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Note: Caldeira-Leggett model describes dynamics of hydrogen atoms on graphene

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The description of complex dynamical processes in many-particle systems can be often reduced to few relevant degrees of freedom (DOFs). Such a reduced description can be formally obtained by partitioning the system into a small subset of important DOFs, referred to as system, and all other DOFs, which constitute a thermal bath.[1] Nonetheless, a rigorous formulation of such a *system-bath partitioning* approach remains an open issue.

A very tempting idea is to assume a simple functional form for the bath DOFs and their coupling to the system part. A particular example is the Caldeira-Leggett (CL) model, where the bath is represented as a collection of harmonic oscillators bilinearly coupled to the system described by a potential $V_S(q)$.[2] For the sake of presentation the system coordinate, q, is kept one-dimensional in the following. The corresponding reduced equations of motion for the system have the form of the generalized Langevin equation (GLE),[3]

$$\dot{p}(t) = F[q(t)] - \int_0^t \xi(t-\tau)p(\tau)\mathrm{d}\tau + R(t), \qquad (1)$$

where $F[q(t)] \equiv -\partial_q V_S[q(t)]$ is the system force. The influence of the bath is thus limited to dissipation, represented by the non-Markovian memory kernel, $\xi(t)$, and fluctuations, $R(t)$, only. In practical applications one usually mimics the latter term by a stochastic zero-centered Gaussian process that is regulated by the fluctuation-dissipation theorem,[4] $\langle R(0)R(t)\rangle = mk_B T\xi(t)$, where k_B is the Boltzmann constant, T is the temperature, and $\langle \ldots \rangle$ stands for a canonical averaging. It is also often practical to work in the frequency domain, where the memory kernel becomes a spectral density, defined as a half-sided Fourier transform, $\hat{\xi}(\omega) \equiv \int_0^\infty \mathrm{d}t\, e^{-i\omega t}\xi(t)$.

Another pathway goes back to Mori, who employed a formal projection operator technique to derive the linear GLE without further approximations.[5] The only difference to Eq. (1) is that the system force takes a harmonic form: $F(q) = -k_B T q/\langle q^2\rangle$, hence referred to as linear GLE. The price to pay is that the system's anharmonicity is projected into the bath.

Recently, some of us considered the general problem of mapping a real system onto a CL model.[6–8] It turned out that such a mapping is not invertible and thus the procedure is not self-consistent, hence termed *invertibility problem*.[6] Practically, the problem was demonstrated for different solution-phase systems, e.g., an HOD molecule in bulk water and the ionic liquid [C$_2$mim][NTf$_2$].[6] There are two important exceptions, however: (i) the CL model's system potential is or is taken effectively harmonic, which corresponds to the Mori projection formalism; (ii) the real system is (approximately) of the CL form. The former exception is not satisfactory if one is interested in non-linear spectroscopy, though it can be well applied to study dissipation dynamics or linear response properties. The latter one, however, suggests that there might exist a broad class of systems generally describable by a CL model, in particular in a solid regime or on a surface. Still, it was surprisingly not easy to find a showcase that possesses a spectrum with features, i.e., a structured curve with many peaks and/or shoulders. Thus, we illustrated this exception in Ref. 8 on the example of I$_2$ in an argon lattice, which was tailored to challenge the parametrization scheme for the spectral densities developed therein, but is not highly relevant in today's research.

Here, we eventually report on a highly relevant system, a hydrogen atom chemisorbed on graphene, that could be mapped onto the CL model. Importantly, a quantum-dynamical treatment based on the CL model has been already used by some of us for describing the sticking dynamics of an H atom to the graphene surface.[9,10] Thus, the possibility of mapping onto the CL model also validates the system-bath treatment therein. Further, the existence of such a mapping opens the doorway for a plethora of methods ranging from fully quantum to purely classical, as it was discussed in, e.g., Ref. 6.

Following Refs. 9 and 10 we adopted the elaborate interaction potential of Kerwin *et al.*[11] The model relies on a *first principle* description of the C–H interaction and on a rather accurate representation of the graphene force field.[12] The C–H potential energy surface, V_{3D}, is taken as a function of three coordinates, namely the heights of the hydrogen atom and of the binding carbon atom above the graphene plane, as well as the projection of their relative position on the surface

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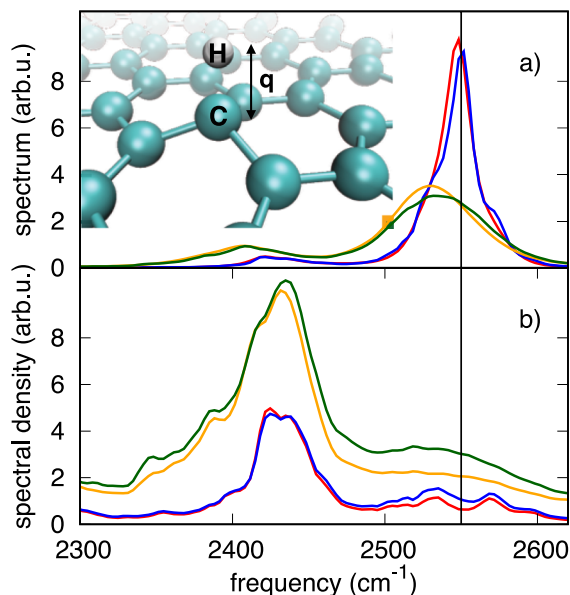b)Electronic mail: sergei.ivanov@uni-rostock.de

FIG. 1. The vibrational spectra are shown in panel (a). GLE: 100 K (red) and 300 K (yellow), explicit MD: 100 K (blue) and 300 K (green). The spectral densities are displayed in panel (b). Non-linear parametrization scheme: 100 K (red) and 300 K (yellow), linear one: 100 K (blue) and 300 K (green). Inset sketches the graphene surface with the chemisorbed H atom and the associated normal mode coordinate, q.

plane. The lattice was modeled with a large cluster of sp^2 C atoms, which was embedded into the rest of the surface by introducing a Langevin thermostat at its edge atoms and coupled with the "C–H system" through a surface oscillator type term.[11]

The model recovers the most important features of the binding of H at graphene in the chemisorption state.[9,10] Normal-mode analysis of the 3D rigid-surface potential gives a bond stretching mode, q, at 2549 cm^{-1}, see inset in Fig. 1. It is highly anharmonic and its characteristic frequency lies well above the Debye frequency of the bath ($\sim$1600 cm^{-1}), thereby making the GLE mapping particularly challenging.[13] This particular stretching mode is chosen to be the system part in Eq. (1). To obtain an analytical representation of the system potential, $V_S(q)$, and thus of the force, $F[q(t)]$, employed in Eq. (1), we extracted a cut of the full system potential along the direction of the aforementioned stretching normal mode, namely along the line $x_k(q) = \frac{1}{\sqrt{m_k}} O_{k1} q$, where x_k are the original Cartesian coordinates of the atoms involved, m_k are their masses, O_{kl} is the orthogonal transformation that diagonalizes the frequency matrix $W_{rs} = (m_r m_s)^{-1/2} \partial^2 V_{3D}/\partial x_r \partial x_s|_{eq}$, and $l = 1$ identifies the stretching normal mode. The resulting cut was fitted to a sixth order polynomial, $V_S(q)/E_h = \Sigma_{n=2}^6 a_n (q/a_0 \sqrt{m_e})^n$, where E_h, a_0, and m_e are the atomic units of energy, length, and mass, and the coefficients read as $a_2 = 6.767 \cdot 10^{-5}$, $a_3 = 1.973 \cdot 10^{-6}$, $a_4 = 3.513 \cdot 10^{-8}$, $a_5 = 5.267 \cdot 10^{-10}$, and $a_6 = 5.304 \cdot 10^{-12}$.

In order to verify the mapping onto the CL model, we performed the self-consistency test as described in Refs. 6

and 8. The idea is to execute explicit molecular dynamics (MD) simulations, compute the vibrational spectrum, and parametrize the spectral density based on the MD data. Then the spectral density is utilized to calculate the vibrational spectrum by means of the GLE[4] as detailed in Ref. 8. The coincidence of the two spectra manifests the success of the CL model. This is illustrated for two temperatures (100 K and 300 K) in Fig. 1(a).[14] Indeed, at both temperatures the match between the two spectra is striking. Importantly the significant difference both in shape and spectral range between the spectra at 100 K and 300 K therein unambiguously tells that the respective anharmonicity of the system potential at 300 K is very pronounced.

In order to determine whether this anharmonicity plays an important role, we have compared the spectral densities for the linear and non-linear GLEs, obtained according to the procedures described in Refs. 7 and 8, respectively. If the spectral densities matched, it would imply that the anharmonicity of the system potential is not important, since the main difference between the approaches is that the system's anharmonicity is projected into the bath in the linear case. Comparing the spectral densities, shown in Fig. 1(b), reveals that they differ in the resonant region, marked by the vertical line therein, especially for the 300 K case. This underlines the importance of using the non-linear parametrization scheme.

In summary, we have demonstrated a highly relevant system that can be described by the CL model and is thus amenable for the plethora of methods based on it. We believe that there exists a broad class of similar systems that share this property.

[1] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley-VCH, 2011).
[2] A. O. Caldeira and A. J. Leggett, Ann. Phys. **149**, 374 (1983).
[3] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, 2001).
[4] M. Ceriotti, G. Bussi, and M. Parrinello, J. Chem. Theory Comput. **6**, 1170 (2010).
[5] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).
[6] F. Gottwald, S. D. Ivanov, and O. Kühn, J. Phys. Chem. Lett. **6**, 2722 (2015).
[7] F. Gottwald, S. Karsten, S. D. Ivanov, and O. Kühn, J. Chem. Phys. **142**, 244110 (2015).
[8] F. Gottwald, S. D. Ivanov, and O. Kühn, J. Chem. Phys. **144**, 164102 (2016).
[9] M. Bonfanti, B. Jackson, K. H. Hughes, I. Burghardt, and R. Martinazzo, J. Chem. Phys. **143**, 124703 (2015).
[10] M. Bonfanti, B. Jackson, K. H. Hughes, I. Burghardt, and R. Martinazzo, J. Chem. Phys. **143**, 124704 (2015).
[11] J. Kerwin and B. Jackson, J. Chem. Phys. **128**, 084702 (2008).
[12] T. Aizawa, R. Souda, S. Otani, Y. Ishizawa, and C. Oshima, Phys. Rev. B **42**, 11469 (1990).
[13] M. Bonfanti, K. H. Hughes, I. Burghardt, and R. Martinazzo, Ann. Phys. **527**, 556 (2015).
[14] Note that linear GLE spectra are not shown as they coincide with the explicit MD results by construction.[6,7]