Reply to "Comment on ‘Theory of Phonon-Assisted Adsorption in Graphene: Many-Body Infrared Dynamics’"

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Based on a new self-energy for atom-phonon interaction, preceding Comment argues about the insufficiency of the mathematical techniques within the Independent Boson Model (IBM) to study physisorption in graphene membranes. In this Reply, we show that the new self-energy reported in the Comment is a perturbative expansion approximated for a 2-phonon process, severely divergent for membrane sizes larger than 100 nm and within its current mathematical form, ill-suited for investigating the physics of physisorption in graphene micromembranes. Additionally, we provide further evidence of the adsorption rate within the IBM that further reinforces the physical soundness of the mathematical techniques reported in Phys. Rev. B 100, 075429 (2019).

The main point of our paper is: adsorption rate of low-energy atoms impinging normally on suspended, µm sized graphene membranes is finite, approximately equal to the adsorption rate predicted by Fermi’s golden rule. To arrive at this conclusion, we have used the Independent Boson Model (IBM) that captures the interaction between the incoming atom and the phonons of the graphene membrane. Our mathematical technique for the calculation of the adsorption rate includes a self-energy formalism within the context of the IBM.

In the Comment, author provides with a new self-energy for the atom-phonon interaction which goes beyond the IBM and includes additional terms that are absent in our work. Author then adapts our method for the calculation of the adsorption rate and extends it to this new self-energy. Within our formalism, he finds that the new self-energy fails to provide with a self-consistent solution. Author thus concludes that the failure of the new self-energy to give self-consistent solution must imply the invalidity of our mathematical formalism.

Additionally, while the Comment dismisses our method as invalid, it does not provide with a mathematical technique that calculates the adsorption rate within this new self-energy. Thus, the Comment eludes the main point of our paper and remains inconclusive about the adsorption rate of incoming atoms.

In this Reply, we will first discuss some of the fundamentally important features of the new self-energy reported in the Comment. We will then argue as to which one is invalid: our mathematical method to compute the adsorption rate or the new self-energy reported in the Comment. Finally, we will conclude our Reply with further evidence of the adsorption rate within the IBM that reinforces the physical soundness of the mathematical technique reported in Ref. 1.

Let us begin with our analysis of the new self-energy reported in the Comment. Throughout our Reply, we will refer to this self-energy as $\Sigma$. Eq. (5) and Eq. (6) of the Comment (see Ref. 2) gives the new self-energy as

\[
\Sigma^c(E) = g_{kb}^2 \sum_q \left( 2\Lambda\lambda_q - 2n_q^2\lambda_q^2 \right) G_{IBM}(E) - \sum_{p,q} \lambda_p\lambda_q \left( 1 + 2n_qn_p + n_q + n_p \right) G_{IBM}(E) \\
+ g_{kb}^2 \sum_q \left( n_q(2\lambda\lambda_q + 1) + 2n_q^2\lambda_q^2 \right) G_{IBM}(E + \omega_q) + \left( (n_q + 1)(1 - 2\Lambda\lambda_q) + 2n_q\lambda_q^2 \right) G_{IBM}(E - \omega_q) \\
+ g_{kb}^2 \sum_q \left( n_q\lambda_q^2(1 - n_q)G_{IBM}(E + \omega_q + \omega_q) - (n_q + 1)\lambda_q^2n_qG_{IBM}(E - \omega_q - \omega_q) \right) \\
+ g_{kb}^2 \sum_{p,q} \left[ n_qn_p\lambda_q\lambda_p G_{IBM}(E + \omega_q + \omega_p) + (n_q + 1)(n_p + 1)\lambda_p\lambda_q G_{IBM}(E - \omega_q - \omega_p) \right. \\
\left. - (n_q + 1)n_p\lambda_q\lambda_p G_{IBM}(E - \omega_q + \omega_p) - (n_p + 1)n_q\lambda_q\lambda_p G_{IBM}(E + \omega_q - \omega_p) \right],
\]

where $g_{kb}$ is the vertex of atom-phonon interaction for a transition of atom from continuum to the bound state and $g_{bb}$ is the vertex of atom-phonon coupling for interaction in the bound state. $\lambda_p = g_{bb}/\omega_p$, $\Lambda = \sum_p \lambda_p$ and $n_q$ is the equilibrium phonon occupation number with Bose-Einstein distribution written as $n_q = 1/(e^{\omega_q/\hbar T} - 1)$.

The Comment (see Ref. [2]) gives the new self-energy as

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+ g_{kb}^2 \sum_q \left( n_q(2\lambda\lambda_q + 1) + 2n_q^2\lambda_q^2 \right) G_{IBM}(E + \omega_q) + \left( (n_q + 1)(1 - 2\Lambda\lambda_q) + 2n_q\lambda_q^2 \right) G_{IBM}(E - \omega_q) \\
+ g_{kb}^2 \sum_q \left( n_q\lambda_q^2(1 - n_q)G_{IBM}(E + \omega_q + \omega_q) - (n_q + 1)\lambda_q^2n_qG_{IBM}(E - \omega_q - \omega_q) \right) \\
+ g_{kb}^2 \sum_{p,q} \left[ n_qn_p\lambda_q\lambda_p G_{IBM}(E + \omega_q + \omega_p) + (n_q + 1)(n_p + 1)\lambda_p\lambda_q G_{IBM}(E - \omega_q - \omega_p) \right. \\
\left. - (n_q + 1)n_p\lambda_q\lambda_p G_{IBM}(E - \omega_q + \omega_p) - (n_p + 1)n_q\lambda_q\lambda_p G_{IBM}(E + \omega_q - \omega_p) \right],
\]

with further evidence of the adsorption rate within the IBM that further reinforces the physical soundness of the mathematical techniques reported in Phys. Rev. B 100, 075429 (2019).
where $\omega_q$ is the energy of the phonon with wave vector $q$ and $T$ is the temperature of the membrane. $G_{\text{IBM}}$ is the bound state Green’s function written within the IBM (given by Eq. (28) and Eq. (29) in Ref. [1]) and $E = E_b + E_k$ with $-E_b$ as the bound state energy and $E_k$ is the incoming energy of the atom.

Our points of disagreement concerning the form of $\Sigma^r(E)$ (given by Eq. (1)) are the following:

1.) While the Comment reports $\Sigma^r(E)$ as an exact closed-form expression for the atom self-energy to quadratic order in the atom-phonon coupling $O(g^2_{kb})$, we see that it is in fact a perturbative expansion in $\Sigma^r(E)$, truncated till a 2-phonon process. The definition of exact self-energy corresponds to summation of infinite number of Feynman diagrams which essentially implies the inclusion of the contribution from infinitely many phonons.

By energy conservation one can readily see that the propagators in Eq. (1): $G_{\text{IBM}}^r(E - \omega_q)$ corresponds to 1-phonon emission with energy $\omega_q$ and $G_{\text{IBM}}^r(E - \omega_q - \omega_p)$, $G_{\text{IBM}}^r(E - \omega_q - \omega_p)$, $G_{\text{IBM}}^r(E - \omega_q + \omega_p)$, $G_{\text{IBM}}^r(E - \omega_q + \omega_p)$ correspond to 2-phonon emission processes with energies $\omega_q$ and $\omega_p$.

(2.) In the first line of Eq. (1), we see that the bound state propagator is written as $G_{\text{IBM}}^r(E)$. By energy conservation, this implies that the energy of the phonon is set to $\omega_q = 0$. However, the vertex of interaction is written as $g^2_{kb}$. We remind ourselves that the definition of the vertex $g_{kb}$ for the model Hamiltonian in Refs. [1][4][2] refers to the transition matrix element.

$$g_{kb} = -\langle b, 1_q|H_i|k, 0 \rangle,$$

where $H_i$ is the Hamiltonian for atom-phonon interaction and $|k, 0\rangle$ represents the initial state of the atom with energy $E_k$ and $|0\rangle$ is the graphene membrane in its ground state with no excitation. $|b\rangle$ is the final bound state with energy $-E_b$ and $|1_q\rangle$ represents excitation of 1 phonon with energy $\omega$ and wave vector $q$. Physically, Eq. (2) corresponds to the transition of atom from $|k\rangle$ to $|b\rangle$ via the emission of 1 phonon of energy $\omega$ and wave vector $q$. A similar definition exists for the vertex $g_{kb}$ which is the transition of the atom within bound states $|b\rangle$ via the emission of phonon of energy $\omega_q$. In other words, if the vertex $g_{kb}$ is used, it would imply an emission of phonon of energy $\omega_q$, which then appears via energy conservation in the expression for the bound state propagator $G_{\text{IBM}}^r(E)$. Therefore, the first line which is written with a propagator $G_{\text{IBM}}^r(E)$, represents a process that involves no emission of phonon $\omega_q$, thus the use of the vertex $g_{kb}$ in such a situation is unjustified. Thus, within the definition of the vertices of atom-phonon coupling, the first line of Eq. (1) is inaccurate.

Armed with arguments (1.) and (2.), let us now proceed to understand the variation of the real part of the self-energy with the infrared (IR) cut-off $\epsilon$. The IR cut-off is related to the size of the graphene membranes by the relation $\epsilon = h v_s / L$, where $v_s$ is the velocity of sound in graphene and $L$ is the size of the membrane. Thus a decreasing $\epsilon$ physically corresponds to increasing membrane sizes. In what follows next, we will stick to the notations, labels and units consistent with the Comment unless otherwise mentioned.

In Fig. 1, we plot the variation of $\bar{\Sigma}^r_{\text{IBM}}$ (dimensionless real part of Eq. (1)) with $\epsilon$. For comparative purposes, we also show the variation of the dimensionless real part of the self-energy within IBM (real part of Eq. (6) in Ref. [1]). Let us summarize our understanding and give further points of disagreements with the Comment as the following:

3.) We note for $\epsilon \leq 0.5$ K, $\bar{\Sigma}^r_{\text{IBM}}$ (blue dashed line) starts to diverge with decreasing $\epsilon$ (increasing size of graphene membranes). In comparison, $\bar{\Sigma}^r_{\text{IBM}}$ within IBM (red line) is well-behaved for the same range of IR cut-off (size of membrane). Comment has reported these severe effects of IR divergence as mere downward shifts in the real part of the self-energy (not to mention, the absolute absence of physical justification for the presence of these IR divergences in a model of weak atom-phonon coupling). Mathematically, such a severe IR divergence signals the breakdown of the perturbation series, which implies that the perturbative expansion given by Eq. (1) is ill-behaved for $\epsilon \leq 0.5$ K (membrane size $> 100$ nm). Furthermore, Kinoshita-Lee-Nauenberg theorem tells us that these IR divergences are physically unreal, hence proper resumations (non-perturbative techniques) need to be implemented to tackle these IR divergences with an effort to gain meaningful physical results. Our formalism of self-energy within the IBM in Ref. [1] is in fact a resummation technique that was implemented to tackle the severe IR divergences which appear with the inclusion of the effects from the atom-phonon coupling in the bound state.
(4.) Previously in point (2.), we mentioned about the inaccuracy of the first line in Eq. (1). It is to be noted that there is a contribution to the leading order divergence in $\Sigma^c$ in the limit of $\epsilon \to 0$ that originates from the term

$$- \sum_q 2n_q \lambda^2_G \delta \exp (E_q) = - \frac{1}{\epsilon^3} \left[ \frac{2g_0^2 \gamma^2}{3} G^{\text{IBM}} (E) \right] \to -\infty.$$  

(3)

With the knowledge of points (3.) and (4.), let us now state our final points of disagreements with the arguments provided in the Comment for the invalidity of our method for the calculation of the adsorption rate.

(5.) Utilizing the real ($\Sigma_r$) and imaginary part of the self-energy ($\Sigma_i$), the adsorption rate $\Gamma$ within our method is given as

$$\Gamma \approx -2Z \Sigma_i (E_p),$$  

(4)

where the quasiparticle weight $Z$ is

$$Z = \left( 1 - \frac{\partial \Sigma_i(E)}{\partial E} \bigg|_{E=E_p} \right)^{-1},$$  

(5)

$E_p$ is the quasiparticle energy that can be solved via

$$E_p - E_k = \Sigma_r (E_p).$$  

(6)

Using the real part of the self-energy $\Sigma^c_r$ (given by real part of Eq. (1)), Comment attempts to find a graphical solution to Eq. (6). For low-energy atoms, author finds no self-consistent solution in the range of $\epsilon \leq 0.4$ K (see Fig. 6 in Comment[2]). This failure is rather obvious for an infinite (divergent) self-energy plugged in the rhs of Eq. (6) (see the IR divergent behavior of $\Sigma^c_r$ in Fig. 1). In contrast, the IBM self-energy which is well-behaved for similar ranges of IR cut-off, succeeds to give self-consistent solution to Eq. (6), also evident from the Fig. 5 and Fig. 6 of the Comment.

Before we conclude, let us provide with an additional calculation of the adsorption rate of low-energy atoms using the self-energy within IBM. This calculation clarifies some of the inaccurate representation of our results provided in the Comment. In Fig. 2, we show the variation of the normalized adsorption rate $\Gamma/\Gamma_0$ as a function of the IR cut-off ($\epsilon$). Here, $\Gamma_0$ is the Fermi’s golden rule result. One can see that for a large range of IR cut-offs that corresponds to membrane sizes 100 nm $\sim$ 10μm, the adsorption rate $\Gamma \approx \Gamma_0$. In the very low IR cut-off regime ($\epsilon \leq 0.1$ K), we find small increments to the adsorption rate ($\Gamma$ is still within 0.27 % of $\Gamma_0$, see inset of Fig. 2). Comment mentions there is a divergence in our results which becomes apparent for $\epsilon \leq 0.1$ K. We point out that this increment in the adsorption rate physically represents the temperature effect of the Bose-Einstein distribution obeyed by the thermal phonons in the graphene membrane. As temperature (or size of the membrane) is increased (decreasing $\epsilon$), there is an enhancement of the probability of emission of low-energy thermal phonons, leading to an increase in adsorption rate[13].

In conclusion, Comment[2] has reported a new self-energy which is a perturbative expansion approximated for a 2-phonon process. This approximation is ill-behaved for low IR cut-offs (large membrane sizes) and suffers from severe divergences. The leading order contribution to the divergence originates from a term that is not allowed within our model in the context of the definition of the vertex of atom-phonon coupling $g_{\text{IB}}$[14]. Owing to this severe IR divergence, this new self-energy fails to predict adsorption rate for membrane sizes greater than 100 nm (IR cut-off $\epsilon \leq 0.5$ K). Unless proper re-summations are performed with appropriate placement of atom-phonon coupling, this divergent self-energy reported in the Comment remains unsuitable for physisorption studies in graphene micromembranes. In contrast, the self-energy within IBM, reported in Ref. 1 is a re-summed self-energy, well-behaved for the same range of IR cut-off (see Fig. 1) and is conclusive about the adsorption rate for a large range of membrane sizes 100 nm $\sim$ 10μm, suitably capturing the physics of temperature and finite size effects. It is important that we point out that within the simple model of IBM implemented for graphene physisorption, our work[1] has revealed that the zero adsorption rate predicted by Ref. [5] is only possible if one considers (i) contribution to adsorption rate from the long time regime, where the effects of Franck-Condon factor sets in and (ii) neglects the effects of thermal phonon emission. Points (i) and (ii) are indeed the regime of study in Ref. [5] and Ref. [4], respectively. However, if we consider the contribution to
adsorption rate from full time regime and do not neglect the effects of thermal phonon emission (which is imminent for finite temperature physics), the adsorption rate will be finite, equal to Fermi’s Golden rule\textsuperscript{11,12}, and in accordance with Bloch-Nordsieck theorem.\textsuperscript{9}

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\textsuperscript{1} S. Sengupta, Phys. Rev. B \textbf{100}, 075429 (2019).
\textsuperscript{2} D. P. Clougherty, arXiv:1910.00361 (2019).
\textsuperscript{3} G. D. Mahan, \textit{Many-Particle Physics} (Plenum Press, New York, 1981).
\textsuperscript{4} D. P. Clougherty, Phys. Rev. B \textbf{96}, 235404 (2017).
\textsuperscript{5} D. P. Clougherty, Phys. Rev. B \textbf{90}, 245412 (2014).
\textsuperscript{6} Y. Zhang and D. P. Clougherty, Phys. Rev. Lett. \textbf{108}, 175302 (2012).
\textsuperscript{7} T. Kinoshita, Journal of Mathematical Physics \textbf{3}, 650 (1962), http://dx.doi.org/10.1063/1.1724268.
\textsuperscript{8} T. D. Lee and M. Nauenberg, Phys. Rev. \textbf{133}, B1549 (1964).
\textsuperscript{9} F. Bloch and A. Nordsieck, Phys. Rev. \textbf{52}, 54 (1937).
\textsuperscript{10} S. Sengupta, V. N. Kotov, and D. P. Clougherty, Phys. Rev. B \textbf{93}, 235437 (2016).
\textsuperscript{11} B. Lepetit and B. Jackson, Phys. Rev. Lett. \textbf{107}, 236102 (2011).
\textsuperscript{12} B. Lepetit and B. Jackson, Phys. Rev. Lett. \textbf{113}, 069602 (2014).