-body radiation at its own temperature $T = T_c$; we denote the source temperature under illumination by $T = T_s$. Suppose further that $a_j(E, \theta) = c_j \Theta(E - E_j)$, where $\Theta(x)$ is the unit step function, the $c_j \in [0, 1]$ are dimensionless absorption coefficients, and $E_j = \Delta E_D$, ΔE_{DA} , and ΔE_A for absorption in the donor material, at the donor-acceptor heterojunction, and in the acceptor material, respectively. Here ΔE_D and ΔE_A are the HOMO-LUMO gaps of the donor and acceptor materials, respectively. Together, these simplifications imply $\Xi_j = c_j \Phi f(\beta E_j)$, where Φ is the incident photon flux and

$$f(x) = \frac{1}{2\zeta(3)} \int_x^{\infty} \frac{u^2}{e^u - 1} du. \quad (8)$$

Here $\zeta(3) = 1.202 \dots$ is Apéry's constant, i.e., the Riemann zeta function $\zeta(x)$ evaluated at $x = 3$. The function $f(x)$ has

a simple physical interpretation for $x = \beta E_j$: It is the fraction of photons in the black-body spectrum with temperature $T = 1/\beta k$ that have energy $E \geq E_j$. We note that $f(x) \approx g(x)$, where

$$g(x) = \frac{1}{2\zeta(3)}(2\zeta(3) + 2x + x^2)e^{-x}. \quad (9)$$

In fact, for $r(x) = f(x)/g(x)$, we have $r_{\min} < r(x) < r_{\max}$ with $r_{\min} = 0.99$ and $r_{\max} = 1.04$, as can be verified numerically.

Equation (9) can be used to understand why recombination at the donor-acceptor interface is the dominant recombination process for BHJ-based cells. We have

$$R_j = R_j^{\text{(eq)}} \exp(\beta_c \Delta\mu) \quad (10)$$

$$= c_j \Phi^{\text{(eq)}} g(\beta_c E_j) r(\beta_c E_j) \exp(\beta_c \Delta\mu). \quad (11)$$

Together, Eqs. (9) and (11) imply

$$\frac{R_{DA}}{R_D} \propto \frac{c_{DA}}{c_D} e^{\beta_c(\Delta E_D - \Delta E_{DA})}. \quad (12)$$

If $\Delta E_D - \Delta E_{DA} \approx 0.3$ eV [22] and $T_c \approx 300$ K, then $e^{\beta_c(\Delta E_D - \Delta E_{DA})} \approx 10^5$. Thus, even if $c_D \gg c_{DA}$, $R_{DA} > R_D$ as long as $c_D \lesssim 10^5 c_{DA}$. In contrast to the BHJ case, $R_D > R_{DA}$ can occur in planar heterojunction cells, if the exciton diffusion length λ is much smaller than the distance d from the photoabsorption site to the heterointerface. In such situations $\Delta\mu_D$ may not be a good representation of $\Delta\mu_{DA}$, with the net result being an additional exponential dependence $R_{DA}/R_D \propto \exp(-d/\lambda)$. Furthermore, the smaller interfacial area in planar heterojunction cells implies a decreased ratio c_{DA}/c_D as compared to BHJ cells.

Substituting $\Xi_j = c_j \Phi g(\beta E_j) r(\beta E_j)$ into Eq. (5) gives

$$\Delta\mu = kT_c \ln \left[\left(\frac{\eta_{\text{ext}}^R}{\eta_{\text{ext}}^G} \right) \left(\frac{\Phi}{\Phi^{\text{(eq)}}} \right) \frac{\sum_j c_j g(\beta_s E_j) r(\beta_s E_j)}{\sum_j c_j g(\beta_c E_j) r(\beta_c E_j)} \right],$$

where $j = D, A$, and DA . We note that

$$\sum_j c_j g(\beta E_j) r(\beta E_j) = r_\beta \sum_j c_j g(\beta E_j), \quad (13)$$

for some r_β with $r_{\min} < r_\beta < r_{\max}$. This follows because the various $r(\beta E_j)$ are themselves constrained to the interval (r_{\min}, r_{\max}) . To establish the connection with V_{oc} , we assume perfect energy-level alignment between the acceptor LUMO and cathode, and between the donor HOMO and anode, such that $\Delta\mu = qV = qV_{oc}$ at open circuit. This gives

$$V_{oc} = \frac{\Delta E_{DA}}{q} \left(1 - \frac{T_c}{T_s} \right) + \frac{kT_c}{q} \ln \left[\left(\frac{\Phi}{\Phi^{\text{(eq)}}} \right) \left(\frac{\eta_{\text{ext}}^R}{\eta_{\text{ext}}^G} \right) \left(\frac{X_s}{X_c} \right) \left(\frac{r_s}{r_c} \right) \right], \quad (14)$$

which is a main result of this paper. The term in Eq. (14) linear in ΔE_{DA} arises from factoring the dominant term $\exp[-\Delta E_{DA}(\beta_s - \beta_c)]$ out of the logarithm. Multiplying ΔE_{DA} we find $1 - T_c/T_s$, the Carnot efficiency for a heat engine operating between temperatures T_s and T_c . The factor X_s/X_c is defined by

$$X = e^{\beta \Delta E_{DA}} \sum_j c_j g(\beta E_j), \quad (15)$$

where X_s and X_c correspond to X with $\beta = \beta_s$ and β_c , respectively; we will see shortly that X_s/X_c is of order unity. Similarly, r_s and r_c correspond to r_β with $\beta = \beta_s$ and β_c , respectively.

Clearly the incident photon flux Φ is proportional to the incident intensity Ψ :

$$\Psi = \int_{E=0}^{\infty} \int_{\Omega} E b(E) dE d\Omega = \frac{12\zeta(4)\Omega n_r}{h^3 c^2 \beta^4}, \quad (16)$$

$$\Phi = \int_{E=0}^{\infty} \int_{\Omega} b(E) dE d\Omega = \frac{4\zeta(3)\Omega n_r}{h^3 c^2 \beta^3} \quad (17)$$

$$= \frac{\zeta(3)}{3\zeta(4)} \beta \Psi, \quad (18)$$

where $\zeta(4) = \pi^4/90$ and Ω is the solid angle subtended by the light source about the cell. This gives

$$\frac{\Phi}{\Phi^{\text{(eq)}}} = \frac{15h^3 c^2}{4\pi^5 n_r k^4 T_c^3 T_s} \Psi, \quad (19)$$

where we have taken $\Omega = 2\pi$ for radiation incident on the face of the cell in equilibrium.

III. INFLUENCE OF X_s/X_c AND r_s/r_c ON V_{oc}

The ratio X_s/X_c is dependent on the energy gaps ΔE_D , ΔE_{DA} , and ΔE_A ; absorption coefficients c_D , c_{DA} , and c_A ; and the temperatures of the light source T_s and solar cell T_c . Through these parameters, X_s/X_c captures the effect of the difference in absorbed and emitted spectra on V_{oc} , this difference in turn being determined by the dominant mechanisms of photogeneration and recombination of excitons, bound polaron pairs, and free charge carriers. Estimating the contribution of X_s/X_c to V_{oc} is straightforward. With polymer-fullerene cells in mind, suppose that absorption (under illumination) is dominant in the donor material, and recombination is dominant at the donor-acceptor heterointerface; this implies that the $j = D$ and $j = DA$ terms are dominant in X_s and X_c , respectively. We next apply $g(x) \approx x^2 e^{-x}/(2\zeta(3))$; for $x = \beta E$ this approximation is within a factor of 3 for $E \geq 1$ eV and $T \leq 6000$ K. Together, the above imply

$$\frac{X_s}{X_c} \approx \frac{c_D T_c^2}{c_{DA} T_s^2}; \quad 1 \ll \frac{c_D}{c_{DA}} \ll e^{\beta_c(\Delta E_D - \Delta E_{DA})}, \quad (20)$$

where we have neglected factors of E_D^2/E_{DA}^2 and $e^{\beta_s(\Delta E_{DA} - \Delta E_D)}$, which are of order unity for the parameter range of interest. Taking $T_c = 300$ K, $T_s = 6000$ K, and $\Delta E_D - \Delta E_{DA} = 0.3$ eV and assuming “ \ll ” corresponds to a separation of at least two orders of magnitude, this implies $0.25 < X_s/X_c < 2.5$, such that $(kT_c/q) \ln(X_s/X_c)$ is on the order of $kT_c/q \approx 25$ meV.

The factor r_s/r_c in Eq. (14) arises when replacing the integral of the black-body spectrum $f(x)$ with the analytic function $g(x)$. Although a closed functional form for r_s/r_c is lacking, we have $|\ln(r_s/r_c)| < \ln(r_{\max}/r_{\min}) < 0.05$. For $T_c \approx 300$ K, this gives $|(kT_c/q) \ln(r_s/r_c)| \lesssim 1$ mV, negligible for most applications.

IV. COMPARISON TO EXPERIMENT

In Fig. 1 we compare Eq. (14) to the experimental data for the open-circuit voltage V_{oc} dependence on temperature T_c , donor HOMO E_D^{HOMO} , acceptor LUMO E_A^{LUMO} , and light intensity Ψ . The experimental data are taken from four separate experimental papers, namely Mihailetchi *et al.* [36], Scharber *et al.* [22], Brabec *et al.* [37], and Koster *et al.* [28], respectively. These studies were selected for consistency in solar cell design: each study investigated cells with structure indium tin oxide/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)/poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]:[6,6]-phenyl C61 butyric acid methyl ester/lithium fluoride/aluminum (ITO/PEDOT:PSS/MDMO-PPV:PCBM/LiF/Al), with the exception that the donor material was varied in Scharber *et al.* [22], the acceptor material was varied in Brabec *et al.* [37], and the LiF layer was omitted in Brabec *et al.* [37].

There is a systematic difference of ~ 0.25 eV in the cyclic voltammetry (CV) data between Scharber *et al.* [22] and Brabec *et al.* [37]. This difference is likely due to differences in calibration, differences in the experimental setup used in the two studies, and to the experimental uncertainty inherent to CV measurements. Fortunately, the first reduction potential of PCBM was measured in both studies. We use this common measurement to shift the data from Brabec *et al.* [37] onto an absolute energy scale consistent with that from Scharber *et al.* [22].

The data in Figs. 1(a) to 1(c), from four separate experiments, are fit using three parameter values. The fitting procedure is as follows: first, $E_{\text{PCBM}}^{\text{LUMO}} - E_{\text{MDMO-PPV}}^{\text{HOMO}} = 1.286 \pm 0.002$ eV is equal to the $T_c = 0$ intercept of a linear fit to Fig. 1(a). $L = -1.42 \pm 0.01$ mV/K is simultaneously extracted from the slope m of the linear fit; here L is defined as

$$L = \frac{k}{q} \ln \left[\left(\frac{\Phi^{(1\text{sun})}}{\Phi^{(\text{eq})}} \right) \left(\frac{\eta_{\text{ext}}^R}{\eta_{\text{ext}}^G} \right) \left(\frac{X_s}{X_c} \right) \left(\frac{r_s}{r_c} \right) \right] \quad (21)$$

$$= m + \frac{E_{\text{PCBM}}^{\text{LUMO}} - E_{\text{MDMO-PPV}}^{\text{HOMO}}}{qT_s}, \quad (22)$$

for 1-sun illumination of a MDMO-PPV:PCBM cell at $T_c = 300$ K.

It is not immediately obvious that V_{oc} should vary linearly with respect to T_c , such that L as defined in Eq. (21) can be treated as a constant and Eq. (22) holds. The short explanation is that the T_c dependence of V_{oc} is completely dominated by the linear factors outside the logarithm in Eq. (14); the T_c dependence of the factors inside the logarithm are negligible by comparison. This can be understood as follows: First, the ratio $\Phi/\Phi^{(\text{eq})}$ contributes a factor of T_c^3 to the denominator in the logarithm in Eq. (14). This is partly balanced by the approximate T_c^2 proportionality of X_s/X_c , see Eq. (20). The remaining factor of T_c would contribute only a variation in slope of $(k/q) \ln(3) \approx 0.1$ mV/K over the entire range of $T_c = 100$ to 300 K. Such a small variation would not be visible on the scale of Fig. 1(a), as can be easily verified numerically. However, even this small contribution is partly balanced by the fact that η_{ext}^R increases with decreasing temperature [38].

$E_{\text{PCBM}}^{\text{LUMO}}$ is necessary to compare Eq. (14) to the data in Fig. 1(b). We find $E_{\text{PCBM}}^{\text{LUMO}} = -4.13 \pm 0.01$ eV from the intercept V_0 of a linear fit with slope $T_c/T_s - 1 = -0.95$ to the V_{oc} versus E_D^{HOMO} data from Scharber *et al.* [22], using the relation

$$E_{\text{PCBM}}^{\text{LUMO}} = \frac{q(V_0 - T_c L)}{1 - \frac{T_c}{T_s}}. \quad (23)$$

This value of $E_{\text{PCBM}}^{\text{LUMO}}$ is used to calculate $E_{\text{PCBM}}^{\text{LUMO}} - E_D^{\text{HOMO}}$ for comparison to the data from Scharber *et al.* [22].

V. DISCUSSION

Linear fits to the data in Fig. 1 were also presented in the original experimental studies [22,28,36,37]. Our contribution is to fit these data within a consistent theoretical framework: The present theory explains the observations from all four experimental studies using parameters based only on data from Mihailetchi *et al.* [36] and Scharber *et al.* [22].

The fact that $E_{\text{PCBM}}^{\text{LUMO}} - E_{\text{MDMO-PPV}}^{\text{HOMO}} = 1.286 \pm 0.002$ eV and $E_{\text{PCBM}}^{\text{LUMO}} = -4.13 \pm 0.01$ eV are extracted as fit parameters in Figs. 1(a) and 1(b) is a strength of the theory: Both of these values are within the range of values reported in the literature [39–44]. The fact that ΔE_{DA} can be extracted from a simple linear fit of V_{oc} versus T_c is particularly noteworthy. The small standard error in the fit parameters indicates that fitting V_{oc}

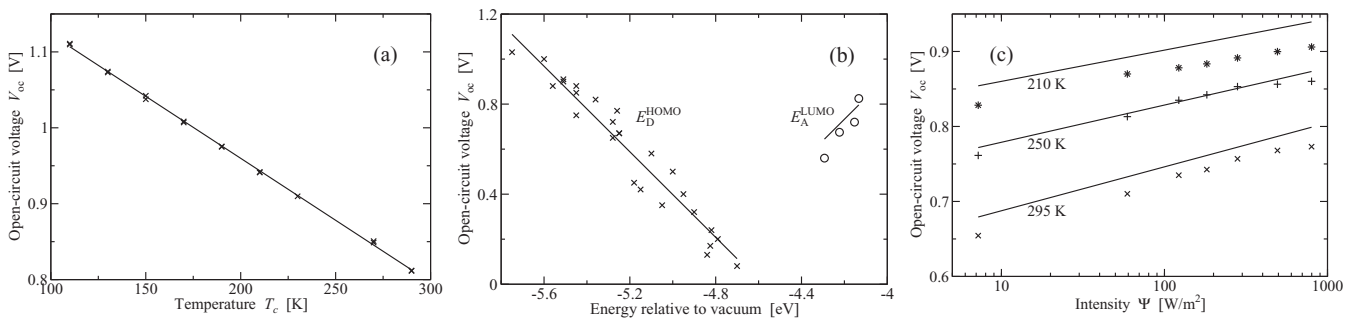


FIG. 1. Comparison of Eq. (14) to experimental dependencies of the open-circuit voltage V_{oc} with (a) the temperature of the cell T_c , (b) the donor HOMO E_D^{HOMO} (\times symbols) and acceptor LUMO E_A^{LUMO} (circles), and (c) light intensity Ψ . Symbols in (c) represent temperatures $T_c = 295, 250$, and 210 K for $\times, +$, and $*$, respectively. Experimental data are from Mihailetchi *et al.* [36], Scharber *et al.* [22], Brabec *et al.* [37], and Koster *et al.* [28], respectively. In all panels, symbols represent experimental data and lines represent the predictions of Eq. 14 with parameters $E_{\text{PCBM}}^{\text{LUMO}} - E_{\text{MDMO-PPV}}^{\text{HOMO}} = 1.286 \pm 0.002$ eV, $L = -1.42 \pm 0.01$ mV/K, and $E_{\text{PCBM}}^{\text{LUMO}} = -4.13 \pm 0.01$ eV.

versus T_c might be useful for extracting ΔE_{DA} for general materials combinations.

The differences between the theory and experiment in Fig. 1(c) are ~ 20 meV on average, representing a discrepancy $\leq kT_c$. These deviations are reasonable considering their small magnitude, and considering the fact that the data in Fig. 1(c) are taken from a different experimental study than the fit parameters. We furthermore note that deviations between the theory and experiment appear to grow with increasing intensity: Such a trend would be consistent with any unaccounted-for heating of the cell due to the light source.

The effects of nonradiative recombination manifest themselves in the $\eta_{\text{ext}}^R/\eta_{\text{ext}}^G$ factor in Eq. (14). Nonradiative losses decreasing η_{ext}^R include optical losses such as a poorly reflective rear mirror [21], conduction pathways through the device such as pinholes or current leakage across device edges, as well as nonradiative recombination mechanisms inherent to the BHJ materials themselves. Under illumination $\eta_{\text{ext}}^G \approx 1$ because photoexcitation dominates over thermal excitation in a properly operating solar cell. The ratio $\eta_{\text{ext}}^R/\eta_{\text{ext}}^G$ for an MDMO-PPV:PCBM cell can be estimated from the parameter L extracted in Sec. IV. Substituting $\Psi = 1000 \text{ W/m}^2$ and $T_c = 300 \text{ K}$ into Eq. (19) gives $\Phi/\Phi^{(\text{eq})} \approx 0.04$. This represents the surprising fact that, although the intensity of sunlight Ψ exceeds that of ambient radiation, the photon flux $\Phi^{(\text{eq})}$ due to a 300 K environment actually exceeds that of sunlight on Earth Φ in terms of number of photons per unit area per unit time. The greatly increased photon flux leaving the surface of the Sun is compensated for by the distance from the Sun to the Earth and the resultant small solid angle subtended by the Sun from the point of view of the Earth. Combined with $L = -1.42 \pm 0.01 \text{ mV/K}$ and taking X_s/X_c and r_s/r_c to be of order unity, we find $\eta_{\text{ext}}^R/\eta_{\text{ext}}^G \approx 10^{-6}$, which is consistent with estimates from the literature [30].

In “the dark,” a solar cell exchanges thermal radiation with the environment until the two reach thermal equilibrium at a common temperature $T = T_s = T_c$. Detailed balance implies both $\Phi = \Phi^{(\text{eq})}$ and $\eta_{\text{ext}}^R = \eta_{\text{ext}}^G$ under these conditions. Furthermore, $X_s = X_c$ and $r_s = r_c$ follow directly from substituting a common $\beta = \beta_s = \beta_c$ into Eqs. (13) and (15), respectively. Overall, each term in Eq. (14) vanishes such that $V_{\text{oc}} = 0$ in the dark; this limit is a simple test supporting the present model.

Any V_{oc} dependence on contact work function was neglected in the derivation of Eq. (14) via an assumption of perfect energy-level alignment between semiconductors and metal contacts: The real situation involves a subtle interplay of injection barriers and band bending [23]. At open circuit, a decreased injection barrier at a contact implies increased carrier density at that contact. Band bending resulting from increased carrier density at the contact has an opposite effect on V_{oc} , as compared to the effect implied by the decreased injection barrier. The net result is that V_{oc} should be independent of contact work function [23], consistent with the present theory.¹ We note, however, that there have been mixed experimental reports of V_{oc} contact dependence and independence [2]. We propose that, for truly symmetric

BHJ-based cells, V_{oc} must equal zero in the case of identical contacts. This supports an interpretation of distinct V_{oc} contact-dependent and contact-independent regimes [2].

In addition to quasi-Fermi-level misalignment at the contacts, it is possible to have spatially heterogeneous quasi-Fermi-levels throughout the device, for instance in the limit of poor charge carrier mobility or short exciton diffusion length. Clearly the open-circuit voltage of a solar cell is unaffected if a resistor is placed in a series with the cell and, in general, poor charge carrier mobility has a stronger influence on J_{sc} and FF than on V_{oc} . Nevertheless, logarithmic corrections to V_{oc} are expected in the case of poor charge carrier mobility or short exciton diffusion length because enhanced recombination in the vicinity of light absorption sites will result in a decreased quasi-Fermi-level splitting at the contacts.

A so-called ideality factor is often reported in the theory of organic solar cells, appearing as a constant factor “ n ” (not to be confused with electron polaron concentration) multiplying kT/q in the logarithmic dependence of V_{oc} on intensity [1–5]. Such an ideality factor can be derived based on Shockley-Read-Hall (SRH) recombination, where charge carriers in the donor and acceptor materials recombine at the heterointerface via intermediate “trap” states [23]. We note that such SRH processes are typically nonradiative, and are thus incorporated in the present theory via η_{ext}^R .

VI. CONCLUSION

In this paper we present a comprehensive theory of the open-circuit voltage of OPV cells, deriving the numerous dependencies of the open-circuit voltage on material and environmental parameters. For a well-designed OPV cell, with efficient exciton dissociation and appropriate absorption coefficients, the energy gap $\Delta E_{DA} = E_A^{\text{LUMO}} - E_D^{\text{HOMO}}$ between the acceptor LUMO and donor HOMO gives the dominant contribution to V_{oc} for OPV cells, as compared to the band gap in inorganic cells. This finding is consistent with existing experimental data and empirical models. Nevertheless, the present theory is distinct from any in the literature, both in terms of its completeness and also in its analytic derivation from first principles.

Key to the applicability of our expression for V_{oc} , Eq. (14), all parameters are directly measurable in experiment. For instance, the factor normalizing the intensity Ψ is given in Eq. (19) in terms of the ambient temperature T_c , index of refraction n_r , and fundamental physical constants. For this reason, the current theory can be used to predict experimental results using parameter values extracted from different experiments. This is demonstrated in Fig. 1, where data from four separate experiments are fit using parameter values obtained from two of the four experiments. As in any line-by-line derivation, the assumptions and approximations are made explicitly; in this way, the places where the theoretical understanding could be improved become immediately apparent, for example, regarding the influence of the contacts on V_{oc} .

Several recommendations can be made for solar-cell optimization and future experiments. First, η_{ext}^R values on the order of 10^{-6} imply a loss in V_{oc} due to the nonradiative recombination of $(kT_c/q) \ln(10^6) > 0.3 \text{ V}$. There is therefore much to be gained in the optimization of the external

¹We note, however, that J_{sc} , FF , and both the voltage and current at the maximum power point are strongly contact dependent.

fluorescence efficiency η_{ext}^R . There are also areas where the basic theory could be improved, principally regarding the role of the metal contacts. Finally, with ~ 0.3 V given away in $E_D^{\text{LUMO}} - E_A^{\text{LUMO}}$, the donor-acceptor heterojunction concept that brought the OPV field to life is now a primary loss mechanism. Heterojunction cells were an important breakthrough to circumvent large exciton binding energies. However, understanding and reducing these binding energies continues to be of critical importance. Simultaneous reductions in exciton binding energies and $E_D^{\text{LUMO}} - E_A^{\text{LUMO}}$ would give a continuous improvement in both V_{oc} and overall

OPV efficiency, with the limiting case being the same 33% Shockley-Queisser efficiency as for inorganic cells.

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- [1] C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia, and S. P. Williams, *Adv. Mater.* **22**, 3839 (2010).
 - [2] C. Deibel and V. Dyakonov, *Rep. Prog. Phys.* **73**, 096401 (2010).
 - [3] B. Walker, C. Kim, and T.-Q. Nguyen, *Chem. Mater.* **23**, 470 (2011).
 - [4] G. Li, R. Zhu, and Y. Yang, *Nat. Photon.* **6**, 153 (2012).
 - [5] A. Mishra and P. Bäuerle, *Angew. Chem. Int. Ed.* **51**, 2020 (2012).
 - [6] I. H. Campbell, T. W. Hagler, D. L. Smith, and J. P. Ferraris, *Phys. Rev. Lett.* **76**, 1900 (1996).
 - [7] I. Hill, A. Kahn, Z. Soos, and R. Pascal, Jr., *Chem. Phys. Lett.* **327**, 181 (2000).
 - [8] V. I. Arkhipov and H. Bässler, *Phys. Status Solidi A* **201**, 1152 (2004).
 - [9] G. Chamberlain, *Sol. Cells* **8**, 47 (1983).
 - [10] C. W. Tang, *Appl. Phys. Lett.* **48**, 183 (1986).
 - [11] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995).
 - [12] M. Hiramoto, M. Suezaki, and M. Yokoyama, *Chem. Lett.* **19**, 327 (1990).
 - [13] J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T.-Q. Nguyen, M. Dante, and A. J. Heeger, *Science* **317**, 222 (2007).
 - [14] T. Ameri, G. Dennler, C. Lungenschmied, and C. J. Brabec, *Energy Environ. Sci.* **2**, 347 (2009).
 - [15] J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, and Y. Yang, *Nat. Commun.* **4**, 1446 (2013).
 - [16] W. Shockley and H. J. Queisser, *J. Appl. Phys.* **32**, 510 (1961).
 - [17] R. T. Ross, *J. Chem. Phys.* **46**, 4590 (1967).
 - [18] G. Smestad and H. Ries, *Sol. Energ. Mat. Sol. Cells* **25**, 51 (1992).
 - [19] T. Markvart, *Appl. Phys. Lett.* **91**, 064102 (2007).
 - [20] T. Markvart, *Phys. Status Solidi A* **205**, 2752 (2008).
 - [21] O. D. Miller, E. Yablonovitch, and S. R. Kurtz, *IEEE J. Photovolt.* **2**, 303 (2012).
 - [22] M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, and C. Brabec, *Adv. Mater.* **18**, 789 (2006).
 - [23] D. Cheyns, J. Poortmans, P. Heremans, C. Deibel, S. Verlaak, B. P. Rand, and J. Genoe, *Phys. Rev. B* **77**, 165332 (2008).
 - [24] S. R. Cowan, A. Roy, and A. J. Heeger, *Phys. Rev. B* **82**, 245207 (2010).
 - [25] N. C. Giebink, G. P. Wiederrecht, M. R. Wasielewski, and S. R. Forrest, *Phys. Rev. B* **82**, 155305 (2010).
 - [26] W. Tress, K. Leo, and M. Riede, *Phys. Rev. B* **85**, 155201 (2012).
 - [27] J. A. Barker, C. M. Ramsdale, and N. C. Greenham, *Phys. Rev. B* **67**, 075205 (2003).
 - [28] L. J. A. Koster, V. D. Mihailetschi, R. Ramaker, and P. W. M. Blom, *Appl. Phys. Lett.* **86**, 123509 (2005).
 - [29] U. Rau, *Phys. Rev. B* **76**, 085303 (2007).
 - [30] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, and J. V. Manca, *Nat. Mater.* **8**, 904 (2009).
 - [31] T. Kirchartz, B. E. Pieters, J. Kirkpatrick, U. Rau, and J. Nelson, *Phys. Rev. B* **83**, 115209 (2011).
 - [32] T. Kirchartz, K. Taretto, and U. Rau, *J. Phys. Chem. C* **113**, 17958 (2009).
 - [33] N. C. Giebink, G. P. Wiederrecht, M. R. Wasielewski, and S. R. Forrest, *Phys. Rev. B* **83**, 195326 (2011).
 - [34] L. J. A. Koster, S. E. Shaheen, and J. C. Hummelen, *Adv. Energ. Mater.* **2**, 1246 (2012).
 - [35] S. Massip, P. M. Oberhumer, G. Tu, S. Albert-Seifried, W. T. S. Huck, R. H. Friend, and N. C. Greenham, *J. Phys. Chem. C* **115**, 25046 (2011).
 - [36] V. D. Mihailetschi, P. W. M. Blom, J. C. Hummelen, and M. T. Rispens, *J. Appl. Phys.* **94**, 6849 (2003).
 - [37] C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, and J. C. Hummelen, *Adv. Funct. Mater.* **11**, 374 (2001).
 - [38] Y. Luo, H. Aziz, R. Klenkler, G. Xu, and Z. D. Popovic, *Chem. Phys. Lett.* **458**, 319 (2008).
 - [39] S. Tuladhar, D. Poplavsky, S. Choulis, J. Durrant, D. Bradley, and J. Nelson, *Adv. Funct. Mater.* **15**, 1171 (2005).
 - [40] B. C. Thompson and J. M. J. Fréchet, *Angew. Chem. Int. Ed.* **47**, 58 (2008).
 - [41] K. Akaike, K. Kanai, H. Yoshida, J. Tsutsumi, T. Nishi, N. Sato, Y. Ouchi, and K. Seki, *J. Appl. Phys.* **104**, 023710 (2008).
 - [42] K. Tvingstedt, K. Vandewal, A. Gadisa, F. Zhang, J. Manca, and O. Inganäs, *J. Am. Chem. Soc.* **131**, 11819 (2009).
 - [43] Z.-L. Guan, J. B. Kim, H. Wang, C. Jaye, D. A. Fischer, Y.-L. Loo, and A. Kahn, *Org. Electron.* **11**, 1779 (2010).
 - [44] J. M. Ball, R. K. M. Bouwer, F. B. Kooistra, J. M. Frost, Y. Qi, E. B. Domingo, J. Smith, D. M. de Leeuw, J. C. Hummelen, J. Nelson, A. Kahn, N. Stingelin, D. D. C. Bradley, and T. D. Anthopoulos, *J. Appl. Phys.* **110**, 014506 (2011).