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Equilibrium time correlation functions are of great importance because they probe the equilibrium dynamical response to external perturbations. We discuss the properties of time correlation functions for several systems that are simple enough to illustrate the calculational steps involved. The discussion underscores the need for avoiding language which misleadingly suggests that thermal equilibrium is associated with a quiescent or moribund state of the system. © *1999 American Association of Physics Teachers.*

I. INTRODUCTION

The traditional operational method for assessing whether a system has achieved thermal equilibrium is to monitor whether a macroscopic quantity has ceased varying and reached a steady-state value. As an example, if a system is placed in contact with a proverbial "heat bath," we might declare that our system has achieved thermal equilibrium and that its temperature has the value T, if the reading of a thermometer has ceased varying and equals T. The occasional fallibility of this operational method is well known; a glass window pane is a striking example of a system that, strictly speaking, has not reached thermal equilibrium even though changes may not be perceptible during the lifetime of even the most alert observer.

Putting aside extreme examples such as the window pane, the characterization of thermal equilibrium in terms of macroscopic quantities that have ceased varying may mistakenly evoke the vision of a quiescent state of the system. At the microscopic level nothing could be further from the truth; the atoms or molecules of our system will continue forever to interact with each other and with the heat bath even though, when examined at the macroscopic level, the system has ceased its evolution. This behavior raises the question, what is a useful construct for assessing the dynamical microscopic activity in a system that has achieved thermal equilibrium? Furthermore, what type of macroscopic measurements can be performed whose outcome is expressible, and thus predictable, in terms of the time dependence of this construct?

To focus our attention, we first consider the example of a macroscopic crystalline sample of sodium chloride at room temperature. What theoretical quantity can provide us with useful insight concerning the dynamical characteristics of the Na^+ and Cl^- ions, which are alternately situated on the sites of a simple cubic lattice,[1] as they vibrate about their lattice sites? We certainly do not expect to determine the time-dependent position vectors of the ions. A more intriguing example is that of a macroscopic crystalline sample of MnO, where the Mn^{2+} and O^{2-} ions occupy the sites of a NaCl type crystal structure.[2] Of particular interest is the fact that each Mn ion has a magnetic moment associated with a spin $S=5/2$, and that as a result of the interactions between the moments, the moments exhibit *antiferromagnetic* ordering below a critical (Néel) temperature $T_c = 116$ K. As we proceed from one Mn lattice site to the next, we may picture the magnetic moment at the first site as anti-parallel to the magnetic moment at the second site. Above T_c the long-range antiferromagnetic ordering can no longer be sustained. Again we ask, what theoretical quantity can provide us with useful insight concerning the *dynamical* characteristics of the Mn ions, both as regards their spatial vibrations about their lattice sites and the orientation of their magnetic moments?

The answers to these questions are given in graduate textbooks on solid-state physics. The density–density time correlation function provides a highly useful characterization of the lattice dynamics of the ions; the spin–spin time correlation function is the construct of choice for characterizing the dynamics of the ion magnetic moments. The independent variables of these correlation functions are the position vectors of a specific pair of ions, the time, and the temperature of the sample. The correlation functions provide highly useful information concerning the lattice and spin dynamics within our system, without inundating us with excessive detail.

Moreover, we can answer our earlier question on the type of macroscopic measurements which can be performed whose outcome is expressible in terms of the time dependence of these time correlation functions. Ever since Van Hove's pioneering papers,[3] it has been known that neutron scattering and neutron magnetic scattering are powerful experimental tools that can establish the form of the time-dependent position and spin correlation functions.[4] Nuclear magnetic resonance techniques[5,6] (NMR), and specifically the measurement of $1/T_1$, the spin-lattice relaxation rate, is another example of a very useful modern experimental technique which is intimately tied to the form of the spin–spin time correlation function. In the most general theoretical formulation,[7] a relation is derived for the spin-lattice relaxation rate in terms of the time correlation function for arbitrary pairs of paramagnetic ions.

Explicit examples of equilibrium correlation functions are given in Secs. II–IV. The usual mathematical form is given by

$$C_{AB}(\mathbf{r}_1,\mathbf{r}_2,t,T)=\langle A(\mathbf{r}_1,0)B(\mathbf{r}_2,t)\rangle, \tag{1}$$

where the angular brace denotes the canonical ensemble average (quantum-mechanical or classical); usually the variables A and B coincide, but that is not required. The theory of transport coefficients[8] is built on the use of time correlation functions, as is the theory of dynamical light scattering,[9] infrared absorption,[10] Raman scattering,[11] dielectric relaxation,[12] NMR line shapes,[7] depolarization of

fluorescence,[13] and sound attenuation,[14] among others.

Although an enormous literature exists, including many seminal articles[15] and useful monographs,[16–19] it appears that the subject of equilibrium time correlation functions has not yet become a part of the standard repertoire of graduate statistical mechanics courses. Perhaps this lack is due to the mathematical complexities associated with calculating the time correlation functions for systems of interest.

In this article we explore the properties of the equilibrium time correlation function for three relatively simple, but nontrivial systems. The purpose of our exploration is to help give the reader a measure of familiarity with the major features of these correlation functions, without becoming intimidated by the complexities associated with realistic systems of research focus. Thus in Sec. II we consider the mathematically simple examples of the classical and quantum linear harmonic oscillators. There are several important conceptual lessons of broad importance that we can learn as we breeze through the almost trivial mathematical steps. In Sec. III we concentrate on the time-dependent spin correlation functions for the kinetic Ising model of Glauber.[20] The conceptual issues are no more intricate than for the harmonic oscillator, and the more challenging mathematical tasks are still manageable as we shall only encounter linear equations of motion for the individual spins. Finally, in Sec. IV we present the major features of the time correlation function for two unit vectors (''spins'') that interact with each other via isotropic Heisenberg exchange. This system, which can be treated by exact analytical methods[21] is a useful starting point before contemplating large arrays of interacting spins for which the calculation of the time correlation function can only be achieved by large-scale computer calculations.[22,23]

The three-part message of this paper that we hope to convey is that there is a rich tapestry of dynamics that proceeds to unfold indefinitely even after a system reaches thermal equilibrium; the time correlation functions provide an optimum theoretical construct for characterizing the dynamics; and a time correlation function appropriately designed for a specific type of experimental probe can be used to predict the outcome of the experiment, and vice versa.

II. LINEAR OSCILLATOR

We consider a one-dimensional harmonic oscillator, described by the Hamiltonian function

$$H(p,x) = p^2/(2m) + (m\omega^2/2)x^2. \tag{2}$$

The simplest example of an equilibrium time correlation function is the equilibrium position autocorrelation function defined by the relation

$$C_{xx}(t,T) = \langle x(0)x(t) \rangle, \tag{3}$$

where the angular brace denotes the canonical ensemble average. It is assumed that the system is in thermal equilibrium with a heat bath at temperature T. We stress that the quantity $x(t)$ in Eq. (3) is to be calculated for an *isolated* oscillator by solving the canonical equations of motion which follow upon using the Hamiltonian function of Eq. (2). In particular, we do not supplement Eq. (2) with terms that describe some applied, external forces or coupling between the oscillator and the heat bath. As we shall see, the latter will manifest itself only in a very subtle, implicit manner, via the weighted average prescribed by the canonical ensemble over the initial values of the position and momentum of the oscillator. We

shall refer to this average as the ''Gibbs approach,'' for which the only signature of the heat bath in thermal equilibrium expressions is the absolute temperature of the bath. The details of the heat bath as well as its coupling to the system of interest (the oscillator) will not be manifested in the partition function and in *equilibrium* time correlation functions. Only when considering *nonequilibrium* time correlations will the heat bath coupling make an explicit appearance. We shall discuss this point on several further occasions in this paper.

The calculation that is to be performed divides into two distinct tasks. First, we establish the most general form of $x(t)$; for the linear oscillator it will be a linear function of the integration constants, which we select as the initial values $x(0)$ and $p(0)$. Second, we perform the classical canonical ensemble average over these initial values. That is, for any quantity $u(p(0),x(0))$, its canonical ensemble average is given by

$$\langle u \rangle = \frac{1}{Z} \int_{-\infty}^{\infty} dp(0) \int_{-\infty}^{\infty} dx(0) u$$
$$\times \exp[-\beta H(p(0),x(0))], \tag{4}$$

where $\beta = 1/(k_B T)$ and Z is the partition function

$$Z = \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dx \exp(-\beta H(p,x)). \tag{5}$$

For the classical oscillator the calculations are particularly simple. Starting from Eq. (2), the steps are very well known, and we have

$$x(t) = x(0)\cos \omega t + \frac{p(0)}{m\omega} \sin \omega t. \tag{6}$$

Substituting this formula in Eq. (3), we arrive at

$$C_{xx}(t,T) = \langle x(0)^2 \rangle \cos \omega t + \frac{\langle x(0)p(0) \rangle}{m\omega} \sin \omega t. \tag{7}$$

Because the exponential function in Eq. (4) is even in $x(0)$ and $p(0)$ and may also be factored as the product of exponential functions of each of these variables, we immediately have

$$\langle x(0)p(0) \rangle = \langle x(0) \rangle \langle p(0) \rangle = 0. \tag{8}$$

We may also sidestep the explicit calculation of the canonical ensemble average of $x(0)^2$; invoking the equipartition theorem we have

$$C_{xx}(0,T) = \langle x(0)^2 \rangle = \frac{k_B T}{m\omega^2}. \tag{9}$$

We thus arrive at our final result

$$C_{xx}(t,T) = \frac{k_B T}{m\omega^2} \cos \omega t. \tag{10}$$

Note that the correlation function is a periodic function of the time with period $\tau = 2\pi/\omega$, coinciding with the period of the oscillator, and in particular, *does not decay with time*. We can say that a classical oscillator in thermal equilibrium proceeds through its oscillatory paces with an amplitude prescribed by the equipartition theorem, namely $(k_B T/(m\omega^2))^{1/2}$.

The mathematical demands of the above calculations were trivial, yet the above derivation is subtle and deserves careful

thought. We explicitly assumed that $x(t)$ in Eq. (3) is given by the classical orbit of an *isolated* oscillator (that is, uncoupled to the heat bath). The heat bath manifests itself solely in Eqs. (8) and (9) which are statements about the relative weights for a given temperature of the initial values of the position and momentum of the oscillator.

For the quantum oscillator the calculations are nearly as simple. The Hamiltonian function of Eq. (2) is replaced by the corresponding Hamiltonian operator, expressed in terms of the operators x, $p = -i\hbar\partial/\partial x$ corresponding to the classical position and momentum variables. The autocorrelation function is still defined by Eq. (3), but $x(0)$ and $x(t)$ are position operators, taken in the Heisenberg representation. That is,

$$x(t) = \exp(-iHt/\hbar)x\exp(iHt/\hbar), \tag{11}$$

and it is also convenient to introduce

$$p(t) = \exp(-iHt/\hbar)p\exp(iHt/\hbar). \tag{12}$$

These time-dependent operators satisfy the Heisenberg equations of motion

$$dx(t)/dt = (-i/\hbar)[x(t),H] = p(t)/m, \tag{13}$$

$$dp(t)/dt = (-i/\hbar)[p(t),H] = -m\omega^2 x(t). \tag{14}$$

The solutions of the latter equations are given in standard textbooks on quantum mechanics; $x(t)$ is given by Eq. (6) except that now $x(0),p(0)$ are no longer c-number integration constants but instead the conjugate operators x, p. The correlation function is again given by Eq. (7), but the quantum canonical ensemble averages are to be taken. We find that $\langle xp \rangle = 0$ and that

$$\langle x^2 \rangle = \mathrm{Tr}(x^2 \exp(-\beta H))/\mathrm{Tr}(\exp(-\beta H))$$

$$= \frac{\hbar}{m\omega}\coth(\beta\hbar\omega/2). \tag{15}$$

To obtain this result it is useful to write x, p in terms of the familiar oscillator raising and lowering operators $\alpha^\dagger, \alpha$, that is,

$$x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(\alpha^\dagger + \alpha), \quad p = i\left(\frac{m\hbar}{2}\right)^{1/2}(\alpha^\dagger - \alpha), \tag{16}$$

where $[\alpha,\alpha^\dagger] = 1$. The Hamiltonian operator then assumes the convenient diagonal form

$$H = \hbar\omega(\alpha^\dagger\alpha + \tfrac{1}{2}). \tag{17}$$

One can then either recall or easily derive the result that the equilibrium occupation number is given by the Planck function

$$\langle\alpha^\dagger\alpha\rangle = \frac{1}{e^{\beta\hbar\omega} - 1}. \tag{18}$$

With Eq. (15) established we immediately arrive at the final result for the autocorrelation function

$$C_{xx}(t,T) = \frac{\hbar}{m\omega}\coth(\beta\hbar\omega/2)\cos\omega t. \tag{19}$$

In the regime where $\hbar\omega/(k_B T) \ll 1$ our general formula reduces to the classical result of Eq. (10). In the opposite (strong quantum) regime $\hbar\omega/(k_B T) \gg 1$, we have

$$C_{xx}(t,T) \approx \frac{\hbar}{m\omega}(1 + 2e^{-\beta\hbar\omega})\cos\omega t. \tag{20}$$

In contrast to the result, Eq. (10), for the classical oscillator, in the low-temperature limit the autocorrelation function of the quantum oscillator remains nonzero, reflecting its residual zero-point motion.

Analogous remarks apply here as for the classical oscillator. The quantum autocorrelation function is a periodic function of the time with period $\tau = 2\pi/\omega$, the Heisenberg operator $x(t)$ has been calculated for an isolated oscillator, and the heat bath plays a role only via the quantum canonical ensemble average of the operator x^2.

III. DYNAMICAL CORRELATIONS IN THE GLAUBER MODEL

A. Introduction

We now discuss the time correlation functions for the Glauber kinetic Ising model, a phenomenological model[20] that incorporates dynamics in a system of Ising spins in contact with a heat bath at temperature T. As is well known, the Ising model[24] provides a useful framework for describing the equilibrium properties of systems for which at each lattice site k, a discrete spin variable, σ_k, can assume either of two discrete values, traditionally chosen as $\sigma_k = \pm 1$. Familiar applications of the Ising model include the equilibrium properties of binary alloys, systems of adsorbed particles, and interacting magnetic moments for models of magnetic materials. For a one-dimensional (1D) ring of N spins with nearest-neighbor interactions, the Ising model Hamiltonian is defined by

$$H[\sigma] = -J\sum_{n=1}^{N}\sigma_n\sigma_{n+1}, \tag{21}$$

where J is the exchange interaction energy and where we adopt the cyclic boundary condition, $\sigma_{N+1} \equiv \sigma_1$. Note that (anti)ferromagnetic interactions are implied by $(J<0)$ $J>0$. We are interested in the thermodynamic limit, $N \to \infty$. The Ising Hamiltonian in Eq. (21) does not yield any intrinsic dynamical properties for the spin variables. To obtain a dynamical model, we could add to the Ising Hamiltonian an explicit term that represents the coupling of the spins to the heat bath. Such a route, however, is fraught with complexities. Instead, Glauber[20] simply *defined* an effective dynamics for Ising spins, one that is phenomenologically based and that takes into account the coupling between the spins which is inherent in the equilibrium model of Eq. (21).

In the Glauber model associated with the nearest-neighbor 1D Ising model of Eq. (21), one defines a time-dependent quantity, $s_n(t)$ which is the ensemble average of σ_n with respect to a nonequilibrium probability distribution function, $P(\{\sigma\};t)$,

$$s_n(t) = \sum_{\{\sigma\}}P(\{\sigma\};t)\sigma_n, \tag{22}$$

where the symbol $\{\sigma\}$ is an abbreviation for a configuration of the complete set of spins and $\Sigma_{\{\sigma\}}$ is defined as the sum over all 2^N configurations of the N spin variables of the system. The equation of motion for these averages can be written as

$$\alpha^{-1}\frac{d}{dt}s_n = -s_n + \frac{\gamma}{2}(s_{n+1}+s_{n-1}),\tag{23}$$

where $\gamma \equiv \tanh(2K)$, with $K \equiv J/(k_B T)$ a dimensionless nearest-neighbor coupling constant, α^{-1} is a characteristic time scale taken as a free parameter of the model, and $s_{N+1} \equiv s_1$. Because the time evolution of the system is determined by a set of N linear, coupled first-order differential equations, we can anticipate that the 1D nearest-neighbor Glauber model is amenable to exact solution. We consider this calculation in Sec. III C after making a few remarks on Eq. (23).

B. The origins of Eq. (23)

Before deriving the equilibrium two-spin time correlation functions, it is useful to briefly review the origins of Eq. (23), the equations of motion of the system. The basic assumption of the Glauber model is that there is a probability per unit time, $w_j(\sigma_j)$, that the heat bath induces a spin–flip transition, $\sigma_j \rightarrow -\sigma_j$ while momentarily leaving all other spins unchanged. Under this assumption, the equation of motion for the probability distribution can be written in the characteristic "gain-loss" form of a master-equation,[19]

$$\frac{d}{dt}P(\{\sigma\};t) = \sum_{j=1}^{N} w_j(-\sigma_j)P(\{\sigma'\}_j;t)$$
$$- \left[\sum_{j=1}^{N} w_j(\sigma_j)\right]P(\{\sigma\};t).\tag{24}$$

The first term in Eq. (24) represents the probability per unit time that the system makes a transition to the configuration $\{\sigma\} \equiv \{\sigma_1,\ldots,\sigma_N\}$ from the configuration $\{\sigma'\}_k \equiv \{\sigma_1,\ldots,-\sigma_k,\ldots,\sigma_N\}$ via single spin flips, while the second term is the probability per unit time that the system makes a transition out of this configuration, also by single spin flips. From Eq. (24), it can then be shown that the equation of motion for s_k is given by

$$\frac{d}{dt}s_k(t) = -2\sum_{\{\sigma\}} \sigma_k w_k(\sigma_k)P(\{\sigma\};t).\tag{25}$$

The dynamical properties of the Glauber model are determined once the form of the transition probability, w_j, is specified. The connection between Eq. (25), which thus far is a general equation of motion based on the sole assumption that the system evolves by a random succession of spin flips, and the Ising model of Eq. (21) comes by imposing the requirement of detailed balance when the system achieves thermal equilibrium. That is, the steady state solution of Eq. (25) must satisfy the relation $w_j(\sigma_j)P_{eq}(\{\sigma\};T) = w_j(-\sigma_j)P_{eq}(\{\sigma'\}_j;T)$, where $P_{eq}(\{\sigma\};T)$ denotes the equilibrium canonical ensemble probability distribution associated with the Ising Hamiltonian of Eq. (21). When only nearest-neighbor spins interact, Glauber has shown[20] that the imposition of detailed balance yields the following temperature- and spin-dependent form of w_j:

$$w_j(\sigma_j,\sigma_{j-1},\sigma_{j+1};T) = \tfrac{1}{2}\alpha[1 - \tfrac{1}{2}\gamma\sigma_j(\sigma_{j+1}+\sigma_{j-1})].\tag{26}$$

According to Eq. (26), there are only three possible values of the spin–flip transition probability, $\tfrac{1}{2}\alpha(1-\gamma)$, $\tfrac{1}{2}\alpha$, and $\tfrac{1}{2}\alpha(1+\gamma)$, depending, respectively, on whether σ_j is parallel

to its nearest neighbors, $\sigma_j = \sigma_{j+1} = \sigma_{j-1}$, the neighboring spins are antiparallel, $\sigma_{j+1} = -\sigma_{j-1}$, or if σ_j is antiparallel to its nearest neighbors, $-\sigma_j = \sigma_{j+1} = \sigma_{j-1}$. This simplifying feature of a restricted dependence on the spin variables makes the Glauber model so useful for the dynamics of cooperative phenomena. Note that for ferromagnetic interactions, $\gamma \rightarrow 1$ as $T \rightarrow 0$, and thus the parallel spin configurations will be significantly longer-lived than the antiparallel ones. Finally, upon combining Eqs. (25) and (26) we arrive at Eq. (23).

C. Calculation of the time correlation function

We now define the equilibrium time correlation function, $C_n(t;T)$, for temperature T which links the spin value at lattice site 0 at time $t=0$ with that at site n at time t:

$$C_n(t;T) = \sum_{\{\sigma\}} P_{eq}(\{\sigma\};T)\sigma_0(0)\sigma_n(t) \equiv \langle\sigma_0(0)\sigma_n(t)\rangle.\tag{27}$$

To simplify the notation we will henceforth abbreviate $C_n(t;T)$ by $C_n(t)$. To simplify the mathematical treatment, we explicitly assume in the following that the system consists of an infinite number of spins and thus possesses translational symmetry. As a consequence, we have that $C_{-n}(t) = C_n(t)$. Finally, we note that at $t=0$, $C_n(t)$ reduces to the equilibrium two-spin static correlation function, which for the 1D nearest-neighbor Ising model is given by[24]

$$C_n(0) = \langle\sigma_0\sigma_n\rangle = u^{|n|},\tag{28}$$

where $u \equiv \tanh K$. Within the framework of the nearest-neighbor Glauber model, the equation of motion satisfied by the $C_n(t)$ can be shown to be given by

$$\alpha^{-1}\frac{\partial}{\partial t}C_n(t) = -C_n(t) + \frac{\gamma}{2}[C_{n-1}(t)+C_{n+1}(t)].\tag{29}$$

We can readily obtain the exact solutions of this infinite set of coupled, linear first-order differential equations by introducing the Fourier transform,

$$C(q,t) \equiv \sum_{n=-\infty}^{\infty} C_n(t)e^{inq}.\tag{30}$$

Once $C(q,t)$ is known, the correlation function can be obtained from the inverse relation,

$$C_n(t) = \frac{1}{\pi}\int_0^{\pi} dq\, C(q,t)\cos(nq) = C_{-n}(t).\tag{31}$$

Combining (29) with (30), it is easy to show that

$$C(q,t) = \chi(q;T)\exp[-\alpha(1-\gamma\cos q)t].\tag{32}$$

where we have followed conventional usage and denoted the initial value by $C(q,0) \equiv \chi(q;T)$.

The quantity $\chi(q;T)$, which measures the spectrum of fluctuations in equilibrium, is referred to as the equilibrium structure factor or as the wave-vector-dependent susceptibility. This quantity is the Fourier transform of the equilibrium two-spin *static* correlation function,

$$\chi(q;T) = \sum_{n=-\infty}^{\infty} C_n(0)e^{inq}.\tag{33}$$

A closed-form expression is easily obtained by substituting Eq. (28) in Eq. (33), thereby yielding a geometric series, with the result

$$\chi(q;T) = \frac{\sqrt{1-\gamma^2}}{1-\gamma\cos q}, \qquad (34)$$

where $\gamma = 2u/(u^2+1)$. We note here that $\chi(0;T) = [(1+\gamma)/(1-\gamma)]^{1/2} = (1+u)/(1-u)$. For the special case of the low-temperature ferromagnetic system, $\chi(q;T)$ diverges as $\gamma \to 1$ and $q \to 0$, that is, long-wavelength fluctuations dominate, because according to Eq. (32) their lifetimes diverge in the small-q limit.

Combining Eqs. (31) and (32), we arrive at the following integral expression for the time correlation function:

$$C_n(t) = \frac{e^{-\alpha t}}{\pi} \int_0^\pi dq\, \chi(q;T) \exp(\alpha\gamma t \cos q)\cos(nq), \qquad (35)$$

where $\chi(q;T)$ is given by Eq. (34). An alternate version of this result can be derived by exploiting the identity

$$\frac{\exp[-\alpha(1-\gamma\cos q)t]}{1-\gamma\cos q} = \int_{\alpha t}^\infty dw\, \exp(-w(1-\gamma\cos q)), \qquad (36)$$

and using the standard [Eq. (9.6.19) of Ref. 25] integral representation of the modified Bessel function, $I_n(x)$,

$$I_n(x) = \frac{1}{\pi}\int_0^\pi dq\, e^{\gamma\cos q}\cos(nq) = I_{-n}(x). \qquad (37)$$

We then find the compact and elegant result

$$C_n(t) = \sqrt{1-\gamma^2}\int_{\alpha t}^\infty dw\, e^{-w}I_n(\gamma w). \qquad (38)$$

For $t=0$ the integrals in Eqs. (35) and (38) are easily evaluated and we arrive at the correct result $C_n(0) = u^{|n|}$. However, for $t \neq 0$ neither integral can be expressed in closed-form in terms of standard transcendental functions.[26] Nevertheless, we can readily obtain useful results. We return to Eq. (35), substitute the infinite series Eq. (33) for $\chi(q;T)$, and use Eq. (37) to obtain the expansion

$$C_n(t) = e^{-\alpha t}\sum_{l=-\infty}^{\infty} u^{|l|}I_{n-l}(\alpha\gamma t). \qquad (39)$$

Note that this result fulfills the requirement $C_n(t) = C_{-n}(t)$. Further, we note that the complete set of equilibrium values, $C_k(0) = u^{|k|}$, explicitly play a role in determining $C_n(t)$. Also note that if we substitute $t=0$, we reproduce the correct result because all of the terms in the series of Eq. (39) vanish, with the exception of those where $l=n$, because $I_m(0) = \delta_{m,0}$, the Kronecker delta. The expansion of Eq. (39) is very useful for numerical purposes, because the modified Bessel function decreases extremely rapidly with increasing order as long as the argument $\alpha\gamma t$ is not too large compared to unity.

For very long times, that is, $\alpha\gamma t \gg 1$, the most convenient method for establishing the leading asymptotic properties of $C_n(t)$ is to work directly with the integral in Eq. (35). We limit our analysis in the following to the case of ferromagnetic coupling. For very long times the most important portion of the integration interval is very small positive values

of the variable q. Thus we may substitute the value $q=0$ in the first factor of the integrand, and we may replace $\cos q$ by $1 - \frac{1}{2}q^2$ and allow q to extend from 0 to $+\infty$. In this manner we arrive at the result

$$C_n(t) \sim \left(\frac{1+\gamma}{1-\gamma}\right)^{1/2}\frac{\exp(-\alpha(1-\gamma)t - n^2/(2\alpha\gamma t))}{(2\pi\alpha\gamma t)^{1/2}}. \qquad (40)$$

Thus, if $\alpha\gamma t \gg 1$, the time correlation function linking two spins, which are a fixed, finite distance apart, is dominated by exponential decay. However, if the temperature is very nearly zero, the decay is dominated by a power law (square root) decay. This power law behavior is a manifestation of critical slowing down, a feature that was already evident in Eq. (32).

Another useful feature of the Glauber model is that it is very helpful in illustrating dynamical critical phenomena. As is well known, fluctuations become correlated over large distances at a critical point. Examining the equilibrium static correlation function of the 1D Ising model, $\langle\sigma_0\sigma_n\rangle = u^{|n|}$, we see that correlations decay exponentially with distance because we can write $\langle\sigma_0\sigma_n\rangle = \exp(-|n|/\xi)$, where the correlation length ξ is given by $\xi^{-1} = -\ln[\tanh(|K|)]$. Note that $\xi \to \infty$ as $T \to T_c = 0$. The fact that the critical temperature T_c is zero is related to the one-dimensional nature of the model. Because the fluctuations become indefinitely large in spatial extent at a critical point, we expect their lifetimes to diverge as well. The *dynamical scaling hypothesis* connects these ideas by stating that the characteristic relaxation time of critical fluctuations should scale with the correlation length. For example, if $\omega_c(q)$ is a characteristic response frequency for wave vector q, the dynamical scaling hypothesis[27] states that near the critical point, $\omega_c = \xi^{-z}F(q\xi)$, where F is a scaling function and z is the dynamical critical exponent.

Determining the dynamical critical exponent is a very difficult task for most systems. We will now show that $z=2$ for the 1D Glauber model. From Eq. (32), we can identify a characteristic response rate for the Glauber model, $\omega_c(q) = \alpha(1-\gamma\cos q)$. As we have seen, for ferromagnetic interactions the system is dominated by long-wavelength fluctuations as $\gamma \to 1$ and $q \to 0$. For small q, we have $\omega_c(q) \approx \alpha(1-\gamma+\frac{1}{2}\gamma q^2)$. It can be shown that $1-\gamma = \tanh(\frac{1}{2}\xi^{-1})\tanh(\xi^{-1})$, so that $1-\gamma \approx \frac{1}{2}\xi^{-2}$ as $\xi \to \infty$. Hence, $\omega_c(q)$ can be written in the dynamic scaling form, $\omega_c(q) = \frac{1}{2}\xi^{-2}(1+(q\xi)^2+\cdots)$ for $q\xi \ll 1$. From this behavior we can simply read off the result, $z=2$.

IV. CLASSICAL HEISENBERG DIMER

We now calculate the form of the time correlation function for a pair of classical spins, a dimer, which interact via the mechanism of isotropic Heisenberg spin exchange. The spins are represented by a pair of unit vectors (c numbers), $\mathbf{s}_1(t)$ and $\mathbf{s}_2(t)$ with $|\mathbf{s}_1(t)| = |\mathbf{s}_2(t)| = 1$. The Hamiltonian describing this system is of the usual exchange form[28]

$$H = -J\mathbf{s}_1(t)\cdot\mathbf{s}_2(t), \qquad (41)$$

where J is the exchange constant in Sec. II. We also can include a term in H which describes the interaction of the spins with an external magnetic field,[29] but for simplicity we will not include such a term here. It should also be noted that H may be rewritten in terms of $S = |\mathbf{S}|$ as

$$H = -(J/2)(S^2 - 2), \qquad (42)$$

where $\mathbf{S} \equiv \mathbf{s}_1(t) + \mathbf{s}_2(t)$.

The dynamical behavior of the spins is determined by the following nonlinear vector equation of motion[28]

$$d\mathbf{s}_1(t)/dt = (1/\tau)\mathbf{s}_1(t) \times \mathbf{s}_2(t),$$

$$d\mathbf{s}_2(t)/dt = -(1/\tau)\mathbf{s}_1(t) \times \mathbf{s}_2(t), \qquad (43)$$

where τ is a parameter with units of time. Equation (43) can be understood in terms of equal and opposite instantaneous torques acting on the separate spins as a result of their exchange interaction. That is, in the absence of an external magnetic field, the total angular momentum of the spins, $\mathbf{S}$, is a conserved quantity.

We now derive the autocorrelation function $C(t,T) \equiv \langle \mathbf{s}_1(0) \cdot \mathbf{s}_1(t) \rangle = \langle \mathbf{s}_2(0) \cdot \mathbf{s}_2(t) \rangle$, where the angular brace denotes the canonical ensemble average based on the Hamiltonian H of Eq. (41). Following the pattern of the preceding sections, our first step consists of solving the equations of motion. This step is easily achieved by noting that $\mathbf{s}_1(t) \times \mathbf{s}_2(t) = \mathbf{s}_1(t) \times (\mathbf{s}_1(t) + \mathbf{s}_2(t)) = \mathbf{s}_1(t) \times \mathbf{S}$, so that we may rewrite Eq. (43) as

$$d\mathbf{s}_1(t)/dt = (1/\tau)\mathbf{s}_1(t) \times \mathbf{S},$$

$$d\mathbf{s}_2(t)/dt = -(1/\tau)\mathbf{s}_2(t) \times \mathbf{S}. \qquad (44)$$

Here we are exploiting the conservation law to allow us to work in a subspace where $\mathbf{S}$ is a constant vector. This subspace offers the great advantage that the equations of motion become linear. Moreover, these equations are formally identical to those arising in the familiar problem of independent spins in an external static magnetic field, whose role is played here by the constant vector $\mathbf{S}$ (up to a constant of proportionality). We recall that such spins precess about the external field with an angular velocity that is proportional to the magnitude of the field. In the present setting the general solution of the first equation of Eq. (44) may be written as

$$\mathbf{s}_1(t) = c\hat{\mathbf{S}} + a[\hat{\mathbf{x}} \cos(St/\tau) - \hat{\mathbf{y}} \sin(St/\tau)], \qquad (45)$$

where a and $c (= \hat{\mathbf{S}} \cdot \mathbf{s}_1(0))$ are a pair of integration constants subject to the constraint $a^2 + c^2 = 1$ to ensure that $\mathbf{s}_1(t)$ is a unit vector. Here $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{S}}$ form a right-handed orthogonal triad, and $\hat{\mathbf{S}}$ is a unit vector in the direction of $\mathbf{S}$. Note that the precessional angular frequency, S/τ, can span the interval $(0, 2/\tau)$ in a *continuous* manner.

Using Eq. (45) the autocorrelation function may be written as

$$C(t,T) = \langle c^2 \rangle + \langle (1 - c^2) \cos(St/\tau) \rangle. \qquad (46)$$

As in our previous examples, the second stage of the calculation consists of doing the canonical ensemble averages in Eq. (46), specifically over the initial values of $\mathbf{s}_1(0)$ and the allowed values of the total spin vector $\mathbf{S}$. The details of these calculations are given elsewhere.[21] The final result is

$$C(t,T) = \frac{1}{2}\left[1 + \coth(\beta J) - \frac{1}{\beta J} \right] - \frac{\beta J}{\exp(2\beta J) - 1}$$

$$\times \int_0^2 dS\, S\left(1 - \frac{S^2}{4} \right) \exp\left(\frac{\beta J S^2}{2} \right) \cos(St/\tau). \qquad (47)$$
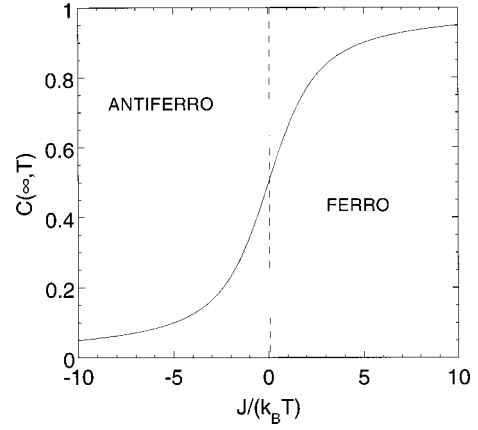
Fig. 1. Dependence on temperature of $C(t\to\infty,T)$, the long-time limit of the autocorrelation function of the classical Heisenberg dimer for ferro- and antiferro-exchange.

For arbitrary values of the time t, the integral in Eq. (47) can be expressed in terms of error functions of complex arguments. However, for numerical work and for establishing the major properties of the result, the integral representation given in Eq. (47) is especially useful.

For $t=0$ the integral in Eq. (47) is easily evaluated and we find that $C(0,T) = 1$. This result is expected because $C(0,T) = \langle \mathbf{s}_1(0) \cdot \mathbf{s}_1(0) = 1 \rangle = 1$. In contrast, in the large-t limit, the integral in Eq. (47) vanishes as a result of the infinite number of oscillations of the cosine factor within the interval of integration $(0,2)$. (In more formal language, this result is a consequence of the Riemann-Lebesgue lemma.[30]) Thus we may identify the first term on the RHS of Eq. (47) with

$$C(\infty,T) = \frac{1}{2}\left[1 - \coth(\beta J) + \frac{1}{\beta J} \right]. \qquad (48)$$

A plot of $C(\infty,T)$ versus $J/k_B T$ is given in Fig. 1. For ferro-exchange, $C(\infty,T)$ decreases monotonically from unity for $T=0$ K to the value $1/2$ for infinite temperature, whereas for antiferro-exchange $C(\infty,T)$ increases monotonically from zero to $1/2$.

In the following it will be useful to consider the Fourier cosine transform of $C(t,T)$ which we denote by $\tilde{C}(\omega,T)$. This pair of functions are related by Fourier's theorem according to

$$\tilde{C}(\omega,T) = \int_0^\infty dt\, C(t,T) \cos \omega t, \qquad (49a)$$

$$C(t,T) = \frac{2}{\pi} \int_0^\infty d\omega\, \tilde{C}(\omega,T) \cos \omega t. \qquad (49b)$$

Using Eqs. (47) and (49a) we have

$$\tilde{C}(\omega,T) = \frac{\pi}{2}\tau\left[2C(\infty,T)\delta(\omega\tau) \right.$$

$$\left. + \frac{\beta J \exp(-\beta J(\omega\tau)^2/2)}{1 - \exp(-2\beta J)} \omega\tau\left(1 - \frac{(\omega\tau)^2}{4} \right) \right]. \qquad (50)$$

The Dirac delta function term is to be expected because of the fact that $C(t,T)$ has a nonzero long-time limit. In Fig. 2
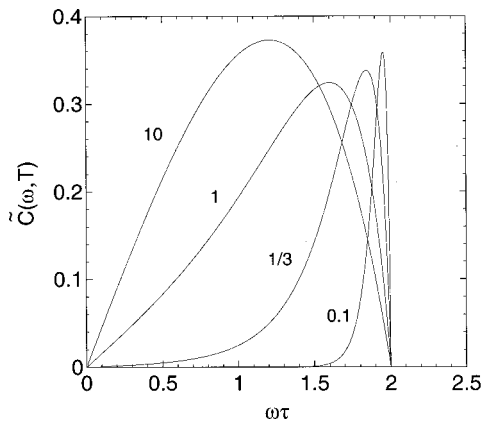
Fig. 2. Fourier cosine transform of the autocorrelation function (arbitrary units) of the classical Heisenberg dimer with ferro-exchange as a function of $\omega\tau$ for the listed values of $k_B T/J$. Not shown is the Dirac delta function associated with $\omega=0$.

Fig. 4. Fourier cosine transform of the autocorrelation function (arbitrary units) of the classical Heisenberg dimer with antiferro-exchange as a function of $\omega\tau$ for the listed values of $k_B T/|J|$. Not shown is the Dirac delta function associated with $\omega=0$.

we plot the second term in the square brackets of Eq. (50) versus $\omega\tau$ for several choices of T for $J>0$. For very low temperatures $(k_B T \ll J)$, this function is sharply peaked around $\omega\tau=2$. This result is to be expected because, if we refer back to Eq. (42), we note that for ferro-exchange, the precessional modes with the highest possible angular frequencies are thermally favored. This behavior implies that for modest values of t, the deviations of $C(t,T)$ from $C(\infty,T)$ should be well approximated by a term proportional to $\cos(2t/\tau)$. This behavior is confirmed as shown in Fig. 3, where we display $C(t,T)=\langle c^2\rangle+\langle(1-c^2)\cos(St/\tau)\rangle$ versus time for several temperatures. In fact, we notice that oscillatory behavior occurs for all temperatures, although the decay of the amplitude of the oscillation is more pronounced the higher the temperature. Also the ''effective period'' of the oscillations increases with increasing temperatures. Both of these features can be correlated to the obvious property seen in Fig. 2 that, as the temperature is increased, $\widetilde{C}(\omega,T)$ retains a skewed shape of increasing width, where the value of $\omega\tau$ corresponding to the peak decreases monotonically to the value $2/\sqrt{3}$ in the high-temperature limit.

Figure 4 is the analogue of Fig. 2 for antiferro-exchange. The most noteworthy features are that the curves broaden with increasing temperature and that the value of $\omega\tau$ corre-
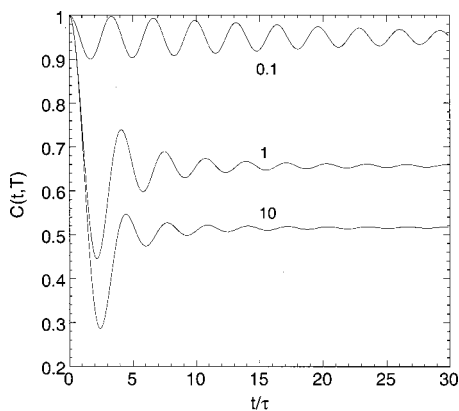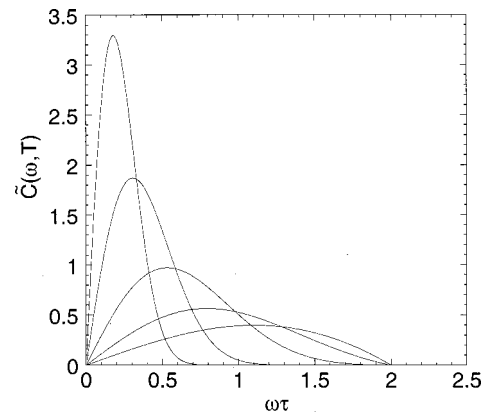
sponding to the peak increases from zero (low temperature limit) to $2/\sqrt{3}$ in the high-temperature limit. For low temperatures the precessional modes with near-zero angular velocity are favored. The corresponding curves for $C(t,T)$ are shown in Fig. 5. Note the very slow variation with time which occurs for low temperatures.

It is common to portray the physics at infinite temperature as entirely uninteresting. However, this is definitely not the case for the dimer. At infinite temperature Eq. (47) reduces to

$$C(t,\infty)=\frac{1}{2}+\frac{1}{2}\int_0^2 dS\, S\left(1-\frac{S^2}{4}\right)\cos(St/\tau). \quad (51)$$

An evaluation of this integral leads to the following closed-form result:

$$C(t,\infty)=\frac{1}{2}-\frac{1}{2t^{*2}}-\frac{3}{4t^{*4}}-\left(\frac{1}{t^{*2}}-\frac{3}{4t^{*4}}\right)$$
$$\times\cos(2t^*)+\frac{3\sin(2t^*)}{2t^{*3}}, \quad (52)$$

where we have introduced $t^*=t/\tau$. Note that the correction terms to the long-time limit (1/2) involve sinusoidal functions of the time with amplitudes that decay according to a
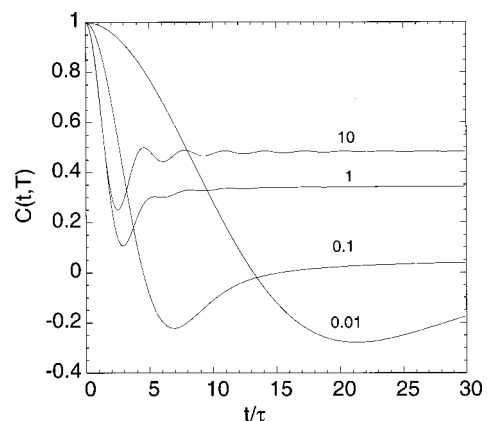

Fig. 3. The autocorrelation function $C(t,T)$ of the classical Heisenberg dimer with ferro-exchange as a function of t/τ for the listed values of $k_B T/J$.

Fig. 5. The autocorrelation $C(t,T)$ of the classical Heisenberg dimer with antiferro-exchange as a function of t/τ for the listed values of $k_B T/|J|$.

low power of t, and not according to the conventional exponential decay. This behavior is implicit in the fact that for all temperatures, including infinite temperature, $\tilde{C}(\omega,T)$ is an *entire function*, that is, an analytical function for all finite values of the complex variable ω. The physical origin of this property is intimately tied to the fact that the total angular momentum of the system is conserved.[21] The more familiar exponential decay for long times would occur if $\tilde{C}(\omega,T)$ were to possess a simple pole at some point in the complex ω plane off the real axis.

For any finite temperature the asymptotic expansion of $C(t,T)$ appropriate for the large-t regime can be derived[21] by repeated integrations by parts of the integral of Eq. (47). The resulting expansion possesses a structure similar to that of Eq. (52), but the expansion terminates after a finite number of terms only for infinite temperature.

The results summarized here for the classical Heisenberg dimer can be generalized in several ways. In Ref. 29 a treatment is given for this system in the presence of a uniform static magnetic field. In Ref. 31 the autocorrelation function is derived for a quantum-mechanical spin dimer, the two spins taking on identical but arbitrary values of spin, and the results are compared to those of the classical dimer. The major difference between these systems is that the quantum autocorrelation function is periodic in time, whereas, as we have just seen, the classical autocorrelation function is not. Analytical results for the autocorrelation function are also available[21] for several other classical Heisenberg spin systems. These include single spins at each vertex of an equilateral triangle, and single spins at the vertices of a regular tetrahedron. The quantum-mechanical version of the equilateral triangle configuration has also been developed in Ref. 32. A much more difficult system to treat, yet one that is nevertheless tractable by analytical methods, is that of classical spins at the vertices of a square with nearest-neighbor interactions only. Numerical results for $N \geq 5$ classical spins, equally spaced on the circumference of a ring, again subjected to the restriction of nearest-neighbor isotropic exchange interactions, have been given in Refs. 23 and 33. It is noteworthy that many features of the classical dimer find their expression in all of these larger arrays of interacting Heisenberg spin systems.

Interest in small arrays of quantum and classical Heisenberg spin systems is fueled in large part by the fact that there is a rapidly growing list[34] of large synthetic organic-based molecules containing relatively small numbers of interacting transition-metal paramagnetic ions. These molecules exhibit very weak intermolecular magnetic interactions. Measurements performed on a bulk sample therefore reflect intramolecular magnetic interactions only. Furthermore, the intramolecular magnetic interactions appear to be well described by the Heisenberg model with isotropic nearest-neighbor exchange. As stated in Sec. I, the time- and temperature-dependent correlation function for pairs of magnetic moments serves as a useful construct for understanding diverse dynamical phenomena, such as spin-lattice relaxation and inelastic neutron scattering. Even the simple model of the classical Heisenberg dimer appears timely given the fact that NMR measurements have recently been performed[35] on a dimer molecular magnet composed of Fe^{3+} ions. The large spin values ($s = 5/2$) of the individual Fe ions makes comparison with the classical Heisenberg dimer very relevant.

V. SUMMARY

We have discussed the equilibrium time correlation functions for three elementary systems. The advantage of considering simple systems is that one can easily grasp the logical steps that are involved in calculating the time correlation functions while avoiding the difficulties associated with the necessary calculations for more complex systems. Interestingly, the characteristics of the time correlation functions differ widely for the three systems that we have analyzed here. Yet in all cases the logical steps are similar no matter how complex the system may be.

ACKNOWLEDGMENTS

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HIGH-CLASS LAB TABLES

Amaldi and Segrè had not been wrong about aluminum. They had simply irradiated different samples of the element on different tables. The hydrogen in the wooden table had slowed down some of the neutrons and enhanced the almost-three-minute activity. As Hans Bethe once noted wittily, the efficiency of slow neutrons ''might never have been discovered if Italy were not rich in marble... . A marble table gave different results from a wooden table. If it had been done [in America], it all would have been done on a wooden table and people would never have found out.''

Richard Rhodes, *The Making of the Atomic Bomb* (Simon & Schuster, New York, 1986), pp. 219–220.