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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, the preceding Comment [Phys. Rev. B **101**, 247401 (2020)] argues about the insufficiency of the mathematical techniques within the independent boson model (IBM) to study physisorption in graphene membranes. In this Reply, I show that the new self-energy reported in the Comment is a perturbative expansion approximated for a two-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, I provide further evidence of the adsorption rate within the IBM that reinforces the physical soundness of the mathematical techniques reported in Phys. Rev. B **100**, 075429 (2019).

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The main point of my paper [1] is as follows: adsorption rate of low-energy atoms impinging normally on suspended micrometer-sized graphene membranes is *finite*, approximately equal to the adsorption rate predicted by Fermi's golden rule. To arrive at this conclusion, I have used the independent boson model (IBM) that captures the interaction between the incoming atom and the phonons of the graphene membrane. My mathematical technique for the calculation of the adsorption rate includes a self-energy formalism within the context of the IBM [1].

In the Comment [2], the author questions the validity of my *finite* adsorption result, and in that attempt, provides with a new self-energy for the atom-phonon interaction which includes additional terms that go beyond the IBM self-energy and are, thus, absent in my work [1]. The author then adapts my method for the calculation of the adsorption rate and extends it to this new self-energy. Within my formalism, he finds that the new self-energy fails to provide a self-consistent solution. The author, thus, concludes that the failure of the new self-energy to give a self-consistent solution must imply the invalidity of my mathematical formalism.

Additionally, although the Comment [2] dismisses my method as invalid, it *does not* provide a mathematical technique that calculates the adsorption rate within this new self-energy. Thus, the Comment [2] eludes the main point of my paper and remains inconclusive about the adsorption rate of incoming atoms.

In this Reply, I will first discuss some of the fundamentally important features of the new self-energy reported in the Comment [2]. I will then show which one is invalid: My mathematical method to compute the adsorption rate or the new self-energy reported in the Comment [2]. Finally, I will conclude my 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 me begin with *my analysis* of the new self-energy reported in the Comment [2]. Throughout my Reply, I will refer to this self-energy as Σ^c. Equations (5) and (6) of the Comment (see Ref. [2]) give the new self-energy as [2]

$$\begin{aligned}
\Sigma^c(E) = g_{kb}^2\Bigg[\sum_q \left(2\Lambda\lambda_q - 2n_q^2\lambda_q^2\right)G^{\mathrm{IBM}}(E) - \sum_{p,q}\lambda_p\lambda_q(1+2n_qn_p+n_q+n_p)G^{\mathrm{IBM}}(E)\Bigg] \\
+ g_{kb}^2\sum_q\left[\left\{n_q(2\Lambda\lambda_q+1)+2n_q^2\lambda_q^2\right\}G^{\mathrm{IBM}}(E+\omega_q)+\left\{(n_q+1)(1-2\Lambda\lambda_q)+2n_q^2\lambda_q^2\right\}G^{\mathrm{IBM}}(E-\omega_q)\right] \\
+ g_{kb}^2\sum_q\left[n_q\lambda_q^2(1-n_q)G^{\mathrm{IBM}}(E+\omega_q+\omega_q)-(n_q+1)\lambda_q^2n_qG^{\mathrm{IBM}}(E-\omega_q-\omega_q)\right] \\
+ g_{kb}^2\sum_{p,q}[n_qn_p\lambda_q\lambda_pG^{\mathrm{IBM}}(E+\omega_q+\omega_p)+(n_q+1)(n_p+1)\lambda_p\lambda_qG^{\mathrm{IBM}}(E-\omega_q-\omega_p) \\
-(n_q+1)n_p\lambda_q\lambda_pG^{\mathrm{IBM}}(E-\omega_q+\omega_p)-(n_p+1)n_q\lambda_q\lambda_pG^{\mathrm{IBM}}(E+\omega_q-\omega_p)],
\end{aligned} \tag{1}$$

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where g_{kb} is the vertex of the atom-phonon interaction for a transition of the atom from continuum to the bound state and g_{bb} is the vertex of atom-phonon coupling for the 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 $n_q = 1/(e^{\omega_q/T} - 1)$, where ω_q is the energy of the phonon with wave-vector q and T is the temperature of the membrane [2]. G^{IBM} is the bound-state Green's function written within the IBM (given by Eqs. (28) and (29) in Ref. [1]), $E = E_k + E_b$ with $-E_b$ as the bound-state energy, and E_k is the incoming energy of the atom [1].

$\Sigma^c(E)$ has additional terms compared to Σ^{IBM} as a result of the inclusion of the noncommutativity of the phonon operator and displacement operator [2]. This noncommutativity was not addressed in my work [1]. Let me analyze Σ^c with a special focus on the effects of the terms appearing as a result of the noncommutativity. Below, I provide my points of disagreement concerning the form of $\Sigma^c(E)$ [given by Eq. (1)] and compare the same with the Σ^{IBM} reported in Ref. [1].

(1) Although the Comment [2] reports $\Sigma^c(E)$ as an *exact* closed-form expression for the atom self-energy to quadratic order in the atom-phonon coupling $\mathrm{O}(g_{kb}^2)$, I see that it is, *in fact*, a perturbative expansion in $\Sigma^c(E)$, truncated to a two-phonon process. The definition of exact self-energy corresponds to a summation of an infinite number of Feynman diagrams which essentially implies the inclusion of the contribution from infinitely many phonons [3]. By energy conservation, one can readily see that the propagators in Eq. (1): $G^{\mathrm{IBM}}(E - \omega_q)$ correspond to one-phonon emission with energy ω_q and $G^{\mathrm{IBM}}(E - \omega_q - \omega_q)$, $G^{\mathrm{IBM}}(E - \omega_q - \omega_p)$, and $G^{\mathrm{IBM}}(E - \omega_q + \omega_q)$ correspond to two-phonon emission processes with energies ω_q and ω_p. Thus, Σ^c is an *approximation* where the noncommutativity of the phonon and displacement operators has been incorporated up to two-phonon processes. However, the Comment [2] does not report Σ^c as an approximation and, furthermore, does not provide the justification of such an approximation. Σ^{IBM}, on the other hand, is also an approximation. It represents a one-phonon self-energy which uses an *exact* propagator for the bound-state G^{IBM} such that it includes all orders in the vertex g_{bb} but is truncated until the first-order phonon process in g_{kb}. This one-phonon approximation in g_{kb} has been justified for my model in Refs. [1,4] within the context of relative magnitudes of the vertices g_{kb} and g_{bb} as $g_{kb} \ll g_{bb}$.

(2) In the first line of Eq. (1), I see that the bound-state propagator is written as $G^{\mathrm{IBM}}(E)$. 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_{kb}^2. I remind myself that the definition of the vertex g_{kb} for the model Hamiltonian in Refs. [1,5,6] refers to the transition-matrix element [6,7],

$$g_{kb} = -\langle b, 1_q | H_i | k, 0 \rangle, \tag{2}$$

where H_i is the Hamiltonian for atom-phonon interaction [1]. $|k, 0\rangle$ represents the initial state of the atom $|k\rangle$ 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 the excitation of one phonon with energy ω and wave-vector q. Physically, Eq. (2) corresponds to the transition of the atom from $|k\rangle$ to $|b\rangle$ via the emission of one phonon of energy ω and wave-vector q [6,7]. A similar definition exists for the vertex g_{bb} which is the transition of the atom within bound-states $|b\rangle$ via the emission of a phonon of energy ω_q [6,7]. In other words, if the vertex g_{kb} is used, it would imply an emission of the phonon of energy ω_q, which then appears via energy conservation in the expression for the bound-state propagator G^{IBM}. Therefore, the first line which is written with a propagator $G^{\mathrm{IBM}}(E)$, represents a process that involves *no* emission of phonon ω_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 terms appearing from the noncommutativity of the phonon and displacement operators in the first line of Eq. (1) are inaccurate.

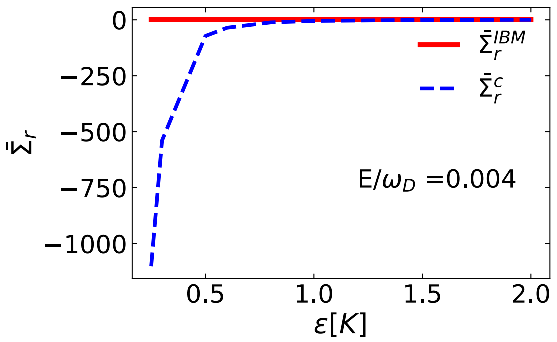

FIG. 1. Variation of the real part of the dimensionless self-energy reported in the Comment [2] ($\bar{\Sigma}_r^c$) vs infrared cutoff ϵ (blue dashed line) for the low-energy atom $E/\omega_D = 0.004$. For $\epsilon < 0.5$ K (membrane size > 100 nm), the self-energy reported in the Comment [2] starts to diverge severely with decreasing ϵ (increasing membrane sizes). Contrary to this, the real part of the self-energy within the IBM [1] (red line) is well behaved for the same ranges of the IR cutoff (membrane sizes) and is around $\bar{\Sigma}_r^{\mathrm{IBM}} \sim 0.7$.

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

In Fig. 1, I plot the variation of $\bar{\Sigma}_r^c$ [dimensionless real part of Eq. (1)] with ϵ. For comparative purposes, I also show the variation of the dimensionless real part of the self-energy within the IBM (real part of Eq. (6) in Ref. [1]). Let me summarize my understanding and give further points of disagreement with the Comment [2] as the following:

(3) I note, for $\epsilon \leqslant 0.5$ K, $\bar{\Sigma}_r^c$ (blue dashed line) starts to diverge with decreasing ϵ (increasing size of graphene membranes). In comparison, $\bar{\Sigma}_r^{\mathrm{IBM}}$ within the IBM (red line) is well behaved for the same range of IR cutoff (size of membrane). The Comment [2] 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 $\epsilon \leqslant 0.5$ K (membrane size > 100 nm). Furthermore, the Kinoshita [8], Lee and Nauenberg [9], and Bloch and Nordsieck [10] theorem tells us that these IR divergences are physically unreal, hence, proper resummations (nonperturbative techniques) need to be implemented to tackle these IR divergences with an effort to gain meaningful physical results. My 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 [1,4].

(4) Previously, in point (2), I mentioned the inaccuracy of the terms appearing as a result of noncommutativity of the phonon and displacement operators in the first line in Eq. (1). It is to be noted that there is a contribution to the leading-order divergence in $\bar{\Sigma}_r^c$ in the limit of $\epsilon \rightarrow 0$ that originates from the term,

$$-\sum_q 2n_q^2\lambda_q^2 G^{\mathrm{IBM}}(E) = -\frac{1}{\epsilon^3}\left[\frac{2g_{bb}^2T^2}{3}G^{\mathrm{IBM}}(E)\right] \rightarrow -\infty. \tag{3}$$

With the knowledge of points (3) and (4), let me now state my final points of disagreement with the arguments provided in the Comment [2] for the invalidity of my method for the calculation of the adsorption rate.

(5) Utilizing the real (Σ_r) and imaginary parts of the self-energy (Σ_i), the adsorption rate Γ within my method is given as

$$\Gamma \approx -2\mathcal{Z}\Sigma_i(E_p), \tag{4}$$

where the quasiparticle weight $\mathcal{Z}$ is

$$\mathcal{Z} = \left(1 - \frac{\partial \Sigma_r(E)}{\partial E}\bigg|_{E=E_p}\right)^{-1}, \tag{5}$$

and E_p is the quasiparticle energy that can be solved via

$$E_p - E_k = \Sigma_r(E_p). \tag{6}$$

Using the real part of the self-energy Σ_r^c [given by the real part of Eq. (1)], the Comment [2] attempts to find a graphical solution to Eq. (6). For low-energy atoms, the author finds no self-consistent solution in the range of $\epsilon \leqslant 0.4$ K (see Fig. 6 in the Comment [2]). This failure is *not because* of the change in sign of the curvature of the real part of the self-energy (as reported by the Comment [2]) but rather from an infinite (divergent) self-energy plugged into the right-hand side of Eq. (6) (see the IR-divergent behavior of Σ_r^c in Fig. 1). In contrast, the IBM self-energy is well behaved for similar ranges of the IR cutoff, and succeeds to give a self-consistent solution to Eq. (6), also evident from Figs. 5 and 6 of the Comment [2].

Before I conclude, let me provide an additional calculation of the adsorption rate of low-energy atoms using the self-energy within the IBM. This calculation clarifies some of the inaccurate representations of my results provided in the Comment [2]. In Fig. 2, I have shown the variation of the normalized adsorption rate Γ/Γ_0 as a function of the IR cutoff (ϵ). Here, Γ_0 is Fermi's golden rule result. One can see that, for a large range of IR cutoffs that correspond to membrane sizes of 100 nm–10 μm, the adsorption rate is $\Gamma \approx \Gamma_0$. In the very low IR cutoff regime ($\epsilon \leqslant 0.1$ K), I find small increments to the adsorption rate (Γ is still within 0.27% of Γ_0, see the inset of Fig. 2). The Comment [2] mentions there is a divergence in my results which becomes apparent for $\epsilon \leqslant 0.1$ K. I 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 ϵ), there is an enhancement of the probability of emission of low-energy thermal phonons, leading to an increase in the adsorption rate [4].

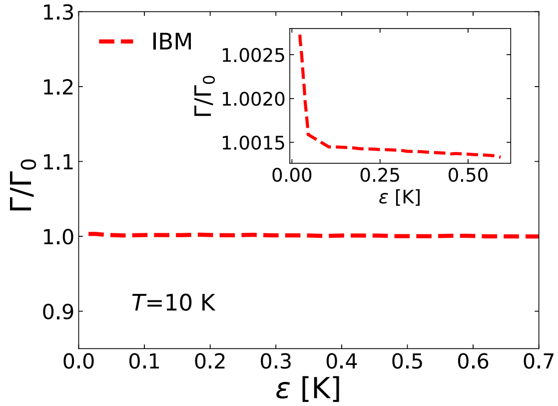

FIG. 2. Within the self-energy in the IBM [1], I plot a variation of the normalized adsorption rate Γ/Γ_0 vs IR cutoff ϵ, Γ_0 is Fermi's golden rule result. Little to no variation is seen with ϵ (i.e., with membrane sizes of the range of 100 nm–10 μm). The inset shows the variation for very low ϵ. A small enhancement (0.27% of Γ_0) in the adsorption rate is seen with decreasing ϵ (increasing membrane sizes), which is related to the enhancement of the probability of the emission of low-energy thermal phonons (obeying Bose-Einsten distribution) at finite temperatures.

In conclusion, the Comment [2] has reported a new self-energy which is a perturbative expansion that includes the noncommutativity of the phonon operator and displacement operator, approximated to a two-phonon process. This *approximation* (although reported as an exact method in the Comment [2]) is ill behaved for low IR cutoffs (large membrane sizes) and suffers from severe IR divergences; tracing back to the original IR problem of the model where perturbative treatment of the self-energy generally leads to IR divergent self-energy, signaling the need for a resummation to be performed on the perturbative series expansion. My method within the IBM [1] is a resummation technique that was, indeed, formulated as a measure to tackle these IR divergences that arise in the perturbative treatment of the problem. Quite naturally, the IR structure of the Σ^{IBM} and $\Sigma^{(c)}$ are starkly different with the merit of Σ^{IBM} being well behaved for micromembranes of graphene samples. An IR safe self-energy is a general as well as a crucial requirement for the calculation of the adsorption rate. As the self-energy reported in the Comment [2] is severely IR divergent for an IR cutoff less than 0.5 K (corresponding to membrane sizes larger than 100 nm), naturally, it *fails* to predict adsorption rates for graphene membrane sizes larger than 100 nm.

Additionally, the Comment [2] has also misplaced the atom-phonon vertex on one of the noncommutativity terms in Σ^c which has resulted in a leading-order IR divergence; these terms are, however, not allowed in our model [1,6,7] within the definition of the atom-phonon vertices. In the absence of such terms, the perturbative series expansion in the Comment [2] is still weakly IR divergent, urging the need of a resummation to be performed on the perturbative series. Unless proper resummations are performed with appropriate placement of atom-phonon coupling, this divergent self-energy reported in the Comment [2] remains unsuitable for physisorption studies in graphene micromembranes. In contrast, the self-energy within the IBM, reported in Ref. [1] is a resummed self-energy [1,4], well behaved for the same range of IR cutoff (see Fig. 1) and is conclusive about the adsorption rate for a large range of membrane sizes of 100 nm–10 μm, suitably capturing the physics of temperature and finite-size effects. Finally, let me address the concluding remark of the Comment [2] which states that the difference between the finite adsorption rate predicted in Ref. [1] with the zero adsorption rates predicted in Refs. [5,6] is due to the self-energy used within the IBM. I *strongly disagree* with this remark. Within the simple model of the IBM, my original work had shown that the zero adsorption rate is only possible if one considers: (i) a contribution to the adsorption rate from the long-time regime where the effects of the Franck-Condon factor sets in and (ii) neglects the effects of thermal phonon emission. Point (ii) and (i) are, indeed, the regime of study in Refs. [5,6], respectively. However, if I consider the contribution to adsorption rate from the 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 [1,11,12], validating the IR-divergence cancellation predicted by the theorem of Bloch-Nordsieck [10]. It would be interesting to know if Σ^c reported in the Comment [2], would also give the same finite adsorption rate as Σ^{IBM} when the following improvements are made within Σ^c, namely, (i) the atom-phonon vertices in the noncommutativity terms are not misplaced, (ii) a full resummation (nonperturbative) formalism is performed on the weakly IR-divergent perturbative series by including the contribution of infinitely many low-energy phonons and not just two-phonons, and (iii) a contribution to the adsorption rate is inclusive for a full-time regime without neglecting thermal phonon emissions.

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