Influence of a Thermal Bath on The Transport Properties of an Open Molecular Junction

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Recent advances in nanotechnology paves the way into molecular electronics, with MJ as an important building block[1, 2]. MJ which are molecular sized quantum dots (QDs) that connect electrical leads, have been the subject of many experimental and theoretical studies [3–9].

One main difference between large QDs and MJ is that in the latter there exist a noticeable electron-phonon coupling. This coupling substantially affects transport properties of the system and may result in phenomena such as Frank-Condon blockade, negative differential resistance, etc[10–12].

Our model consists of a single level MJ which connects two leads. Moreover, electrons on the MJ are coupled to a single frequency phonon mode. This phonon mode is in contact to another thermal phonon bath. The Hamiltonian of this system is

\[ \hat{H} = \hat{H}_m + \hat{H}_{leads} + \hat{H}_{tun} + \hat{H}_{bath} + \hat{H}_{m-bath}, \]  

\[ \hat{H}_m = \epsilon_d \hat{n}_d + \Omega \hat{b} \hat{b}^\dagger + \lambda \Omega \hat{n}_d \left( \hat{b} + \hat{b}^\dagger \right), \]  

\[ \hat{H}_{leads} = \sum_{k,\alpha \in \{ R, L \}} \epsilon_{k,\alpha} \hat{a}^\dagger_{k,\alpha} \hat{a}_{k,\alpha}, \]  

\[ \hat{H}_{tun} = \sum_{k,\alpha \in \{ R, L \}} V_{k,\alpha} \hat{a}^\dagger_{k,\alpha} h.c., \]  

\[ \hat{H}_{bath} = \sum_{\nu} \Omega_\nu \hat{b}^\dagger_\nu \hat{b}_\nu, \]  

and

\[ \hat{H}_{m-bath} = \sum_{\nu} \gamma_\nu (\hat{b}^\dagger \hat{b} + \hat{b}^\dagger \hat{b}^\dagger + \hat{b}^\dagger + \hat{b}^\dagger + \hat{b}), \]

where \( \hat{c} (\hat{c}^\dagger) \) is the annihilation (creation) operator of electrons on MJ, \( \hat{n}_d = \hat{c}^\dagger \hat{c} \) is the number operator and \( \epsilon_{d0} \) is the onsite energy of electrons on the MJ. \( \hat{b}(\hat{b}^\dagger) \) is the
annihilation (creation) operator of phonons on MJ, \( \Omega \) is the phonon frequency and \( \lambda \) determines electron-phonon coupling. Moreover, \( \hat{a}_{\alpha} (\hat{a}^{\dagger}_{\alpha}) \) annihilates (creates) an electron in the state \( k \) of the lead \( \alpha \) (\( \alpha = R, L \)), and \( V_{k,\alpha} \) determines the electron hopping between MJ and the leads. \( \hat{b}_{\nu} (\hat{b}^{\dagger}_{\nu}) \) is the annihilation (creation) operator of mode \( \nu \) of the thermal bath, \( \Omega_{\nu} \) is the energy of this mode, and \( \gamma_{\nu} \) determines the coupling strength of this mode with MJ phonons.

Performing the Lang-Firsov transformation as \( e^{\hat{S}} \hat{H} e^{-\hat{S}} \) (where \( \hat{S} \equiv \lambda \hat{n}_{\alpha} (\hat{b}^{\dagger}_{\nu} - \hat{b}_{\nu}) \)), renormalizing the onsite energy to \( \epsilon_{\alpha} = \epsilon_{\alpha 0} - \lambda^{2} \Omega \) and following the standard steps for deriving a Markovian ME in the limit of weak lead to MJ coupling, would result in the dynamics of the density matrix (DM) of the system (where by system we mean MJ electrons and phonons). It is straightforward to show that the rate of change of DM (\( \frac{d\rho}{dt} \)) at any time is diagonal, provided that DM is diagonal at that time. Therefore, if the initial DM is diagonal, by mathematical induction we conclude that the DM will remain diagonal at all times. In such cases where all the off-diagonal terms vanish, the ME can be stated as the rate of change of the diagonal elements of DM as follow

\[
\frac{d}{dt} P_{0m} = \sum_{m',\alpha} \Gamma_{\alpha} \left( 1 - f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) \right) |\hat{X}_{mm'}|^{2} P_{1,m'} - f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) |\hat{X}_{mm'}|^{2} P_{0m} + \hat{\mathcal{L}}_{b}(P_{0m}),
\]

\[
\frac{d}{dt} P_{1m} = \sum_{m',\alpha} \Gamma_{\alpha} \left( f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) - 1 + f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) \right) |\hat{X}_{mm'}|^{2} P_{0,m'} - f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) |\hat{X}_{mm'}|^{2} P_{1,m} + \hat{\mathcal{L}}_{b}(P_{1m}),
\]

where \( P_{im} \) (\( i \), \( m \) represent diagonal elements of DM and determine the probability of having \( i \) electrons in MJ and \( m \) phonons being excited. Moreover, \( \hat{X} \equiv \exp[\lambda (\hat{b}^{\dagger}_{\nu} - \hat{b}_{\nu})] \), and \( f_{\alpha}(\omega) = \frac{1}{e^{\beta_{\alpha}(\omega + \mu_{\alpha})} - 1} \) is the Fermi distribution of lead \( \alpha \), in which \( \mu_{\alpha} \) is chemical potential of the lead and \( \beta_{\alpha} \) is its inverse temperature. \( \Gamma_{\alpha} \) determines the tunneling rate of electrons between MJ and lead \( \alpha \), which is defined to be \( \Gamma_{\alpha} (\omega) = \sum_{k} 2\pi |V_{k,\alpha}|^{2} \delta (\epsilon_{k} - \omega) \). In wide band limit (WBL), we take \( \Gamma_{\alpha} \) to be independent of \( \omega \). \( \hat{\mathcal{L}}_{b}(P_{im}) \) is

\[
\hat{\mathcal{L}}_{b}(P_{im}) = \Gamma_{P} [1 + N_{bath}(\Omega)] [m + 1] P_{i,m+1} - m P_{i,m}], \quad \Gamma_{p} \equiv \gamma_{p} \Omega_{p} \equiv \frac{1}{k_{B} T_{p}}
\]

in which \( N_{bath}(\Omega) = \frac{1}{e^{\beta_{b}(\Omega)} - 1} \) is the number of phonons with frequency \( \Omega \) in the thermal bath (given by Bose-Einstein distribution function), in which \( \beta_{b} = \frac{1}{k_{B} T_{b}} \) is the inverse temperature of the phonon bath. Moreover, \( \Gamma_{p} = \sum_{\nu} 2\pi \gamma_{p}^{2} \delta (\Omega - \Omega_{\nu}) \), determines the thermalization rate of MJ phonons.

It is noticeable that Eqs. 7 and 8 reduce to the ME given by Kosov, if we set \( \Gamma_{p} = 0 \). On the other hand, if we remove the leads, these equations would determine the dynamic of a phonon system coupled to a thermal bath.

The number of electrons in MJ is \( N_{e} = \sum_{\alpha} P_{1m} \). The electrical currents from the leads to the MJ determine the rate of change of electron population, i.e., \( \frac{dN_{e}}{dt} = \sum_{\alpha} I_{\alpha} \). Comparison with Eq. 8, the relation for current from lead \( \alpha \) to the MJ is obtained as

\[
I_{\alpha} = \Gamma_{\alpha} \sum_{m' \neq m} \left[ -f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) |\hat{X}_{mm'}|^{2} P_{1,m'} + f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) |\hat{X}_{mm'}|^{2} P_{0,m'} \right], \quad \text{(10)}
\]

and the total current passing through the MJ is \( I = (I_{L} - I_{R})/2 \).

The number of phonons in MJ is \( N_{ph} = \sum_{m} m (P_{0m} + P_{1m}) \). The heating rate of MJ is \( q = \Omega \frac{dN_{ph}}{dt} \). This \( q \) is sum of two terms \( q_{0} \) and \( q_{1} \), where \( q_{0} = \sum_{m} \Omega m \frac{dP_{0m}}{dt} \), \( q_{1} = \sum_{m} \Omega m \frac{dP_{1m}}{dt} \). Each of these heat transfer/ generation rates can be decomposed to terms that come from electronic current and thermal bath coupling. For the first part we use the index \( i \), while the second part is shown by the index \( b \). Comparison with Eqs. 7 and 8 suggests that we have the following relations for heat transfer rates:

\[
q_{0i} = \sum_{\alpha, m', m} \Omega_{\alpha} m \Gamma_{\alpha} \left[ 1 - f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) \right] |\hat{X}_{mm'}|^{2} P_{1,m'} - f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) |\hat{X}_{mm'}|^{2} P_{0,m'},
\]

\[
q_{1i} = \sum_{\alpha, m', m} \Omega_{m} \Gamma_{\alpha} \left( f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) - 1 + f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) \right) |\hat{X}_{mm'}|^{2} P_{0,m'} - f_{\alpha} (\Omega (m' - m) + \epsilon_{\alpha}) |\hat{X}_{mm'}|^{2} P_{1,m},
\]

\[
q_{ib} = \sum_{\alpha, m} \Omega_{m} \Gamma_{\alpha} [1 + N_{bath}(\Omega)] [(m + 1) P_{i,m+1} - m P_{i,m}] + \Gamma_{p} N_{bath}(\Omega) |m P_{i,m+1} - m P_{i,m}|, \quad i = 0, 1
\]

In steady state the probabilities don’t change, consequently, \( q_{0i} = -q_{ib} \), which means that any heat that is produced (consumed) by electrical current, is transferred to (compensated by) the phonon thermal bath.

In order to better understand the role of thermal bath, it would be useful to assign an effective temperature to the MJ according to the Bose-Einstein distribution function

\[
T_{MJ} = \frac{\Omega_{p}}{k_{B} \ln \frac{N_{ph} + 1}{N_{ph}}}.
\]

With these tools, we can investigate the effect of a thermal bath on the electrical current and study the heat transfer between the bath and MJ, which is the subject of the next section.
FIG. 1. The current as a function of bias voltage, for the NTB case (solid-black curve), and the cases where a thermal bath is coupled to the MJ. The lead temperature is $T_l = 0.1$ and the temperatures of thermal bath are indicated in the plot. For the cases where we have thermal bath, $\Gamma_p = 0.01$.

FIG. 2. The effective temperature of the MJ, $T_{MJ}$, as a function of bias voltage for the same situations as Fig. 1.

III. NUMERICAL RESULTS

In this section we represent our numerical results. We work in a system of units in which $e = \hbar = 1$. Also, the Boltzmann constant, $k_B$, is taken to be 1. We set the phonon frequency to be our energy unit, i.e., $\Omega = 1$. These automatically set our units of time and electrical current. Moreover, $\lambda = 1$ and the bias voltage is applied symmetrically, so that $\mu_L = -\mu_R = V/2$, and we consider $\epsilon_d = 0$. In this work, we don’t consider the temperature gradient between the leads and set both leads to be at the same temperature $T_i$. Finally, the tunneling rates between MJ and the leads are assumed to be $\Gamma_L = \Gamma_R = 0.01$.

The first case we investigate is when the leads temperature is low. Fig. 1 shows the current through MJ as a function of bias voltage, for the lead temperature $T_l = 0.1$. In this figure, the solid-black curve corresponds to the case where we have no thermal bath coupled to our MJ (the NTB case). Other curves represent the situation in which the MJ is also coupled to the thermal bath with coupling strength determined by $\Gamma_p = 0.01$. As it is shown in this figure, when the temperature of bath, $T_b$, is greater than the lead temperature $T_l$, up to some critical bias voltage (which we show by $V_c$) the current is less than its value for the NTB case, i.e., the thermal bath reduces the current. However, for higher bias voltages, the current is greater than that of NTB case and the thermal bath increases the current. On the other hand, for the case where $T_b < T_l$, the current is always greater than the NTB case. In order to understand this behavior, in Fig. 2 the effective temperature of MJ, $T_{MJ}$, is depicted for similar parameters as Fig. 1. Electron current through MJ excites phonons and increases $T_{MJ}$. As long as $T_{MJ}$ in the NTB case is less than $T_b$, coupling to the bath results in a heat flow from the bath to the junction, which means there would be more phonons to resist electron current (in other words, the so called Franck-Condon blockade is increased). Moreover, this heat flow increases $T_{MJ}$ with respect to the NTB case. On the other hand, when by increasing the bias voltage and exciting more phonons in the MJ, $T_{MJ}$ in the NTB case gets larger than $T_b$, the direction of heat flow would become from the MJ to the bath, which means less phonons and consequently less resistance and lesser $T_{MJ}$. This discussion clarifies that $V_c$ is the voltage at which $T_{MJ}$ in the NTB case equals $T_b$. For the case where $T_b < T_l$, even at zero bias $T_{MJ} > T_b$, and increasing the voltage just increases $T_{MJ}$, therefore the heat flow is always from MJ to the bath, and the current is always greater than the NTB case.

In Fig. 3, the rates of MJ heating due to current ($q_I$) and thermal bath ($q_b$) as functions of bias voltage for $T_l = 0.1$ and $T_b = 0.05$, 2. Other parameters are same as Fig. 1.
FIG. 4. The current as a function of bias voltage, for the NTB case (solid-black curve), and the cases where a thermal bath is coupled to the MJ. The lead temperature is \( T_l = 1.5 \) and the temperatures of thermal bath are indicated in the plot. For the cases where we have thermal bath, \( \Gamma_p = 0.01 \).

thermal bath (\( q_b \)) are depicted as functions of bias voltage for \( T_l = 0.1 \) and \( T_b = 0.05 \). As it is seen, the signs of heat flows are in consistence with the foregoing discussion. Moreover, for \( T_b = 2 \) at the critical bias voltage \( V_c \), both \( q_I \) and \( q_b \) vanish and there would be no heat flow between MJ and bath. For \( T_b = 0.05 \) where the lead temperature is greater than bath, \( q_b \) is always negative, which means that the heat flows from the MJ to the leads. On the other hand, \( q_I \) is always positive in this case and electron current heats the MJ up.

The same behavior is seen when the leads are at high temperature, except that since the electrons get distributed around the chemical potential of leads, the step-wise behavior that is the finger print of the phonon side-bands disappears. In Fig.4 the current and in Fig.5 the effective temperature of MJ as functions of bias voltage are shown for \( T_l = 1.5 \) and \( T_b = 0.5 \) and 3. When \( T_b < T_l \) the bath sucks the phonons from MJ, therefore the current is increased while \( T_{MJ} \) is decreased with respect to the NTB case. On the other hand, for \( T_b > T_l \), if the bias voltage is lesser (greater) than a critical voltage \( V_c \), the current is decreased (increased) and \( T_{MJ} \) is increased (decreased) with respect to the NTB case.

We expect that by increasing \( \Gamma_p \) (or in other words, increasing the coupling strength between the bath and MJ), the phonons on our MJ get thermalized. This means that \( T_{MJ} \) becomes less voltage dependent and stays close to \( T_B \). This behavior is depicted in Fig.6 where \( T_{MJ} \) is plotted for low temperature leads (\( T_l = 0.1 \)) and bath temperature of \( T_b = 2 \), for three cases of \( \Gamma_p = 0.01 \), \( \Gamma_p = 0.05 \) and \( \Gamma_p = 0.1 \).

As we already mentioned, the critical voltage \( V_c \) is the voltage at which the effective temperature of MJ in the NTB case equals the bath temperature (and it is independent of \( \Gamma_p \)). Consequently, by computing \( T_{MJ} \) as a function of bias voltage and inverting the curves, one can obtain \( V_c \) as a function of \( T_b \) for a given lead temperature. This is done in Fig.7 for two values of \( T_l = 0.1 \) and 1.5. For the bath temperatures below \( T_l \), there is no such critical voltage.

IV. CONCLUSIONS

In conclusion, we considered a current carrying MJ coupled to a single frequency phonon mode that can be either isolated from other environments or be coupled to another phononic thermal bath. For the bath temperatures greater than the leads temperature, we showed...
that at bias voltages lower than a critical value $V_c$, the thermal bath would heat up the MJ and reduces the current. However, for higher bias voltages, the thermal bath cools down the MJ and increases the current. This critical bias voltage is the bias voltage at which the effective temperature of MJ in the NTB case is equal to the bath temperature. On the other hand, if the bath temperature is less then the leads, there would be always a heat flow from the MJ to the bath, and the bath helps increasing the electrical current through MJ. This behavior is seen for both low and high temperature leads, with the difference that in the former, the step-wise behavior in the current-voltage characteristic which stems from the phonon side-bands is clearly seen.

If we increase the coupling strength of the MJ phonons with the thermal bath, $T_{MJ}$ looses its dependence on bias voltage and stays close to $T_b$, or in other words, the phonons get thermalized, as we physically expect.

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