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Self-Diffusion via Sine-Gordon Solitons

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Theoretical evidence is presented that for temperatures so low that k_BT is much less than the rest energy of a soliton, the mean square displacement of a diffusing particle of an infinite sine-Gordon chain behaves as $t^{1/2}$ for times much longer than microscopic times but much shorter than the soliton lifetime τ. For times much greater than τ, *linear* behavior is suggested. Finite-size effects are discussed in the context of recent computer simulation studies.

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The problem of the dynamical behavior of interacting particles subject to interactions with a heat bath which can be simulated by random forces of the Langevin type has applicability to a wide variety of systems in physics, chemistry, and biology.[1] One such nontrivial system with essential nonlinearities is the sine-Gordon chain, which consists of a chain of particles, each moving in a sinusoidal potential and interacting with each other via nearest-neighbor spring forces. We will deal with the simplest case, where the natural length of the spring is equal to the period of the sinusoidal potential. Though there exist particular solutions to the dynamical equations of motion of the system in the absence of random forces,[2] we still do not have an exact solution for the system in the presence of random thermal-noise forces.

Schneider and Stoll[3] recently published results of a computer study of the dynamics of the sine-Gordon chain in the presence of random forces which indicated that the asymptotic long-time (t) behavior of the mean square displacement $\langle x^2\rangle$ of a particle was proportional to $t^{4/3}$. On the other hand, exact solutions[4,5] for the chain of harmonically coupled particles (and thus the sine-Gordon chain with the periodic potential removed) lead to a $t^{1/2}$ behavior. It is *tempting* to suggest that the addition of a periodic potential to the chain of harmonically coupled particles (thus producing the sine-Gordon chain) cannot lead to an *increase* in the exponent of t (from $\frac{1}{2}$ to $\frac{4}{3}$), since the periodic potential should *impede* rather than aid diffusion (as in the case of the single, noninteracting Brownian particle[6]). In other words, we would expect an exponent of $\frac{1}{2}$ or less instead of the exponent of $\frac{4}{3}$. However, the *combination* of the periodic potential and the harmonic coupling produce unique excitations such as the "kink" or the "soliton." One might think that the sine-Gordon chain could exhibit surprising effects contrary to one's intuition. Clearly, this system deserves a more quantitative treatment.

In this paper, we produce theoretical evidence that for the infinite sine-Gordon chain, at least in the limit that the temperature $T\to 0$ K, the *exponent remains equal to* $\frac{1}{2}$ as long as the *soliton's lifetime is neglected.* A *finite lifetime* τ leads, within our approximate model, to an *exponent of unity* (i.e., linear behavior) for times $\gg\tau$.

In order for our model to be valid, we require that $k_BT\ll E_0$, the rest energy of a soliton. This inequality leads to a low soliton density n_s. We can neglect both interactions among solitons and higher-energy excitations. Finally, we can assume that a particle will oscillate in a minimum of the periodic potential until a soliton passes by and leads to the particle's jumping forward or backward one lattice spacing. Diffusion of the *particles* is thus governed by the diffusion of the *solitons*, which can be treated as a system of pseudoparticles of mass $M_0=E_0/c_0^2$, where c_0 is the sound velocity along the chain. The assumption of strong coupling (expressible as $c_0\gg\omega_0 a$, where ω_0 is the characteristic frequency of oscillation of a single particle in the sinusoidal potential and a is the lattice constant, set equal to unity in the paper) allows us to use a continuum approximation.

After presenting our results for an infinite chain, we shall present some results for a finite chain and discuss their relevance to the recent computer simulation work of Schneider and Stoll.[3] In particular, one can qualitatively account for their results on the basis of self-diffusion of particles governed by a combination of both freely moving and diffusing solitons, in which case the $t^{4/3}$ fit of their data would result from a mixture of t^2 behavior and t behavior.

de Gennes's theory of reptation of a polymer chain[7] is directly applicable to this model. It will be shown to lead to the result

$$\langle x^2\rangle=n_s\langle|y|\rangle, \tag{1}$$

where y is the displacement of a single soliton in a time t.

Equation (1) can be understood in simple terms as follows: The solitons produce a random walk in x, so that $\langle x^2\rangle$ equals the average number of *uncorrelated* jumps which have taken place in the time interval 0 to t. Multiple back and forth jumps produced by a *single* soliton are *correlated* and contribute either one uncorrelated jump or none at all (accordingly as the number of passes is odd or even). The average number of uncorrelated jumps is equal to the number of solitons which lie within a distance $\langle|y|\rangle$ from the given particle—$n_s\langle|y|\rangle$.

With a Gaussian distribution for y (which obtains here),

$$\langle x^2\rangle=n_s(2\langle y^2\rangle/\pi)^{1/2}\,. \tag{2}$$

If the *solitons* are not damped, $\langle y^2\rangle\propto t^2$ and $\langle x^2\rangle\propto t$: The *particles* diffuse via a simple random walk. When damping is taken into account, $\langle y^2\rangle$ behaves as $2D_st$ for times much greater than the inverse damping rate (η^{-1}).[8] Here D_s is the diffusion constant of the solitons. Then,

$$\langle x^2\rangle\to n_s(4D_st/\pi)^{1/2}\text{ as }t\to\infty. \tag{3}$$

According to Kawasaki,[9] for low temperatures,

$$n_s=(M_0/m)(8E_0/\pi k_BT)^{1/2}\exp(-E_0/k_BT)\,. \tag{4}$$

There have been a number of interesting recent works[10-13] on the mobility of solitons in the presence of an external force acting on all the particles of the chain. If we assume the Einstein relation between the mobility and the diffusion constant to hold, they all lead to

$$D_s=\tfrac{1}{4}\pi k_BT/\eta M_0 \tag{5}$$

for low T. This classical result confirms the picture of the solitons behaving like a gas of diffusing independent particles of mass M_0.

We thus obtain, in the limit $t\to\infty$,

$$\langle x^2\rangle=\left(\frac{E_0}{mc_0}\right)\left(\frac{2t}{\eta}\right)^{1/2}\exp\left(\frac{-E_0}{k_BT}\right). \quad (6)$$

This result should be compared with the exact result for the chain of harmonically coupled particles[4,5]:

$$\langle x^2\rangle=\left(\frac{k_BT}{mc_0}\right)\left(\frac{t}{2\pi\eta}\right)^{1/2}. \quad (7)$$

We note that Eq. (6) does *not* reduce to Eq. (7) in the limit that the periodic potential vanishes. This result should not be altogether surprising since our theory assumes that $E_0\gg k_BT$.

While our results do not apply for intermediate amplitudes of the periodic potential V_p, it is reasonable to conjecture that the exponent of $\frac{1}{2}$ obtains for all finite values of V_p.

So far we have neglected the effect of a finite soliton lifetime τ.[14] Detailed calculations[15] with a model which neglects soliton-soliton correlations leads to $\langle x^2\rangle\to n_s(D_s/\tau)^{1/2}\, t$ for $t\gg\tau$. This result can be understood as follows: For large t, the dominant contribution to $\langle x^2\rangle$ comes from solitons which have been both created and destroyed in the time interval 0 to t. The rate at which solitons are created, per unit length of chain, is given by n_s/τ. Those solitons which have an opportunity to pass the given diffusing particle come from within a distance from the particle equal to the mean free path $(D_s\tau)^{1/2}$.[16] Hence

$$\langle x^2\rangle\sim(n_st/\tau)(D_s\tau)^{1/2}$$

or

$$\langle x^2\rangle\sim n_s(D_s/\tau)^{1/2}t. \quad (8)$$

Thus, for $t\ll\tau$, $\langle x^2\rangle\propto t^{1/2}$. For intermediate times $t\sim\tau$, the leading correction of the $t^{1/2}$ behavior goes as $t^{3/2}$. The exponent $(\frac{3}{2})$ is close to that of Schneider and Stoll $(\frac{4}{3})$ but probably merely by coincidence because of the importance of finite-size effects in their work.

We now discuss the effects of *finite chain length* L. We will assume that L is much smaller than the mean free path l of a soliton. For freely moving solitons $(t\ll\eta^{-1})$, l is given by $\bar{v}\tau$, where $\bar{v}$ is the average soliton velocity. For diffusing solitons $(t\gg\eta^{-1})$, l is given by $(D_s\tau)^{1/2}$. The time τ_L which it takes for a soliton to traverse the full length of chain is given $L/\bar{v}$ and L^2/D_s for the two respective regimes. The inequality $l\gg L$ implies that $\tau\gg\tau_L$. We will further *restrict our attention to times* $t\gg\tau_L$, so that a soliton makes many traversals of the full chain length in a time t. Finally, we will assume that solitons are *reflected at the ends of the chain as antisolitons*.

We find the following results:

(i) For free solitons $(t\ll\eta^{-1})$,

$$\langle x^2\rangle\sim\begin{cases} n_s\bar{v}^2t^2/L, & \text{for } t\ll\tau & (9a)\\ n_s\bar{v}^2\tau t/L, & \text{for } t\gg\tau, & (9b)\end{cases}$$

Result (9a) can be understood as follows: A single soliton will traverse the chain t/τ_L times in a time t. The single (uncorrelated) jump distance in the random walk is given, then, by t/τ_L, not by unity as it is for the infinite chain. The total number of uncorrelated jumps for $t\ll\tau$ is given by the number n_sL of solitons present at one time. Thus $\langle x^2\rangle\sim n_sL(t/\tau_L)^2$, from which (9a) follows.

When $t\gg\tau$, the single-uncorrelated-jump distance is limited to τ/τ_L. The total number of uncorrelated jumps is now equal to $n_sL\,t/\tau$. Then $\langle x^2\rangle\sim n_sL(t/\tau)(\tau/\tau_L)^2=n_s\bar{v}^2\tau t/L$.

(ii) For diffusing solitons $(t\gg\eta^{-1})$,

$$\langle x^2\rangle\sim n_sD_st/L \text{ for all } t. \quad (10)$$

In the case $t\ll\tau$, this result can be obtained by multiplying the number of uncorrelated jumps (n_sL) by the square of the single-uncorrelated-jump distance (D_st/L^2). In the case $t\gg\tau$, the first factor is given by n_sLt/τ, while the latter factor is given by $D_s\tau/L^2$. The form of the result is thus independent of t!

Interestingly, Eq. (10) may also be obtained under the condition that the solitons *die at the ends*. This remarkable result follows from the fact that in this case, the single-uncorrelated-jump distance is given by unity, while the number of uncorrelated jumps is given by $n_sLt/\tau_L=n_sD_st/L$. (Here it is assumed that solitons are continuously being created all along the length of the chain so as to maintain the equilibrium soliton density n_s.)

How does the finite-size work of Schneider and Stoll relate to the above results? A number of factors characterize their system:

(1) They are observing behavior over time scales only a few times τ_L (not $t\gg\tau_L$). (See Ref. 3, Fig 3.)

(2) They have $k_BT/E_0\geqslant0.2$. Thus, their system may not be at temperatures so low that our approximate model can apply quantitatively.

(3) According to Ref. 3, Fig. 3, there is a significant fraction of fast-moving (v close to the speed of sound c_0) solitons which seem to propagate freely, as well as a significant fraction of

slow-moving solitons which seem to propagate diffusively.

(4) No soliton-anitsoliton annihilations are evident in Ref. 3, Fig. 3. At best, we can assume that they are examining time intervals comparable to τ or less.

(5) There are only a small number of solitons (~8) along the entire length of chain. Thus, the statistics may be insufficient to apply results of theories which neglect fluctuations in the number of solutions.

As a first approximation, we may assume that in the Schneider-Stoll work $\tau_L \ll t \ll \tau$. Their results might be explained as follows: The freely moving solitons will produce t^2 behavior [see Eq. (9a)], while the diffusing solitons produce t behavior [see Eq. (9b)]. A mixture of the two might produce behavior which is close to $t^{4/3}$.

In order to test the theory presented in this paper, it would be worthwhile and interesting to perform computer simulation calculations on a sine-Gordon chain having parameters which lie in the well-defined regimes characterized in this paper.

We now outline the mathematical development of de Gennes's theory.[7] We work with his discrete model and transfer over to the continuum afterwards. Let $P(m, t)$ be the probability that a particle has moved m spaces in a time t. Let

$$\langle e^{im\varphi}\rangle = \sum_m P(m, t) e^{im\varphi}. \tag{11}$$

With a low soliton concentration,

$$\langle e^{im\varphi}\rangle = \langle\langle e^{im\varphi}\rangle\rangle^{N_s}, \tag{12}$$

where N_s is the number of solitons among a collection of N particles and the double angular brackets $\langle\langle\rangle\rangle$ represent an average, assuming only one soliton is present. Now, one soliton can lead to $m=0$, ±1 only. Thus,

$$\langle\langle e^{im\varphi}\rangle\rangle = p_{ll} + p_{rr} + e^{i\varphi} p_{lr} + e^{-i\varphi} p_{rl}, \tag{13}$$

where p_{ll} equals the probability that the soliton started to the left of the particle *and* ended up at time t to the left of the particle, etc.

We let $p_n(t)$ be the probability that a soliton has traveled n spaces in a time t. Then,

$$p_{ll} = p_{rr} = N^{-1} \sum_{n,m>0} p_{n-m}(t) = \tfrac{1}{2} - (2N)^{-1} \sum_n |n| p_n(t),$$

$$p_{lr} = p_{rl} = N^{-1} \sum_{\substack{n>0 \\ m<0}} p_{n-m}(t)$$

$$= (2N)^{-1} \sum_n |n| p_n(t) = (2N)^{-1} \langle |n| \rangle. \tag{14}$$

Thus

$$\langle\langle e^{im\varphi}\rangle\rangle = 1 - N^{-1}(1-\cos\varphi)\langle |n| \rangle. \tag{15}$$

In the limit $N_s, N \to \infty$, with $n_s = N_s/N$,

$$\langle e^{im\varphi}\rangle = \exp[-n_s(1-\cos\varphi)\langle |n|\rangle], \tag{16}$$

from which it follows that

$$p(m, t) = \exp(-n_s\langle |n|\rangle) I_m(n_s\langle |n|\rangle) \tag{17}$$

and

$$\langle m^2 \rangle = n_s \langle |n| \rangle, \tag{18}$$

where $I_m(z)$ is the modified Bessel function of mth order.[17]

Replacing m by x and n by y produces Eq. (1).

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