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[1] such as ferroelectric transitions,[2] optical bistability,[3] bistability in Josephson junctions,[4] bistability in light-induced chemical reactions,[5] and other systems.[6] The liquid-gas transition also exhibits supercooling and superheating,[7] 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[8] that the simple jump phenomena corresponds to "Maxwell construction," familiar from van der Waal's theory of liquid-gas phase transitions,[9] whereas the hysteresis phenomena 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[10-12] as well as the time scale over which the control parameters of the system are changed. Recently Gilmore[8] 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 ψ, which is assumed to obey the Fokker-Planck equation

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial \psi}[A(\psi)P]+\frac{\partial^2}{\partial \psi^2}[D(\psi)P]. \quad (1)$$

The macroscopic equation for the order parameter is

$$\dot{\psi}=-A(\psi). \quad (2)$$

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

$$A(\psi)=0. \quad (3)$$

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

$$P_{st}(\psi)=N\exp\left(-\frac{1}{D}\int^{\psi}A(\psi)d\psi\right)\equiv N\exp\left(-\frac{\Phi}{D}\right), \quad (4)$$

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

$$\delta\dot{\psi}=-\frac{1}{T_1}\delta\psi, \quad \frac{1}{T_1}=A'(\psi), \quad (5)$$

where ψ 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 ψ_1 and ψ_2 and one unstable solution ψ_3 as shown in Fig. 1. We will denote the external control or drive parameter by μ. 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 $\mu=\mu_m$ at which the jump phenomena occurs (without hysteresis) corresponds to the situation:

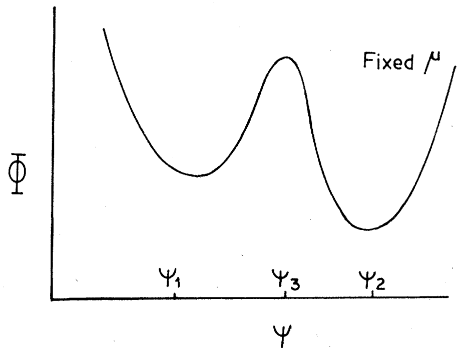

FIG. 1. A schematic plot of the potential Φ (Eq. 4) as a function of ψ for a fixed control parameter μ with two minima (ψ_1, ψ_2) and one maxima (ψ_3).

$$\Phi(\psi_1) = \Phi(\psi_2) . \tag{6}$$

Note that T_1 is infinite at the points μ_{c1} and μ_{c2}. This is an example of critical slowing down at the spinodal curve where one of the Φ minima disappears.[13]

The observation of hysteresis rather than jump behavior depends on how big the rate of change of the drive parameter is relative to the relaxation $1/T_1$ and decay $1/T_2$ rates. This implies that the time scale τ_μ of the change of μ should be much larger than the relaxation rate to a given minimum, i.e., roughly $\tau_\mu \gg T_1$. Moreover, the system must not have time to jump over to the competing minimum, i.e., $T_2 \gg \tau_\mu$ as we will see more precisely later. Stating the first condition more precisely, if $\mu \to \mu + \delta\mu$ then the order parameter changes $\psi \to \psi + \delta\psi$ gradually, i.e., adiabatically following the changing μ such that the same equation is obeyed:

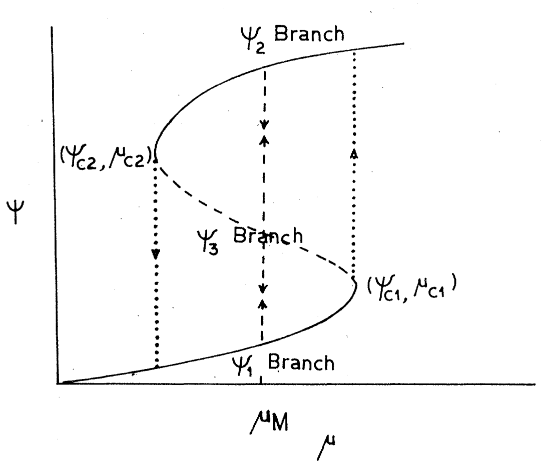

FIG. 2. The extrema of Φ (Fig. 1) as a function of μ. The solid lines represent stable branches (ψ_1, ψ_2) and dashed line (ψ_3 branch) represents unstable solutions.

$$A(\psi, \mu) = 0 , \quad A(\psi + \delta\psi, \mu + \delta\mu) = 0 . \tag{7}$$

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

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

where Δt is a typical rise time for the control parameter pulse. It should be noted that (8) is violated near the critical points μ_{c1} and μ_{c2} since $T_1 \to \infty$.

The time T_2 can be calculated from the considerations of the mean first passage time for a Markov process. For this purpose ψ_3 can be taken as essentially the absorbing boundary of the process, since once ψ takes the value ψ_3, the transition from the minimum ψ_1 to ψ_2 occurs. The mean first passage time is given by[14]

$$\langle t(\psi) \rangle = \int_0^\infty dt \, P_{\mathfrak{D}}(\psi, t) , \tag{9}$$

where $P_{\mathfrak{D}}(\psi, t)$ is the probability that the system is to be found in the region to the left of the maximum ψ_3, given that it was initially in that region, which we will denote by $\mathfrak{D}$. The mean first passage time can be expressed in terms of the eigenfunctions of the operator

$$L = \frac{\partial}{\partial\psi}[A(\psi) \cdots] + \frac{\partial^2}{\partial\psi^2}[D(\psi) \cdots] , \tag{10}$$

$$L\chi_n = \lambda_n \chi_n , \quad L^\dagger \phi_n = \lambda_n^* \phi_n ,$$

as

$$\langle t(\psi) \rangle = \int_{\mathfrak{D}} \sum \frac{\chi_n(\psi')\phi_n(\psi) d\psi'}{\lambda_n} . \tag{11}$$

Of course if initially ψ is characterized by a distribution $P_0(\psi)$, then the mean first passage time is obtained by averaging (9) with respect to $P_0(\psi)$. The mean first passage as defined by (9) is known to satisfy[14]

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

On solving (12) we obtain

$$\langle t(\psi) \rangle = -\int_{\psi_3}^{\psi} \frac{d\psi''}{DP_{st}(\psi'')} \int_{-\infty}^{\psi''} d\psi' P_{st}(\psi') , \tag{13}$$

in agreement with recent results.[8,15]

We will now define T_2 by

$$T_2 = \langle t(\psi_1) \rangle . \tag{14}$$

The integrals appearing in (13) can be asymptotically evaluated by expanding the potential function in the neighborhood of the maxima and minima

$$\Phi(\psi)=\Phi(\psi_1)+\frac{(\psi-\psi_1)^2}{2}\Phi''(\psi_1)+\frac{(\psi-\psi_1)^3}{6}\Phi'''(\psi_1)+\cdots\,, \tag{15}$$

$$\Phi(\psi)=\Phi(\psi_3)-\frac{(\psi-\psi_3)^2}{2}|\Phi''(\psi_3)|+\frac{(\psi-\psi_3)^3}{6}\Phi'''(\psi_3)+\cdots\,, \tag{16}$$

Simple algebra shows that

$$T_2=\pi[\Phi''(\psi_1)|\Phi''(\psi_3)|]^{-1/2}\exp(K)\,, \tag{17a}$$

$$K=\frac{1}{D}[\Phi(\psi_3)-\Phi(\psi_1)]\,. \tag{17b}$$

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 invalid near the critical points μ_{c1} and μ_{c2} where the second derivatives of Φ 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 ψ_3 and ψ_1 approach each other, as happens near the critical points μ_{c1} or μ_{c2}, then $\langle t\rangle\to 0$. Hence in the neighborhood of μ_{c1}

$$\langle t\rangle\cong(\psi_1-\psi_{c1})\frac{\partial\langle t\rangle}{\partial\psi}\bigg|_{\psi_{c1}}=\left(\frac{\psi_{c1}-\psi_1}{D}\right)\int_{-\infty}^{\psi_{c1}}d\psi'\exp\left(-\frac{\Phi(\psi')-\Phi(\psi_{c1})}{D}\right)\approx\frac{(\psi_{c1}-\psi_1)}{D}\int_{-\infty}^{\psi_{c1}}d\psi'\exp\{-(\psi'-\psi_{c1})^3\Phi'''(\psi_{c1})/6D\}\,,$$

which on evaluation leads to

$$T_2=\frac{(\psi_{c1}-\psi_1)}{D}(0.83)\left(\frac{6D}{|\Phi'''(\psi_{c1})|}\right)^{1/3} \tag{18}$$

$$=\frac{\sqrt{2}}{D}|\mu_{c1}-\mu|^{1/2}(0.83)\left(\frac{6D}{|\Phi'''(\psi_{c1})|}\right)^{1/3}\left(\frac{\partial^2\mu}{\partial\psi_{c1}^2}\right)^{-1/2}. \tag{19}$$

T_2 is now directly expressed in terms of the control parameter μ. Note that near the critical point $1/T_1$ can also be expressed in a similar form

$$\frac{1}{T_1}=\sqrt{2}\,|\mu_{c1}-\mu|^{1/2}|\Phi'''(\psi_{c1})|\left(\frac{\partial^2\mu}{\partial\psi_{c1}^2}\right)^{-1/2}. \tag{20}$$

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

$$\frac{1}{6}\frac{|\Phi'''(\psi_{c1})|}{D}(\psi_3-\psi_1)^3\ll 1\,, \tag{21}$$

which, from the order-parameter equation, can be reexpressed as a condition on $(\mu-\mu_{c1})$:

$$|\mu-\mu_{c1}|\ll\left(\frac{3}{8\sqrt{2}}\frac{D}{|\Phi'''(\psi_{c1})|}\right)^{2/3}\frac{\partial^2\mu}{\partial\psi_{c1}^2}\,. \tag{22}$$

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 μ is $(\delta P_{st}/\delta\mu)\dot{\mu}$, we have

$$\frac{1}{P_{st}}\left|\frac{\partial P_{st}}{\partial\mu}\dot{\mu}\right|>\frac{1}{T_2}\Rightarrow|\dot{\mu}|>\left(\frac{1}{D}\left|\frac{\partial\Phi}{\partial\mu}\right|T_2\right)^{-1}. \tag{23}$$

The condition for jump behavior to occur is clearly (23) with the direction of the inequality reversed; the system in a given Φ minimum $[\Phi(\psi_1)]$ then hops over to the competing minimum $[\Phi(\psi_2)]$ as soon as $\Phi(\psi_1)$ 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 μ, as would be done in practice when making estimates, then we must have

$$\frac{\delta T_2}{T_2}\approx\frac{1}{D}\left|\frac{\partial}{\partial\mu}[\Phi(\psi_3)-\Phi(\psi_1)]\delta\mu\right|\ll 1\,, \tag{24}$$

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[16] like (18), (23), and (24) lead to a large range for the time scale τ_μ 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^K 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

$$\left|\Delta t\frac{\partial A}{\partial\mu}\right|^{-1}\frac{|\psi|}{T_1}\gg\dot{\mu}\gg\frac{D}{T_2}\left|\frac{\partial\Phi}{\partial\mu}\right|^{-1}, \tag{25a}$$

which should be compared with the hysteresis window given by Gilmore

$$\frac{1}{T_1}\gg\dot{\mu}\gg\frac{1}{T_2}\,. \tag{25b}$$

The prefactors in (25a) multiplying the characteristic times come from the detailed physical arguments involving the change of Φ produced by changes in the drive parameter μ. The condition (25b) stated by Gilmore does not include these prefactors. In general, the condition (25b) is more stringent than our conditions (25a) as we will see, for example, in the case of a laser with a saturable absorber.[17-20]

The analysis presented above holds for both equilibrium and nonequilibrium phase transitions provided the order parameter for such systems would be characterized by the Fokker-Planck equation (1). For equilibrium phase transitions we may identify

$$\exp(-\Phi/D) \to \exp(-F/k_B T)\,,$$

where F is the free energy of the system.

We will now study some examples of first-order phase transitions—one of which corresponds to equilibrium and the others to the nonequilibrium case. Consider now a first-order phase transition characterized by the Φ function[2,6]

$$\frac{\Phi(P)}{\Delta v} = A(T-T_0)P^2 - BP^4 + CP^6 - EP \quad (A,B,C>0)\,. \tag{26}$$

This expression for example may represent the excess free energy per unit volume of a ferroelectric with P representing the electric polarization and E the electric field. In such a case both temperature and field hysteresis have been reported.[2] On introducing the scaled variables

$$p = \left(\frac{3C}{B}\right)^{1/2} P\,, \quad e = \left(\frac{27C^3}{B^5}\right)^{1/2} E\,, \quad t = \frac{3AC}{B^2}(T-T_0)\,, \tag{27}$$

expression (26) becomes

$$\frac{\Phi(P)}{\Delta v} = \frac{B^3}{9C^2}\left(p^2 t - p^4 + \tfrac{1}{3}p^6 - pe\right)\,, \tag{28}$$

and the scaled order-parameter equation is

$$2pt + 2p^5 - 4p^3 - e = 0\,. \tag{29}$$

For temperature hysteresis $e=0$, the minima and maxima of the free energy Φ are given by ($t>0$)

$$p_1 = 0\,, \quad p_2^2 = 1 + (1-t)^{1/2}\,, \quad p_3^2 = 1 - (1-t)^{1/2}\,. \tag{30}$$

In such a case the factor K [Eq. (17b)] becomes

$$K = \frac{4B^3}{27C^2}(1-t)^{3/2}\frac{\Delta v}{k_B T}\,. \tag{31}$$

Using the experimentally[2] reported parameters B, C, we find that $B^3/9C^2 \sim 10^6$ and that $K \sim 10^{18}-10^{20}$. T_2 is determined by e^K times a typical relaxation time scale. This time scale is not determined by thermodynamic arguments, but rather by microscopic theory, and is expected to be of the order 10^{-6} sec-10^{-10} sec. T_2 is therefore very large, essentially due to the largeness of K. Even for field hysteresis, T_2 will be astronomical since the factor in the exponent continues to be large. The hysteresis window in the present case[21] 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.[17] The dynamics of a laser with saturable absorber is described by the following Fokker-Planck equation for the intensity,[18-20] with the order parameter being the intensity $\psi \equiv I$, the control parameter being the net gain term $|\eta|$, and the diffusion constant being ψ dependent (for details see Ref. 18).

$$\frac{\partial P}{\partial(2\nu t)} = 2\frac{\partial}{\partial\psi}\left[\left(\psi f - \frac{\eta_1}{2}\right)P\right] + \eta_1\frac{\partial^2}{\partial\psi^2}(\psi P)\,, \tag{32}$$

where

$$f = \tfrac{1}{2}[\beta_1\beta_2\psi^2 - \beta_1(\theta + |\eta|)\psi + |\eta|\,]\,. \tag{33}$$

The parameters β_1, β_2 are the saturation parameters in the laser active medium and the saturable absorber. The hysteresis region corresponds to $0<\theta\ll 1$ and $0 \le |\eta| \le \beta_1\theta^2/4\beta_2$. 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:

$$-2\left(\psi f - \frac{\eta_1}{2}\right)\frac{\partial}{\partial\psi}\langle t\rangle + \eta_1\psi\frac{\partial^2}{\partial\psi^2}\langle t\rangle = -\frac{1}{2\nu}\,, \tag{34}$$

which can be integrated to yield

$$\langle t(\psi)\rangle = \frac{1}{2\nu\eta_1}\int_\psi^{\psi_3}\frac{d\psi}{P_{st}(\psi)\psi}\int_0^\psi d\psi' P_{st}(\psi')\,, \tag{35}$$

where

$$P_{st}(\psi) = N\exp\left(-\frac{2}{\eta_1}\int^\psi f\,d\psi\right). \tag{36}$$

ψ_3 is the root of $f(\psi)=0$ for which $\int f d\psi$ is maximum. The time T_2 can now be shown to be given by

$$T_2 \sim \langle t(0)\rangle = \frac{1}{2\nu\eta_1}\left(\frac{\pi\eta_1}{2|f'|}\right)^{1/2}\exp\left(\frac{2}{\eta_1}\int^{\psi_3} f\,d\psi\right) \times \operatorname{erf}\left[\left(\frac{|f'|}{\eta_1}\right)^{1/2}\psi_3\right]\,, \tag{37}$$

which can be evaluated from the knowledge of the system parameters. For typical values of the parameters $\nu \sim 10^6$ Hz, $\beta_1 = \tfrac{1}{2}\beta_2 = 10^{-6}$, $|\eta| = \tfrac{1}{3}\times 10^{-2}$, and $\theta = 0.28$ we find that the time T_2 is not astronomical for the present problem. It is of the order of a few tens of seconds, so that with $|\dot{\eta}|\Delta t \sim |10T_1|\dot{\eta}|$, the hysteresis conditions for transition from $\psi = 0$ to $\psi \neq 0$ are now given by $10^{-5} \ll |\dot{\eta}| \ll 10^{5}$ and the critical region corresponds to $|\Delta\eta/\eta| \sim 10^{-2}$. On the other hand Gilmore's condition (25b) yields, $10^{-1} \ll |\dot{\eta}| \ll 10^{10}$.

Finally we also mention that in a recent paper we have examined nonequilibrium first-order phase transitions in irradiated Josephson junctions.[4] In particular the existence of bistable behavior has been shown. Using our equations we have estimated[22] the times T_1 and T_2 which turn out to be of the order of 10^{-6} sec and 10^{90} sec — and hence our equations allow a very wide range[23] 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).

[3]H. M. Gibbs, S. L. McCall, and T. N. C. Venkatesan, Phys. Rev. Lett. 36, 1135 (1976); R. Bonifacio and L. A. Lugiato, Phys. Rev. A 18, 1129 (1978); G. S. Agarwal, L. M. Narducci, R. Gilmore, and D. H. Feng, *ibid.* 18, 620 (1978) and the references therein.

[4]S. R. Shenoy and G. S. Agarwal, Phys. Rev. Lett. 44, 1524 (1980); see also M. Milani, R. Bonifacio, and M. Scully, Nuovo Cimento Lett. 26, 353 (1979).

[5]A. Nitzan and J. Ross, J. Chem. Phys. 59, 241 (1973); G. Nicolis and I. Prigogine, *Self-organization in Nonequilibrium Systems* (Wiley, New York, 1977).

[6]M. Agu and Y. Teramachi, J. Appl. Phys. 49, 3645 (1978).

[7]R. E. Heist and H. Reiss, J. Chem. Phys. 59, 665 (1973).

[8]R. Gilmore, Phys. Rev. A 20, 2510 (1979).

[9]See, for example, K. Huang, *Statistical Mechanics* (Wiley, New York, 1963), Chap. 8.

[10]R. Landauer, J. Appl. Phys. 33, 2209 (1962).

[11]H. A. Kramers, Physica (Utrecht) 7, 284 (1940).

[12]J. S. Langer, Ann. Phys. (N.Y.) 54, 258 (1969).

[13]K. Binder, in *Fluctuations, Instabilities and Phase Transitions*, edited by T. Riste (Plenum, New York, 1975), p. 53.

[14]R. L. Stratonovitch, *Topics in the Theory of Random Noise*, trans. by R. A. Silverman (Gordon and Breach, New York, 1963), Vol. I, Chap. 4, Sec. 6.

[15]D. L. Weaver, Physica (Utrecht) 98A, 359 (1979).

[16]The inequalities (8) and (23) differ from the ones given by Gilmore (Ref. 8).

[17]V. N. Lisitsyn and V. P. Chebotayev, Zh. Eksp. Teor. Fiz. Pis'ma Red. 7, 1 (1968) [JETP Lett. 7, 3 (1968)]; V. S. Letokhov and V. P. Chehotayev, *Non-Linear Laser Spectroscopy* (Springer, New York, 1977), p. 98.

[18]A. P. Kazantsev and G. I. Surdutovich, Zh. Eksp. Teor. Fiz. 58, 245 (1970) [Sov. Phys.—JETP 31, 133 (1970)].

[19]J. F. Scott, M. Sargent III, and C. D. Cantrell, Opt. Commun. 15, 13 (1975).

[20]Reference 1, p. 238.

[21]Experimentally (Ref. 2) the field variation rate for which hysteresis was observed was 60 $\sec^{-1}$, well within the window.

[22]S. R. Shenoy and G. S. Agarwal, Phys. Rev. B (in press).

[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. 32, 136 (1980)].