Observability of hysteresis in first-order equilibrium and nonequilibrium phase transitions

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The general conditions under which a system undergoing a first-order phase transition will exhibit hysteresis behavior, rather than simple jump behavior, are obtained. These are expressed in terms of the intrinsic time scales of the system and the time scale of variation of the control parameter. The size of the critical region is estimated. Estimates of the characteristic times are made for some equilibrium and nonequilibrium systems to show hysteresis behavior.

In the theory of systems exhibiting first-order phase transitions, a question which often arises is—Does the system show a simple jump behavior at the transition point or does the system exhibit hysteresis behavior? The latter behavior occurs in a wide class of equilibrium and nonequilibrium phase transitions such as ferroelectric transitions, optical bistability, bistability in Josephson junctions, bistability in light-induced chemical reactions, and other systems. The liquid-gas transition also exhibits supercooling and superheating, however, a simple jump behavior is ordinarily seen. It appears that for nonequilibrium phase transitions of first order, the hysteresis-type of behavior predominates.

It has been pointed out that the simple jump phenomena corresponds to "Maxwell construction," familiar from van der Waal's theory of liquid-gas phase transitions, whereas the hysteresis phenomenon corresponds to what is known as the "delay convention." The question of whether the Maxwell construction prevails over the delay convention or vice versa, depends on the dynamical behavior of the system, i.e., on certain-characteristic time scales associated with the system as well as the time scale over which the control parameters of the system are changed. Recently Gilmore has also examined some of these questions and has pointed out that the time rate of change of the control parameter is an important time scale which has to be compared with the other time scales in the problem. In this paper we report some of our results on the existence of the hysteresis behavior of the system which differ in several respects from Gilmore's treatment.

In what follows we assume that the dynamics of the system is such that the phase transition behavior of the system could be characterized by a single order parameter \( \psi \), which is assumed to obey the Fokker–Planck equation

\[
\frac{\partial P}{\partial t} = \frac{\partial}{\partial \psi} \left[ A(\psi) P \right] + \frac{\partial^2}{\partial \psi^2} \left[ D(\psi) P \right].
\]

The macroscopic equation for the order parameter is

\[
\dot{\psi} = -A(\psi).
\]

For most systems \( D(\psi) \) is independent of \( \psi \) and we will assume this, later showing for a specific example that the analysis carries through even if \( D \) depends on \( \psi \). The most probable values of the order parameter in the steady state are given by

\[
A(\psi) = 0.
\]

It is easily shown that the stationary solution of (1) is

\[
P_{st}(\psi) = N \exp \left( -\frac{1}{D} \int^\psi A(\psi') d\psi' \right) = N \exp \left( -\frac{\psi}{D} \right),
\]

where \( N \) is a normalization constant. The maxima and minima of the probability distribution are given by (3). Generally if the fluctuation term \( D \) is very small, then the mean-field description (3) will be good. Note the similarity of (4) to the Einstein fluctuation formula for the description of fluctuations in thermal equilibrium systems. Note also that the relaxation of the system around the steady state is described by

\[
\ddot{\psi} = \frac{1}{T_1} \dot{\psi} - \frac{1}{T_1} A'(\psi),
\]

where \( \psi \) is a solution of (3). Equation (3) may admit many solutions, the stable solutions correspond to the ones for which \( A' \) is positive. In order to be more specific in discussing existence of hysteresis vs jump phenomena, we will assume that (3) admits two stable solutions \( \psi_1 \) and \( \psi_2 \) and one unstable solution \( \psi_3 \), as shown in Fig. 1. We will denote the external control or drive parameter by \( \mu \). We have denoted in Fig. 2 the hysteresis behavior by the dots with arrows and the simple jump behavior by the dashed line. The value of \( \mu = \mu_0 \) at which the jump phenomena occurs (without hysteresis) corresponds to the situation:
$$A(\psi, \mu) = 0, \quad A(\psi + \delta \psi, \mu + \delta \mu) = 0. \quad (7)$$

Thus, on carrying out Taylor series expansions the condition $|\delta \psi/\psi| \ll 1$ becomes

$$\left| \frac{\delta A}{\delta \mu} \right| \ll \frac{1}{T_1}, \quad \delta \mu \sim (\mu \Delta t), \quad (8)$$

where $\Delta t$ is a typical rise time for the control parameter pulse. It should be noted that (8) is violated near the critical points $\mu_1$ and $\mu_2$ since $T_1 \rightarrow \infty$.

The time $T_2$ can be calculated from the considerations of the mean first passage time for a Markov process. For this purpose $\phi_1$ can be taken as essentially the absorbing boundary of the process, since once $\psi(t)$ takes the value $\phi_1$, the transition from the minimum $\psi_1$ to $\phi_2$ occurs. The mean first passage time is given by

$$\langle \tau(\phi) \rangle = \int_0^\infty dt P_2(\psi, \tau), \quad (9)$$

where $P_2(\psi, \tau)$ is the probability that the system is to be found in the region to the left of the maximum $\phi_2$, given that it was initially in that region, which we will denote by $D$. The mean first passage time can be expressed in terms of the eigenfunctions of the operator

$$L = \frac{\partial}{\partial \psi} \left[ A(\psi) \phi_n \right] + \frac{\partial^2}{\partial \psi^2} \left[ D(\psi) \phi_n \right], \quad (10)$$

$$L \phi_n = \lambda_n \phi_n, \quad L \phi_n = \lambda_n \phi_n,$$

as

$$\langle \tau(\phi) \rangle = \int_D \sum \phi_n(\phi') d\phi'. \quad (11)$$

Of course if initially $\phi$ is characterized by a distribution $P(\phi)$, then the mean first passage time is obtained by averaging (9) with respect to $P(\phi)$. The mean first passage as defined by (9) is known to satisfy

$$-A(\psi) \frac{\partial}{\partial \psi} \langle \tau(\phi) \rangle + D(\psi) \frac{\partial^2}{\partial \psi^2} \langle \tau(\phi) \rangle = -1. \quad (12)$$

On solving (12) we obtain

$$\langle \tau(\phi) \rangle = -\int_{\phi_3}^{\phi_2} \frac{d\phi''}{DP_{\phi''}(\phi'')} \int_{\phi_{\text{min}}}^{\phi''} d\phi'' P_{\phi''}(\phi''), \quad (13)$$

in agreement with recent results. \(^8,^{15}\)

We will now define $T_2$ by

$$T_2 = \langle \tau(\phi_1) \rangle. \quad (14)$$

The integrals appearing in (13) can be asymptotically evaluated by expanding the potential function in the neighborhood of the maxima and minima
\[ \Phi(\psi) = \Phi(\psi_1) + \frac{(\psi - \psi_1)^2}{2} \Phi''(\psi_1) + \cdots, \quad (15) \]
\[ \Phi(\psi) = \Phi(\psi_1) - \frac{(\psi - \psi_1)^2}{2} \Phi''(\psi_1) + \cdots, \quad (16) \]

Simple algebra shows that
\[ T_2 = \pi [\Phi''(\psi_1) / |\Phi''(\psi_1)|]^{-1/2} \exp(K), \quad (17a) \]
\[ K = \frac{1}{D} \left[ \Phi(\psi_1) - \Phi(\psi_1^2) \right]. \quad (17b) \]

Note that the first passage time (17a) is equal to one half of the reaction time obtained by Kramers.\(^{11}\) It is evident from (15) that (17) is valid near the critical points \( \mu_{c1} \) and \( \mu_{c2} \) where the second derivatives of \( \Phi \) are zero. Hence in the neighborhood of such critical points, we should retain the next-order term in (15). It is also evident from (13) that as \( \psi_1 \) and \( \psi_2 \) approach each other, as happens near the critical points \( \mu_{c1} \) or \( \mu_{c2} \), then \( \langle \psi \rangle \rightarrow 0 \). Hence in the neighborhood of \( \mu_{c1} \)

\[
\langle \psi \rangle \approx \left( \psi_1 - \psi_2 \right) \frac{\partial \langle \psi \rangle}{\partial \psi_1} |_{\psi_1} \]
\[ = \left( \psi_1 - \psi_2 \right) \int_{-\infty}^{\infty} d\psi' \exp \left[ -\frac{\Phi(\psi') - \Phi(\psi_1)}{D} \right] \approx \left( \psi_1 - \psi_2 \right) \int_{-\infty}^{\infty} d\psi' \exp \left[ -\frac{(\psi' - \psi_1)^2}{2D} \right] \Phi''(\psi_1)/6D, \]
which on evaluation leads to
\[ T_2 = \frac{\left( \psi_1 - \psi_2 \right)}{D} \left( \frac{6D}{|\Phi''(\psi_1)|} \right)^{1/3}, \quad (18) \]
\[ = \sqrt{\frac{6}{D}} \frac{\mu_{c1} - \mu}{|\Phi''(\psi_1)|} \left( \frac{6D}{|\Phi''(\psi_1)|} \right)^{1/3} \left( \frac{\partial^2 \mu}{\partial \psi^2} \right)^{1/3} \quad \text{(19)}. \]

\( T_2 \) is now directly expressed in terms of the control parameter \( \mu \). Note that near the critical point \( 1 / T_1 \) can also be expressed in a similar form
\[ \frac{1}{T_1} = \sqrt{\frac{6}{D}} \left[ \mu - \mu_{c2} \right] \left( \frac{\partial^2 \mu}{\partial \psi^2} \right)^{1/3} \quad \text{(20)}. \]

Equation (19) for \( T_2 \) is valid only when the maxima and minima are close enough, i.e., within a critical region defined by \( K \ll 1 \), across the spinodal curve, where \( K \) is defined in Eq. (17). Thus
\[ \frac{1}{D} \left( \frac{\partial^2 \mu}{\partial \psi^2} \right)^{1/3} \left( \psi_1 - \psi_2 \right)^{1/3} \ll 1, \quad (21) \]
which, from the order-parameter equation, can be reexpressed as a condition on \( \mu - \mu_{c2} \):

\[ |\mu - \mu_{c1}| \ll \left( \frac{3}{6\sqrt{2}} \left| \frac{D}{\Phi''(\psi_1)} \right| \right)^{1/3} \frac{\partial^2 \mu}{\partial \psi^2} \quad \text{(22)}. \]

The critical region within which mean-field theory breaks down is likely to be of this order or smaller.

\( T_2 \) is the time in which the intrinsic random fluctuations kick the system from a given minimum, over the intervening barrier, into the other minimum. It is therefore a "smearing time" for the hysteresis curve. The control parameter must vary fast enough so that the minimum, in which the system sits, moves along at a faster rate than the decay rate \( 1 / T_2 \) of the state. Since the rate of change of \( P_{st} \) due to the changing \( \mu \) is \( (\partial P_{st}/\partial \mu) \mu \), we have
\[ \frac{1}{P_{st}} \left( \frac{\partial P_{st}}{\partial \mu} \right) \mu > \frac{1}{T_2} \Rightarrow |\mu - (1 / D) (\partial \Phi / \partial \mu) T_2 |^{-1}. \quad (23) \]

The condition for jump behavior to occur is clearly (23) with the direction of the inequality reversed; the system in a given \( \Phi \) minimum \( \{ \Phi(\psi_0) \} \) then hops over to the competing minimum \( \{ \Phi(\psi_1) \} \) as soon as \( \Phi(\psi_0) \) falls below it. If the time \( T_2 \) above is taken to be the intrinsic decay rate in the absence of a time variation in \( \mu \), as would be done in practice when making estimates, then we must have
\[ \frac{\delta T_2}{T_2} = \frac{1}{D} \left( \frac{\partial \Phi}{\partial \mu} \right) \left( \phi(\psi_1) - \phi(\psi_2) \right) \delta \mu \ll 1, \quad (24) \]
i.e., the changes in \( T_2 \) due to the \( \mu(t) \) variation must be relatively small.

For most systems for which hysteresis is observed it turns out that \( T_2 \) is extremely large, whereas \( T_1 \) is quite small and hence the inequalities\(^{12}\) like (18), (23), and (24) lead to a large range for the time scale \( T_2 \) of the control parameter. In fact in most cases the range appears so large that the Maxwell construction would never prevail. However, the presence of impurities and surfaces could affect the diffusion constant and the form of the potential, leading to a significant change in \( T_2 \) due to the \( e^F \) factor. Thus in these inhomogeneous nucleation\(^{7,12}\) situations simple reproducible behavior could take over. The conditions (18), (23), and (24) can be combined to lead to the hysteresis window defined by
\[ \left| \frac{\delta \mu_{c1}}{\delta \mu} \right| \ll \left| \frac{\delta \mu_{c2}}{\delta \mu} \right| \ll \left| \frac{\delta \mu_1}{\delta \mu} \right| \ll \left| \frac{\delta \mu_2}{\delta \mu} \right| \ll 1, \quad (25a) \]
which should be compared with the hysteresis window given by Gilmore
\[ \left| \frac{\delta \mu_{c1}}{\delta \mu} \right| \ll \frac{1}{T_1} \ll \frac{1}{T_2}, \quad (25b) \]
The prefactors in (25a) multiplying the character-
The thermodynamic arguments, but rather by microscopic theory, and is expected to be of the order $10^{-6}$ sec--$10^{-10}$ sec. $T_s$ is therefore very large, essentially due to the largeness of $K$. Even for field hysteresis, $T_s$ will be astronomical since the factor in the exponent continues to be large. The hysteresis window in the present case is very wide. The critical region, estimated from (21) is $(e - e_c)/e_c \sim 10^{10}$.

We next consider an example of a nonequilibrium first-order phase transition, where hysteresis behavior has been reported. The dynamics of a laser with saturable absorber is described by the following Fokker-Planck equation for the intensity, 

$$\frac{\partial \rho}{\partial t} = \frac{2}{\eta} \frac{\partial}{\partial \psi} \left[ \left( \psi - \frac{\eta_1}{2} \right)p \right] + \eta_2 \frac{\partial^2}{\partial \psi^2} (\rho p) ,$$

where

$$f = \frac{1}{2} \left[ \beta_1 \beta_2 \psi^2 - \beta_1 (\theta + |\eta|) \psi + |\eta| \right].$$

The parameters $\beta_1, \beta_2$ are the saturation parameters in the laser active medium and the saturable absorber. The hysteresis region corresponds to $0 < \theta < 1$ and $0 \leq |\eta| \leq \beta_2 / 4 \beta_2$. It is clear that the macroscopic (mean field) behavior is given by $\psi = 0$, or $f = 0$. It can be shown that the mean first passage time now satisfies the equation:

$$-2\left( \frac{\psi - \eta_1}{2} \right) \frac{\partial}{\partial \psi} (f) + \eta_2 \frac{\partial^2}{\partial \psi^2} (f) = -\frac{1}{2v} ,$$

which can be integrated to yield

$$\langle \psi(t) \rangle = \frac{1}{2v \eta_1} \int_0^{T_s} \frac{d \psi}{P_{st}(\psi)} \int_0^\psi d\psi' P_{st}(\psi') ,$$

where

$$P_{st}(\psi) = N \exp \left( -\frac{2}{\eta_1} \int_\psi^\infty f d\psi \right) ,$$

$\psi_0$ is the root of $f(\psi) = 0$ for which $\int f d\psi$ is maximum. The time $T_s$ can now be shown to be given by

$$T_s = \frac{1}{2v \eta_1} \left( \frac{\pi \eta_1}{2 |f'|} \right)^{1/2} \exp \left( \frac{2}{\eta_1} \int_\psi^\infty f d\psi \right) \times \text{erf} \left( \frac{\left( f/\eta_1 \right)^{1/2}}{\sqrt{2}} \psi_0 \right) ,$$

which can be evaluated from the knowledge of the system parameters. For typical values of the parameters $\nu \sim 10^9$ Hz, $\beta_2 = 10^{-3}$, $|\eta| = 10^{-3}$, and $\theta = 0.28$ we find that the time $T_s$ is not astronomical for the present problem. It is of the order
of a few tens of seconds, so that with $|\Delta | \Delta \theta \sim 10^7 |\Delta | \Delta \theta$, the hysteresis conditions for transition from $\theta = 0$ to $\theta = 0$ are now given by $10^{-6} \ll |\Delta | \Delta \theta \ll 10^6$ and the critical region corresponds to $|\Delta \phi/\Delta \eta| \sim 10^{-3}$. On the other hand Gilmore's condition (25b) yields, $10^{-4} \ll |\Delta | \Delta \theta \ll 10^2$.

Finally we also mention that in a recent paper we have examined nonequilibrium first-order phase transitions in irradiated Josephson junctions. In particular the existence of bistable behavior has been shown. Using our equations we have estimated $T_1$ and $T_2$ which turn out to be of the order of $10^{-4}$ sec and $10^{10}$ sec — and hence our equations allow a very wide range over which the control parameter (the intensity of the irradiated microwave power in this case) could be varied to see hysteresis.

In summary the observability of hysteresis depends on the rate of variation of the control parameter within a window determined by the intrinsic time constants of the system. It would be interesting to study systems in which one could obtain both hysteresis and jump behavior by the variation of an external parameter.

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1 For a general discussion of nonequilibrium phase transitions and applications of Fokker-Planck equations, see H. Haken, Synergetics (Springer, New York, 1977).
2 W. Merz, Phys. Rev. 76, 1221 (1949); 91, 513 (1953).
9 See, for example, K. Huang, Statistical Mechanics (Wiley, New York, 1963), Chap. 8.
11 H. A. Kramers, Physica (Utrecht) 7, 284 (1940).
16 The inequalities (8) and (23) differ from the ones given by Gilmore (Ref. 8).
20 Reference 1, p. 238.
21 Experimentally (Ref. 2) the field variation rate for which hysteresis was observed was $60 \text{ sec}^{-1}$, well within the window.
23 For the optical bistability $T_2$ has recently been shown to be of the order $10^{27}$ sec [K. Kondo, M. Mabuchi, and H. Hasegawa, Opt. Commun. 22, 136 (1980)].