Fluctuation-Dissipation Theorem for Metastable Systems

G. Báez,[1,2,*] H. Larralde,[1] F. Leyvraz,[1] and R. A. Méndez-Sánchez[1]

[1]*Centro de Ciencias Físicas UNAM, AP 48-3, 62210, Cuernavaca, Morelos, México*

[2]*Laboratorio de Sistemas Dinámicos, Departamento de Ciencias Básicas, Universidad Autónoma Metropolitana-Azcapotzalco, AP 21-267, Coyoacán 04000, México D.F., México*

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We show that an appropriately defined fluctuation-dissipation theorem, connecting generalized susceptibilities and time correlation functions, is valid for times shorter than the nucleation time of the metastable state of Markovian systems satisfying detailed balance. This is done by assuming that such systems can be described by a superposition of the ground and first excited states of the master equation. We corroborate our results numerically for the metastable states of a two-dimensional Ising model.

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There have been many efforts to extend the concepts and methods used to describe systems in equilibrium to systems which are not in equilibrium but are either stationary or evolve very slowly [1,2]. A particular class of "slowly evolving" out of equilibrium systems are those which are in a metastable state and, due to their ubiquity, their characterization is of special interest. Usually it is thought that the macroscopic properties of a metastable system can be treated as if it were in equilibrium. In particular, even relations such as the fluctuation-dissipation theorem (FDT) [3–5] are generally assumed to be valid for systems in a metastable state. However, metastable systems are actually far from equilibrium and there is no reason to expect the validity of this theorem for such systems, even if their evolution is very slow. Indeed, the FDT does not apply to systems such as finite-range spin glasses, domain growth processes, structural glasses, and others (see Ref. [6] and references therein). In this Letter we use a dynamical approach to show why it is justified to apply results from equilibrium to metastable states for the case of Markovian stochastic dynamics, and we derive the FDT for these systems from the microscopic dynamics.

Since the phenomenology of metastable states has been assumed to be similar to that of equilibrium systems, most of the efforts have focused on understanding the mechanisms by which a system decays from the metastable state to equilibrium by nucleation processes (growing of a second phase) [7–11]. However, a theory for the description of metastable states *per se* is still lacking [12]. This is partly because the phenomenon of metastability is a relative and rather complicated concept [13]. Penrose and Lebowitz [11] made a detailed characterization of the principal properties observed in the behavior of systems in a metastable state, which can be summarized as follows: In a metastable state, a system behaves similarly to a hypothetical pure thermodynamic phase, although the intensive parameters have values such that the equilibrium state would consist of a different phase or a coexistence of different phases. When the system is isolated, the metastable state remains for a very long time. The response to small and slow perturbations leads to small and reversible changes in the systems. For large or rapid changes, the system may escape irreversibly from the metastable state. Beyond qualitative characterizations, there is not a clear and general definition of metastability [14]. In this work we use a definition of a metastable state similar to that introduced by Davies [15,16] for Markovian systems satisfying detailed balance, in terms of the eigenvectors of the corresponding time independent master equation [17]. Using this definition and the Kubo formalism for linear response theory [3–5], we obtain a metastable fluctuation-dissipation theorem valid for times short compared with the nucleation time of the system.

In the following we limit ourselves to the dynamics of Markovian systems with a finite (possible large) number of states. Those can be described by a master equation to which we associate an operator $\hat{L}_0$,

$$\dot{P}(t) = \hat{L}_0 P(t). \tag{1}$$

If the system is characterized by a set of discrete random variables $\vec{\sigma}$, then $P(t)$ is a vector of components $p(\vec{\sigma}, t)$ which correspond to the probability that the system is in the state specified by $\vec{\sigma}$ at time t. When Eq. (1) is solved by separation of variables, we obtain the time independent master equation

$$\hat{L}_0 \psi_j = -\Omega_j \psi_j, \tag{2}$$

where Ω_j and ψ_j are the eigenvalues and eigenvectors of $\hat{L}_0$, respectively. Because of conservation of probability there exists a stationary solution $\psi_0(\vec{\sigma})$ associated to the eigenvalue $\Omega_0 = 0$, namely, $\psi_0(\vec{\sigma}) = p^e(\vec{\sigma})$. Here p^e is the Boltzmann probability distribution of the system in the equilibrium state, which we assume to be the only stationary solution of the master equation. If detailed balance holds then $\hat{L}_0$ is self-adjoint with respect to the following internal product,

$$(R, Q) = \sum_{\vec{\sigma}} \frac{R(\vec{\sigma})Q(\vec{\sigma})}{\psi_0(\vec{\sigma})}, \tag{3}$$

with R and Q two arbitrary functions with finite norm [18]. For $R = \psi_0$ and $Q = \psi_j$, Eq. (3) implies $\sum_{\vec{\sigma}} \psi_j(\vec{\sigma}) = \delta_{0,j}$, i.e., $\psi_0(\vec{\sigma})$ is normalized and $\psi_{j\neq 0}(\vec{\sigma})$ sum to zero.

We assume now that it is possible to choose the parameters of the system in such a way that one of the eigenvalues of $\hat{L}_0$, labeled by $-\Omega_1$, corresponds to a decay that is much slower than the observational times. This is $0 < \Omega_1 \ll 1 \ll \Omega_j$, for $j \geq 2$, in appropriate units. This assumption means that we neglect the case of having several different metastable states. The extension to finitely many metastable states is straightforward, but not the one to systems with a divergent number of metastable states (glasses, spin glasses, etc.).

Let us now prepare the system in any configuration $\vec{\sigma}'$. Since the set of eigenfunctions is complete (as follows from the self-adjointness of $\hat{L}_0$), we can represent the corresponding probability distribution as

$$\delta_{\vec{\sigma},\vec{\sigma}'} = \psi_0(\vec{\sigma}) + \sum_{j=1}^{\infty} \frac{\psi_j(\vec{\sigma}')\psi_j(\vec{\sigma})}{\psi_0(\vec{\sigma}')}, \tag{4}$$

and hence, for $1/\Omega_2 \ll t \ll 1/\Omega_1$, one gets a nearly stationary state (which essentially does not vary in time for $t \ll 1/\Omega_1$),

$$e^{\hat{L}_0 t}\delta_{\vec{\sigma},\vec{\sigma}'} \approx \psi_0(\vec{\sigma}) + G(\vec{\sigma}')\psi_1(\vec{\sigma}), \tag{5}$$

where $G(\vec{\sigma}') = \psi_1(\vec{\sigma}')/\psi_0(\vec{\sigma}')$. That the right-hand side (r.h.s) of Eq. (5) is a probability distribution follows from the norm and positivity preserving properties of $\exp(\hat{L}_0 t)$. When $G(\vec{\sigma}') \ll 1$, the state given by Eq. (5) is the equilibrium state, since the second term in the r.h.s is negligible. On the other hand, when $G(\vec{\sigma}') \gg 1$ the state is sharply localized in a zone of configurations $\{\vec{\sigma}\}_m$ (hereafter, the metastable *zone*) and very small outside this zone. Then, this quasistatic probability distribution represents the metastable state. Notice that in this situation G is independent of $\vec{\sigma}'$ since any configuration prepared within the metastable zone is expected, on physical grounds, to evolve into the same intermediate metastable state $p^m(\vec{\sigma})$. The case $G(\vec{\sigma}') \sim 1$, leads to configurations which have comparable probabilities of evolving into either the equilibrium or metastable state. We assume that this set of "saddle points" is negligible compared to the sets of both, equilibrium and metastable configurations.

Now consider a system which can be prepared in a metastable initial state described by

$$p^m(\vec{\sigma}) = \psi_0(\vec{\sigma}) + G\psi_1(\vec{\sigma}); \qquad G \gg 1. \tag{6}$$

As $p^m(\vec{\sigma})$ is negligible outside the metastable zone, we approximate $p^m(\vec{\sigma})$ as

$$p^m(\vec{\sigma}) \approx \begin{cases} \psi_0(\vec{\sigma}) + G\psi_1(\vec{\sigma}), & \text{for } \vec{\sigma} \in \{\vec{\sigma}\}_m, \\ 0, & \text{for } \vec{\sigma} \in \{\vec{\sigma}\}_m, \end{cases} \tag{7}$$

with $G \gg 1$. The last equation coincides with the definition of the metastable state given by Davies [15,16], where the reader can find greater detail.

Using the definition of G and the fact that it is constant within the metastable zone one gets $\psi_1(\vec{\sigma}) = G\psi_0(\vec{\sigma})$ for $\vec{\sigma} \in \{\vec{\sigma}\}_m$. On the other hand, using that $p^m(\vec{\sigma}) = 0$ outside the metastable zone, we get $\psi_1(\vec{\sigma}) = -1/G\psi_0(\vec{\sigma})$ for $\vec{\sigma} \notin \{\vec{\sigma}\}_m$ Thus, the first excited state $\psi_1(\vec{\sigma})$, and hence, the metastable state, is specified in terms of the equilibrium distribution for (almost) all configurations of the system since it is locally proportional to the Boltzmann distribution in both metastable and nonmetastable zones. The proportionality coefficients are given by G and $-1/G$, respectively.

This simple picture of metastability allows us to go beyond the description of the distributions characterizing the metastable states. In particular, we now derive a FDT through linear response theory for these states. We now consider the perturbed master equation,

$$\dot{P} + h\dot{P}_1 = (\hat{L}_0 + he^{i\omega t}\hat{L}_1)(P + hP_1), \tag{8}$$

where $\hat{L}_1$ is the perturbative term generated by an oscillatory external field and P is the probability distribution in the absence of the perturbing external field, whose evolution is described by Eq. (1).

Now, if the system is initially in its metastable state—described by Eq. (6)—after some algebra we obtain the following general expression for the changes in the probability distribution $P_1(\vec{\sigma}, t)$, to first order in h,

$$\begin{aligned} P_1(\vec{\sigma}, t) = h \int_0^t e^{\hat{L}_0(t-t')}\hat{L}_1[\psi_0(\vec{\sigma}) + G\psi_1(\vec{\sigma})]e^{i\omega t'}dt' \\ + h \int_0^t e^{\hat{L}_0(t-t')}\hat{L}_1 G\psi_1(\vec{\sigma})e^{i\omega t'}(e^{-\Omega_1 t'} - 1)dt'. \end{aligned} \tag{9}$$

This expression is exact for all times. Since $\hat{L}_1$, ψ_0, and ψ_1 are independent of t', the integrations are trivial. Expanding $P_1(\vec{\sigma}, t)$ in the basis of eigenvectors of $\hat{L}_0$, the equilibrium case is recovered for $t \to \infty$. For times $t \ll 1/\Omega_1$, the second integral vanishes and the first integral yields the total change of the probability distribution starting from the metastable initial condition.

We introduce for any ρ the following notation:

$$\langle B(t)\rangle_\rho = \sum_{\vec{\sigma}} B(\vec{\sigma})\rho(\vec{\sigma}, t). \tag{10}$$

We can calculate the changes of the average value of any physical quantity $B(\vec{\sigma})$ as $\langle B(t)\rangle_{P_1}$ where P_1 is taken from Eq. (9).

By taking the corresponding Laplace-Fourier transform of $\langle B(t)\rangle_{P_1}$, we can define [19] the metastable susceptibility of the system as

$$\chi(s) = \sum_{\vec{\sigma}} B(\vec{\sigma}) \sum_j \psi_j(\vec{\sigma}) \left\{ \frac{(\psi_j, \hat{L}_1(\psi_0 + G\psi_1))}{(s + \Omega_j)} - \frac{\Omega_1(\psi_j, \hat{L}_1 G\psi_1)}{(s + \Omega_j)(s + \Omega_1 - i\omega)} \right\}. \tag{11}$$

Then, in linear approximation, the metastable susceptibility consists of two terms. The first term is similar to the equilibrium case, but this time the initial condition is the probability distribution of the metastable state. The second is a memory term corresponding to a convolution with the external field.

We now define $\psi_j(h)$ as the eigenfunctions of the operator $L_0 + h\hat{L}_1$. To first order in h we have the following relation connecting $\hat{L}_1\psi_i(0)$ with the derivatives of $\psi_1(h)$ with respect to h:

$$\hat{L}_1\psi_i(0) = -\hat{L}_0 \frac{\partial\psi_i}{\partial h}\bigg|_{h=0} - \Omega_i(0)\frac{\partial\psi_i}{\partial h}\bigg|_{h=0} - \frac{\partial\Omega_i}{\partial h}\bigg|_{h=0}\psi_i(0). \tag{12}$$

We substitute Eq. (12) in the scalar products of Eq. (11) and use the appropriate proportionality between $\psi_1(\vec{\sigma})$ and $\psi_0(\vec{\sigma})$. We then split the sum over $\vec{\sigma}$ in a sum over the stable zone and one over the metastable zone [see Eq. (7)], noting that if the system has a metastable state as defined above, then the higher excited states satisfy $\sum_{\vec{\sigma}_m} \psi_j(\vec{\sigma}_m) = \sum_{\vec{\sigma}\notin\{\vec{\sigma}_m\}} \psi_j(\vec{\sigma}) \approx 0$, for $j \geq 2$. This must be the case as $\sum_{\vec{\sigma}\in\{\vec{\sigma}_m\}} P(\vec{\sigma}, t) = 1$ for times shorter than the nucleation time $1/\Omega_1$.

We now define $E(\vec{\sigma})$ as the energy of the system appearing in the Boltzmann distribution and introduce, for each probability distribution $\rho(\vec{\sigma}, t)$, the following dynamical correlation

$$\left\langle \dot{B}(t)\frac{\partial E}{\partial h}\right\rangle_\rho = \sum_{\vec{\sigma}} \frac{\partial E(\vec{\sigma})}{\partial h}\rho(\vec{\sigma}, t)\sum_{\vec{\sigma}'} B(\vec{\sigma}')\dot{p}(\vec{\sigma}', t'|\vec{\sigma}, t), \tag{13}$$

where $p(\vec{\sigma}', t'|\vec{\sigma}, t)$ is the conditional probability that the configuration $\vec{\sigma}'$ occurs at time t' given that it was in $\vec{\sigma}$ at time t. After several pages of algebra one then gets for the metastable susceptibility

$$\chi(s) = \beta\mathcal{L}\left[\left\langle \dot{B}(t)\frac{\partial E}{\partial h}\right\rangle_{p^m} + \Omega_1\Delta\left\langle B(t)\frac{\partial}{\partial h}(E - kT\ln\Omega_1)\right\rangle + \Omega_1\int_0^t d\tau\, e^{iw(t-\tau)}\Delta\left\langle \dot{B}(t)\frac{\partial E}{\partial h}\right\rangle + o(\Omega_1)\right], \tag{14}$$

where $\beta = 1/kT$ and $\Delta\langle A\rangle = \langle A\rangle_{p^m} - \langle A\rangle_{p^e}$.

To obtain the metastable fluctuation-dissipation theorem it is enough to show that the second and third terms in Eq. (14) vanish as the coexistence curve is approached (first order correction in Ω_1). Since $B(t)$ and $\dot{B}(t)$ remain bound, the terms related to them are negligible because $\Omega_1 \ll 1$. Indeed, the principal correction is given by the term of the order of $\partial\ln\Omega_1/\partial h$. Since Ω_1 is the nucleation rate [10], it is given roughly by $\exp(-\beta W)$ where W is the nucleation barrier. Usually W is roughly R_c^{d-1}, where R_c is the critical droplet radius and diverges algebraically as the supersaturation h_0 goes to zero. Here the total strength of the external field is given by the fixed initial field h_0 plus the perturbation h (h_0 in the Ising model is the external magnetic field). From this it follows that $\partial\Omega_1/\partial h$ also diverges algebraically in h, whereas Ω_1 goes to zero as a stretched exponential. *Thus we have established the central result of this work, a fluctuation-dissipation theorem for the metastable states.*

In order to check the FDT for metastable states, we will show that the susceptibility obtained by perturbing the metastable state of a two-dimensional Ising model with a magnetic field of fixed frequency agrees with that obtained by taking the Fourier-Laplace transform of the correlations of the fluctuations in the metastable state, given by the first term in the r.h.s. of Eq. (14). Our programs where proved checking the well known FDT in equilibrium (see Fig. 1). We obtained the autocorrelation of the magnetization by a Monte Carlo simulation for a two-dimensional Ising model evolving by Glauber dynamics [17] on a square lattice with periodic boundary conditions. The set of external parameters (temperature T, coupling J, and static magnetic field h_0) was chosen to give long-lived metastable states ($\sim 10^4$ Monte Carlo time steps per spin) when starting with all spins opposite to the magnetic field. As suggested in Refs. [20,21], we used $T = \frac{2}{3}T_c J$, where T_c is the critical temperature and J is the coupling between nearest neighbor spins. The external magnetic field h_0 was chosen by trial. For all calculations we allowed the system to evolve until a long-lived state opposite to the field was reached. Then we computed the average of the fluctuations of the magnetization with respect to the metastable equilibrium value, over a set of 100 realizations.

In Fig. 1 we show the magnetic susceptibilities as a function of the frequency. The open squares correspond to the classical magnetic susceptibility for the equilibrium state, obtained by the definition of linear response theory. The crosses correspond to the same quantity for the metastable state. Both quantities were averaged over ten realizations. The dashed lines correspond to the

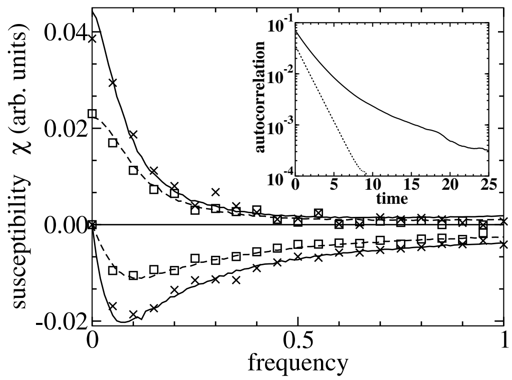

FIG. 1. Magnetic susceptibility for a two-dimensional Ising model with 10^4 spins; temperature $T = 1.52$, external magnetic field $h_0 = 0.1$, and coupling $J = 1$. As usual, the real part is the positive quantity and the imaginary part is the negative quantity. The crosses correspond to the metastable computation by the perturbative method and the open squares to the corresponding equilibrium computation. The solid lines and the dashed lines were obtained by transforming the metastable and equilibrium autocorrelations of the magnetization. The inset shows the autocorrelation of the magnetization. The solid lines and the dashed lines correspond to the metastable and equilibrium correlations, respectively.

equilibrium magnetic susceptibility computed using Laplace-Fourier transformation of the corresponding autocorrelations (per spin) of the magnetization given in the inset (dashed line). Finally, the solid lines correspond to the magnetic susceptibility obtained by transforming the appropriate autocorrelation function in the metastable state (continuous line in the inset). We find the same good level of agreement for the equilibrium and metastable cases. It is interesting to observe that the behavior of the correlations is very different in both cases.

In summary, by using a formal definition of a metastable state for the case of Markovian systems with a finite number of states we have shown that the FDT indeed holds for times shorter than the nucleation time. We also evaluated the size of the leading corrections. Since many systems have Markovian dynamics on sufficiently long time scales, this result has quite a broad range of applicability. A crucial hypothesis was the existence of one single low-lying excited state of the operator $\hat{L}_0$. This means that nucleation is the slowest physical process, a condition often satisfied in practice. Detailed calculations and numerical simulations will be given elsewhere [22].

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*Electronic address: baez@fis.unam.mx

[1] F. Sciortino and P. Tartaglia, Phys. Rev. Lett. **86**, 107 (2001).
[2] A. F. Izmailov and A. S. Myerson, Physica (Amsterdam) **267A**, 34 (1999).
[3] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[4] R. Kubo, in *Some Aspects of the Statistical Mechanical Theory of Irreversible Processes*, University of Colorado Lectures in Theoretical Physics (Interscience Publishers, New York, 1959), Vol. 1, p. 120.
[5] R. Kubo, Rep. Prog. Phys. **29**, 255 (1966).
[6] T. S. Grigera and N. E. Israeloff, Phys. Rev. Lett. **83**, 5038 (1999).
[7] M. Volmer and A. Weber, Z. Phys. Chem. (Leipzig) **119**, 277 (1926).
[8] W. L. Bragg and E. J. Williams, Proc. R. Soc. London, Ser. A **145**, 699 (1934).
[9] R. Becker and W. Döring, Ann. Phys. (Leipzig) **24**, 719 (1935).
[10] J. S. Langer, Ann. Phys. (N.Y.) **41**, 108 (1967).
[11] O. Penrose and J. L. Lebowitz, J. Stat. Phys. **3**, 211 (1971).
[12] O. Penrose and J. L. Lebowitz, in *Fluctuation Phenomena*, edited by E.W. Montroll and J. L. Lebowitz, Studies in Statistical Mechanics (North-Holland, Amsterdam 1979), Vol. 7.
[13] P. G. Debenedetti, *Metastable Liquids* (Princeton University, Princeton, 1996).
[14] E. J. Neves and R. H. Schonmann, Commun. Math. Phys. **137**, 209 (1991).
[15] E. B. Davies and Ph. A. Martin, Helv. Phys. Acta **54**, 106 (1981).
[16] E. B. Davies, Proc. London Math. Soc. **45**, 133 (1982); J. London Math. Soc. **26**, 541 (1982); J. Stat. Phys. **27**, 657 (1982).
[17] R. J. Glauber, J. Math. Phys. (N.Y.) **4**, 294 (1963).
[18] N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1992).
[19] Notice that this definition uses Fourier-Laplace instead of Fourier transform since the metastable states decay for $t \rightarrow \infty$.
[20] J. D. Gunton and M. Droz, in *Introduction to the Theory of Metastable and Unstable States*, Lecture Notes in Physics (Springer-Verlag, Berlin, 1983), Vol. 183.
[21] S.-K. Ma, *Statistical Mechanics* (World Scientific, Philadelphia, 1985).
[22] G. Báez *et al.* (to be published).