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Temporal and Spatial Chaos in a van der Waals Fluid Due to Periodic Thermal Fluctuations

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The Mel'nikov technique is applied to prove the existence of deterministic chaos in two problems for a van der Waals fluid. The first problem shows that temporal chaos results as a result of small time periodic fluctuations about a subcritical temperature when the fluid is initially quenched in the unstable spinoidal region. The second problem shows that spatial chaos arises from small spatially periodic flunctions in an infinite tube of fluid if the ambient pressure is appropriately chosen. \approx 1985 Academic Press. Inc.

0. INTRODUCTION

In recent years several papers and monographs have discussed the application of the Mel'nikov [26] technique to establish the existence of deterministic chaos in periodically forced evolution equations. In this regard we mention the work of Greenspan and Holmes [10], Gruendler [11], Guckenheimer and Holmes [12], Holmes [15–17], Holmes and Marsden [18–21], Kirchgraber [23], Lichtenberg and Lieberman [25], Moser [27], and Nicolaevsky and Shchur [29]. The purpose of this paper is to show how the Mel'nikov method can be used in analyzing two problems arising from van der Waals' [34] theory of phase transitions.

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The first problem concerns the dynamics of spinodal decomposition. Assume we have a van der Waals type fluid with isotherms as shown in Fig. 1. We will consider a general class of constitutive functions with properties motivated by the specific van der Waals constitutive relation (see, for example, Fermi [9])

$$p(w,\theta) = \frac{R\theta}{w-b} - \frac{a}{w^2}, \qquad (0.1)$$

R, *b*, *a* are positive constants, ρ is the density, $w = 1/\rho$ is the specific volume, and θ is the absolute temperature. Figure 1 sketches isotherms of *p* for θ above, equal to, and below the critical temperature $\theta_{crit} = 8a/27bR$. For $\theta_0 < \theta_{crit}$, $p(w, \theta)$ has the features

(i)
$$p_w(w, \theta_0) < 0$$
 on $(b, \alpha) \cup (\beta, \infty)$,
(ii) $p_w(w, \theta_0) > 0$ on (α, β) , (0.2)
(iii) $p_w(\alpha, \theta_0) = p_w(\beta, \theta_0) = 0$.

The domain (b, α) corresponds to the fluid being liquid; the domain (β, ∞) corresponds to the fluid being vapor; the domain (α, β) is the unstable region and is referred to as the spinodal region. We have also noted the point w_0 where $p_{ww} = 0$ on the graph of the θ_0 isotherm $(w_0$ is the zero of $R\theta_0w^4 + a(w-b)^3 = 0)$.

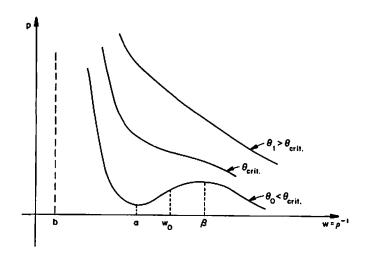


FIG. 1. Van der Waals isotherms.

The fluid flow is thought of as taking place along the (Eulerian) x-axis in a tube of unit cross section of fixed volume. If $\theta_1 > \theta_{crit}$ then $w = w_0$ will describe a stable homogeneous configuration for the dynamic equations discussed in Section 1. We then instantaneously quench the fluid by reducing the temperature to $\theta_0 < \theta_{crit}$. The homogeneous state w_0 will now be in the unstable spinodal region of the θ_0 isotherm. The first part of this paper examines the effect of a small time-periodic fluctuation of the absolute temperature about θ_0 . Specifically we show how the loss of stability of w_0 is accompanied by temporal chaos in that the first two hydrodynamic modes of w possess a Poincaré-Birkhoff-Smale horseshoe in their dynamics (see Smale [32]).

Crucial to our analysis is the presence of a small viscous contribution to the stress. This does not mean that we expect the inviscid problem not to contain horseshoes but only that the comparatively straightforward Mel'nikov method used here is inapplicable. Inviscid problems will need methods involving exponentially small Mel'nikov functions and Arnold diffusion. Such work is currently in progress [22].

Also, as noted above, we work with a finite-dimensional approximation to the governing equations of hydrodynamics (actually a finite-dimensional Hamiltonian structure with a viscous damping contribution adjoined). As Holmes and Marsden [18] have already presented an infinite-dimensional Mel'nikov theory, it is not the infinite-dimensionality of our problem that forces us to make the finite-dimensional approximation. The difficulty arises from the fact that their theory requires the existence (and rather specific information regarding) a homoclinic orbit lying in a two-dimensional manifold for the inviscid, unperturbed, infinite-dimensional problem. While Holmes and Marsden were able to exhibit such an orbit for the vibrating beam problem they considered, the corresponding existence question of a homoclinic orbit for the van der Waals fluid is as yet open.

The second problem considered is the effect of a small thermal perturbation of the form $\theta(x) = \theta_0 + \epsilon \cos qx$, ϵ small, on the equilibrium configuration of an infinite tube of fluid under a given applied load. We shall show that in this case there are solutions with the features of both metastable and co-existing phases that exhibit spatial chaos.

The paper is divided into four sections. The first section recalls the one-dimensional Lagrangian description of compressible fluid flow and shows how the governing hydrodynamic equations can be written in a perturbed Hamiltonian form. The second section presents a finite mode approximation to the original Hamiltonian, develops the finite mode approximation to the evolution equations, sketches the relevant Holmes-Marsden-Mel'nikov theory, and shows how it applies to the first problem of temporally chaotic solutions for the van der Waals fluid. The third section considers the equilibrium states of a van der Waals fluid and the chaotic solutions formed as a result of spatial thermal perturbations. Finally in the fourth section we show that van der Waals fluid theory is directly applicable to an elastic bar model of Ericksen [6] where a nonmonotone stress-strain constitutive relation is used.

1. ONE-DIMENSIONAL LAGRANGIAN DESCRIPTION OF COMPRESSIBLE FLUID FLOW

The Holmes and Marsden [18] theory depends heavily on the evolution equations possessing a perturbed Hamiltonian structure. For this reason it is advantageous to use a Lagrangian description of the fluid motion. Since the motion is assumed to be planar so that the flow depends only on the one cartesian coordinate x and the time t a Lagrangian description is particularly simple (see, for example, Zel'dovich and Raizer [37, p. 5] or Courant and Friedrichs [5, p. 30]).

Let us denote the Eulerian coordinate of a reference fluid particle by x_1 . Then the mass X of a column of fluid of unit cross section between the reference fluid particle and the Eulerian coordinates of a general fluid particle x is

$$X = \int_{x_1}^x \rho(\zeta, t) \, d\zeta. \tag{1.1}$$

Here $\rho(x, t)$ is the fluid density at position x and time t. Relation $(1.1)^{\prime}$ defines for each fixed (X, t) the values of x(X, t) implicitly. Furthermore, differentiation of (1.1) shows $1 = x_X(X, t)\rho(x(X, t), t)$. Set $\rho(x(X, t), t) = \tilde{\rho}(X, t), w(X, t) = \tilde{\rho}(X, t)^{-1} = x_X(X, t)$ (the specific volume), and $u(X, t) = x_I(X, t)$ (the velocity). In this case the equations of balance of mass and momentum are, respectively,

$$\frac{\partial w}{\partial t} = \frac{\partial u}{\partial X},\tag{1.2}$$

$$\frac{\partial u}{\partial t} = \frac{\partial \tau}{\partial X},\tag{1.3}$$

where τ is the Piola stress. We have assumed there are no body forces. In addition, as we will be varying the temperature of the fluid, we assume the equation of balance of energy is identically satisfied via immersion of the fluid in a "heat bath."

Balance law (1.3) must be supplemented by a constitutive relation for τ . We assume the fluid is thermoelastic, slightly viscous, isotropic, with an additional stress component given by the van der Waals-Korteweg theory of capillarity. (A discussion of the van der Waals-Korteweg theory may be found in van der Waals [34], Felderhof [7], Widom [35], the monograph of Truesdell and Noll [33], and the paper of Aifantis and Serrin [1].) Specifically we write

$$\tau = -p(w,\theta) + \mu u_X - A w_{XX} \tag{1.4}$$

where $w = 1/\rho$ as before, p is the pressure, A is a positive constant (for simplicity), and $\mu \ge 0$ is an assumed constant viscosity (again for simplicity). The term $-Aw_{XX}$ is the van der Waals-Korteweg addition to usual visco-thermoelastic stress.

We now substitute (1.4) into (1.3) and find that x(X, t) satisfies the equation

$$x_{ii} = -p(x_X, \theta)_X + \mu x_{iXX} - A x_{XXXX}.$$
 (1.5)

We now wish to consider a finite tube of unit cross section which contains a total mass $2\pi/q$ of fluid in a volume $(2\pi/q)w_0$. Here q > 0 is a constant which we shall subsequently restrict. From the incremental relation w dX = dx of (1.1) we see that this constraint may be written as

$$\int_0^{2\pi/q} w(X,t) \, dX = \frac{2\pi w_0}{q}. \tag{1.6}$$

We now introduce the change of variables $\overline{X} = qX$, $\overline{t} = qt$, $\overline{x}(\overline{X}, t) = qx(X, t)$ so that (1.5) becomes (with overbars deleted)

$$x_{tt} = -p(x_X, \theta)_X + \epsilon \mu_0 q x_{tXX} - A q^2 x_{XXXX} \qquad (1.7)$$

where we have set $\mu = \epsilon \mu_0, \epsilon, \mu_0$ positive constants. The mass-volume constraint (1.6) becomes

$$\int_{0}^{2\pi} w(X,t) \, dX = 2\pi w_0. \tag{1.8}$$

Next we note (1.7) has the "dissipative" Hamiltonian structure

$$x_{t} = D_{u}H(x, u; \theta),$$

$$u_{t} = -D_{x}H(x, u; \theta) + \epsilon \mu_{0}qu_{XX},$$
(1.9)

where

$$H(x, u; \theta) = \frac{1}{\pi} \int_0^{2\pi} \left[\frac{u^2}{2} + \psi(x_X, \theta) + \frac{Aq^2}{2} x_{XX}^2 \right] dX, \quad (1.10)$$

 D_u , D_x denote the variations with respect to u, x, respectively, and

$$\psi(\xi,\theta) = -\int_{w_0}^{\xi} p(s,\theta) \, ds.$$

2. TEMPORAL CHAOS ARISING IN THE SPINOIDAL REGION

Assume we have a van der Waals fluid with constitutive relation for p given in (0.1). (In fact, we only used the properties of p described in (0.2) and the usual graphical features of the van der Waals isotherms shown in Fig. 1.) We will now study the behavior near the "quenched" equilibrium solution $w = w_0$, u = 0 of (1.5) (i.e., $x_X = w_0$, $x_t = 0$) where the absolute temperature θ is given by the relation

$$\theta(X,t) = \theta_0 + \epsilon \gamma \cos \omega t \cos X \tag{2.1}$$

where t, X represent the new scaled variables introduced in Section 1. To perform the perturbation analysis we expand $p(w, \theta)$ about (w_0, θ_0) in a Taylor series and truncate at cubic terms. In this manner we set

$$p(w,\theta) = p(w_0,\theta_0) + p_w(w_0,\theta_0)(w - w_0) + p_\theta(w_0,\theta_0)(\theta - \theta_0) + p_{w\theta}(w_0,\theta_0)(w - w_0)(\theta - \theta_0) + \frac{p_{www}}{3!}(w_0,\theta_0)(w - w_0)^3 + \frac{p_{ww\theta}}{2}(w_0,\theta_0)(w - w_0)^2(\theta - \theta_0)$$
(2.2)

where $p_{\theta\theta}(w_0, \theta_0) = p_{w\theta\theta}(w_0, \theta_0) = p_{\theta\theta\theta}(w_0, \theta_0) = 0$ by (0.1) and $p_{ww}(w_0, \theta_0) = 0$ by the definition of w_0 . As w_0 is in the spinodal region we see

$$p_w(w_0, \theta_0) > 0, \qquad p_{www}(w_0, \theta_0) < 0.$$
 (2.3)

We expand w, u in Fourier sine and cosine series, respectively, on $[0, 2\pi]$ and use (1.8) to obtain

$$w(X, t) = x_X(X, t)$$

= $w_0 + x_1(t)\cos X + x_2(t)\cos 2X + x_3(t)\cos 3X + \dots$
 $u(x, t) = x_t(X, t) = u_1(t)\sin X + u_2(t)\sin 2X + u_3(t)\sin 3X + \dots$
(2.4)

If we substitute (2.1), (2.2), (2.4) into (1.10) we find that

$$H(x,u) = H_2(x,u) + R(x,u),$$

where $H_2(x, u)$ is given by

$$H_{2}(x, u) = \frac{u_{1}^{2}}{2} + \frac{u_{2}^{2}}{2} - \frac{p_{w}}{2}(w_{0}, \theta_{0})(x_{1}^{2} + x_{2}^{2}) - \frac{p_{www}}{32}(w_{0}, \theta_{0})(x_{1}^{4} + x_{2}^{4} + 4x_{1}^{2}x_{2}^{2}) - p_{\theta}(w_{0}, \theta_{0})\epsilon\gamma\cos\omega tx_{1} - \frac{p_{w\theta}}{2}(w_{0}, \theta_{0})\epsilon\gamma\cos\omega tx_{1}x_{2} - \frac{p_{ww\theta}}{24}(w_{0}, \theta_{0}) \times (3\epsilon\gamma\cos\omega tx_{1}^{3} + 6\epsilon\gamma\cos\omega tx_{1}x_{2}^{2}) + \frac{Aq^{2}}{2}(x_{1}^{2} + 16x_{2}^{2}), (2.5)$$

and R(x, u) is a remainder term which vanishes when $x_n = u_n = 0$, $n \ge 3$.

If we neglect the effect of the higher modes $n \ge 3$, (1.9) becomes the following two-degrees-of-freedom Hamiltonian system.

$$\begin{aligned} x_{1} &= \frac{\partial H_{2}}{\partial u_{1}} = u_{1}, \\ x_{2} &= \frac{\partial H_{2}}{\partial u_{2}} = u_{2}, \\ u_{1} &= \frac{-\partial H_{2}}{\partial x_{1}} = \left(p_{w}(w_{0},\theta_{0}) - Aq^{2} \right) x_{1} + \frac{p_{www}}{32} (w_{0},\theta_{0}) (4x_{1}^{3} + 8x_{1}x_{2}^{2}) \right. \\ &+ \epsilon \left\{ p_{\theta}(w_{0},\theta_{0}) \gamma \cos \omega t + \frac{1}{2} p_{w\theta}(w_{0},\theta_{0}) \gamma \cos \omega t x_{2} \right. \\ &+ \frac{p_{ww\theta}}{24} (w_{0},\theta_{0}) (9\gamma \cos \omega t x_{1}^{2} + 6\gamma \cos \omega t x_{2}^{2}) \right\} - \epsilon \mu_{0} q u_{1}, \\ u_{2} &= -\frac{\partial H_{2}}{\partial x_{2}} = \left(p_{w}(w_{0},\theta_{0}) - 4Aq^{2} \right) x_{2} + \frac{p_{www}}{32} (4x_{2}^{3} + 8x_{1}^{2}x_{2}) \right. \\ &+ \epsilon \left\{ \frac{p_{w\theta}}{2} (w_{0},\theta_{0}) \gamma \cos \omega t x_{1} + \frac{p_{ww\theta}}{24} (w_{0},\theta_{0}) (12\gamma \cos \omega t x_{1}x_{2}) \right\} \\ &- 4\epsilon \mu_{0} q u_{2}. \end{aligned}$$

$$(2.6)$$

If we set $z = (x_1, x_2, u_1, u_2)^T$, (2.6) has the form

$$\dot{z}(t) = f_0(z) + \epsilon f_1(z, t) \tag{2.7}$$

where f_1 is $2\pi/\omega$ periodic in t and the unperturbed ($\epsilon = 0$) system

$$\dot{z}(t) = f_0(z)$$
 (2.8)

is Hamiltonian.

If we linearize the undriven system ((2.7) with $\gamma = 0$) about z = 0 we obtain

$$\dot{z}_L(t) = L z_L(t) \tag{2.9}$$

where L is given by

$$L = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ p_w - Aq^2 & 0 & -\epsilon\mu_0 q & 0 \\ 0 & p_w - 4Aq^2 & 0 & -4\epsilon\mu_0 q \end{bmatrix}_{(w_0,\theta_0)}$$

The eigenvalues of L are given by

$$\begin{aligned} &\lambda_1 \\ &\lambda_2 \\ &\lambda_2 \\ &= \frac{-\epsilon\mu_0 q}{2} \pm \frac{1}{2} \left[\epsilon^2 \mu_0^2 q^2 - 4 \left(A q^2 - p_w \right) \right]_{(w_0,\theta_0)}^{1/2}, \\ &\lambda_3 \\ &\lambda_4 \\ &\lambda_4 \\ &= -2\epsilon\mu_0 q \pm \left[4\epsilon^2 \mu_0^2 q^2 - \left(4A q^2 - p_w \right) \right]_{(w_0,\theta_0)}^{1/2}. \end{aligned}$$

$$(2.10)$$

We thus see that when

$$\frac{p_{w}(w_{0},\theta_{0})}{4A} < q^{2} < \frac{p_{w}(w_{0},\theta_{0})}{A}$$
(H.1)

and $\epsilon > 0$ is sufficiently small the first mode is unstable with $\lambda_1 > 0$, $\lambda_2 < 0$ and the second and higher modes are stable with

$$\frac{\lambda_3}{\lambda_4} = \pm i \left[4Aq^2 - p_w(w_0, \theta_0) \right]^{1/2} - r(\epsilon),$$
 (2.11)

where $r(\epsilon) > 0$ and $r(\epsilon) = O(\epsilon)$. We shall assume from here on that (H.1) holds.

When $\epsilon = 0$, the linearized system (2.9) possesses two imaginary eigenvalues given by (2.11) with r = 0. We now make the nonresonance hypothesis

$$\omega^2 \neq 4Aq - p_w(w_0, \theta_0). \tag{H.2}$$

In this case (2.6) possess a nontrivial $2\pi/\omega$ periodic solution $p_{\epsilon}(t)$. (See, for example, Hale [13, p. 154]. The analogous infinite dimensional result is more delicate; see Holmes and Marsden [18, Appendix A].) If we linearize (2.6) about $p_{\epsilon}(t)$, the linear variational equation has the form

$$\dot{y}_{1} = v_{1},$$

$$\dot{v}_{1} = \left(p_{w}(w_{0},\theta_{0}) - Aq^{2}\right)y_{1} + \frac{\epsilon p_{w\theta}}{2}(w_{0},\theta_{0})(\gamma \cos \omega t)y_{2} - \epsilon \mu_{0}qv_{1} + O(\epsilon^{2})$$

$$\dot{y}_{2} = v_{2},$$

$$\dot{v}_{2} = \left(p_{w}(w_{0},\theta_{0}) - 4Aq^{2}\right)y_{2} + \frac{\epsilon p_{w\theta}}{2}(w_{0},\theta_{0})(\gamma \cos \omega t)y_{1} - 4\epsilon \mu_{0}qv_{2} + O(\epsilon^{2})$$
(2.12)

where the $O(\epsilon^2)$ terms have coefficients that are $2\pi/\omega$ periodic in t. If we make the change of dependent variables

$$(y_1, v_1, y_2, v_2)^T = E(\tilde{y}_1, \tilde{v}_1, \tilde{y}_2, \tilde{v}_2)^T,$$

where

$$E = \begin{bmatrix} 1 & 1 & 0 & 0 \\ a & -a & 0 & 0 \\ 0 & 0 & i & -i \\ 0 & 0 & -\omega_0 & -\omega_0 \end{bmatrix}, \qquad \begin{array}{c} a \stackrel{\text{def}}{=} \left(p_w(w_0, \theta_0) - Aq^2 \right)^{1/2}, \\ & \stackrel{\text{def}}{=} \left(p_w(w_0, \theta_0) - 4Aq^2 \right)^{1/2}, \end{array}$$

so that the columns of X are the eigenvectors of $(Df_0/Dz)(p_{\epsilon}(t))$ (a constant matrix) then $\tilde{z} = (\tilde{y}_1, \tilde{v}_1, \tilde{y}_2, \tilde{v}_2)^T$ satisfies the "diagonalized" system

$$\dot{\tilde{z}} = C\tilde{z} + \epsilon \Phi_1(t)\tilde{z} + \epsilon^2 \Phi_2(t)\tilde{z}$$

with

$$C = \operatorname{diag}(a, -a, -i\omega_0, -i\omega_0),$$

$$\Phi_1\left(t + \frac{2\pi}{\omega}\right) = \Phi_1(t), \qquad \Phi_2\left(t + \frac{2\pi}{\omega}\right) = \Phi_2(t)$$

and

 $2\Phi_{1}(t)$

$$= \begin{bmatrix} -\mu_0 q & \mu_0 q & \frac{ip_{w\theta}\gamma\cos\omega t}{a} & -\frac{ip_{w\theta}\gamma\cos\omega t}{2} \\ \mu_0 q & -\mu_0 q & -\frac{ip_{w\theta}\gamma\cos\omega t}{a} & \frac{ip_{w\theta}\gamma\cos\omega t}{2} \\ -\frac{p_{w\theta}\gamma\cos\omega t}{2\omega_0} & -\frac{p_{w\theta}\gamma\cos\omega t}{2\omega_0} & -4\mu_0 q & -4\mu_0 q \\ -\frac{p_{w\theta}\gamma\cos\omega t}{2\omega_0} & -\frac{p_{w\theta}\gamma\cos\omega t}{2\omega_0} & -4\mu_0 q & -4\mu_0 q \end{bmatrix}_{(w_0,\theta_0)}$$

We then apply standard perturbation of spectra results (for example, see Exercise 1.10 of Hale [13, p. 267]) to conclude the characteristic multipliers of (2.12) $\rho_i(\epsilon)$ have the form $\rho_i(\epsilon) = e^{\mu_i(\epsilon)T}$ with $T = 2\pi/\omega$ and

$$\mu_{1}(\epsilon) = aT - \frac{\epsilon\mu_{0}q}{2} + o(\epsilon),$$

$$\mu_{2}(\epsilon) = -aT + \frac{\epsilon\mu_{0}q}{2} + o(\epsilon),$$

$$\mu_{3}(\epsilon) = +i\omega_{0}T - 2\epsilon\mu_{0}q + o(\epsilon),$$

$$\mu_{4}(\epsilon) = -i\omega_{0}T + 2\epsilon\mu_{0}q + o(\epsilon).$$
(2.13)

This is illustrated in Fig. 2.

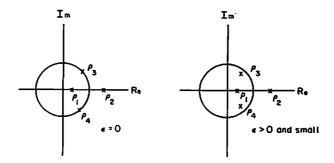


FIG. 2. The location of the characteristic multipliers for (2.12).

In summary we record the following observations regarding (2.6), (2.7):

(0.1) The system $\dot{z}(t) = f_0(z)$ is Hamiltonian.

(0.2) (2.7) possesses a nontrivial $2\pi/\omega$ periodic solution $p_{\epsilon}(t)$ of order ϵ for ϵ small.

(0.3) The characteristic multipliers ρ_i for (2.7) linearized about $p_{\epsilon}(t)$, i.e., the characteristic multipliers for

$$\dot{z}(t) = \frac{Df_0}{Dz}(p_{\epsilon}(t)) \cdot z(t) + \epsilon \frac{Df_1}{Dz}(p_{\epsilon}(t), t) \cdot z(t)$$

are of the form $\rho_i(\epsilon) = e^{\mu_i(\epsilon)T}$ where $\mu_i(\epsilon)$ are given by (2.13).

We also note

(0.4) The unperturbed ($\epsilon = 0$) system $\dot{z}(t) = f_0(z)$ has a two-dimensional invariant symplectic manifold Σ containing the homoclinic orbit connecting the origin to itself:

$$z_{0}(t) = \begin{bmatrix} \frac{2a}{(-p_{www})^{1/2}} \operatorname{sech} at \\ 0 \\ -a^{2} \frac{2}{(-p_{www})^{1/2}} \operatorname{sech} at \tanh at \\ 0 \end{bmatrix}_{(w_{0},\theta_{0})}$$

Now let $z(t, t_0, z_0, \epsilon)$ denote the solution of (2.7) satisfying $z(t_0, t_0, z_0, \epsilon) = z_0$ and define the Poincaré map $P_{t_0}^{\epsilon}$ by $P_{t_0}^{\epsilon} z_0 = z(t + 2\pi/\omega, t_0, z_0, \epsilon)$. The periodic solution $p_{\epsilon}(t)$ corresponds to a fixed point $p_{\epsilon}(t_0)$ of the Poincaré map. The linearization of $P_{t_0}^{\epsilon}$ at $p_{\epsilon}(t_0)$, denoted by $DP_{t_0}^{\epsilon}(p_{\epsilon}(t_0))$, has eigenvalues equal to the characteristic multipliers ρ_i given by (2.13).

LEMMA 1. Corresponding to the characteristic multipliers ρ_1 , ρ_2 there are unique invariant manifolds $W^u(p_{\epsilon}(t_0))$, $W^{ss}(p_{\epsilon}(t_0))$, the unstable and strongly stable manifolds, respectively, of $p_{\epsilon}(t_0)$ for the map $P_{t_0}^{\epsilon}$ such that

(i) $W^{u}(p_{\epsilon}(t_{0})), W^{ss}(p_{\epsilon}(t_{0}))$ are tangent to the eigenspaces of ρ_{1}, ρ_{2} , respectively, at $p_{\epsilon}(t_{0})$;

(ii) they are invariant under $P_{I_0}^{\epsilon}$;

(iii) if $z \in W^u(p_{\epsilon}(t_0))$ then $\lim_{n \to \infty} (P_{t_0}^{\epsilon})^n z = p_{\epsilon}(t_0)$ and if $z \in W^{ss}(p_{\epsilon}(t_0))$ then $\lim_{n \to \infty} (P_{t_0}^{\epsilon})^{-n} z = p_{\epsilon}(t_0)$.

(iv) For any finite t^* , $W^u(p_{\epsilon}(t_0))$ is C^r close as $\epsilon \to 0$ to the homoclinic orbit $z_0(t)$, $-\infty < t \le t_*$, and for any finite t^* , $W^{ss}(p_{\epsilon}(t_0))$ is C^r close as $\epsilon \to 0$ to $z_0(t)$, $t^* \le t < \infty$. Here r is any fixed integer $0 \le r < \infty$.

Proof. Since the unperturbed $\epsilon = 0$ system of (2.7) possesses a twodimensional center manifold the standard stable manifold perturbation theorem does not apply directly. Instead we use a result from the theory of ρ -pseudo hyperbolic maps of Hirsch, Pugh, and Shub [14, Sect. 5] though the result also follows from the paper of Sell [31].

DEFINITION. A linear map $\mathcal{T}: \mathbb{R}^n \to \mathbb{R}^n$ is called ρ -pseudo hyperbolic if its spectrum lies off the circle of radius ρ .

Corresponding to the spectral decomposition is a \mathscr{T} invariant splitting of \mathbb{R}^n , $\mathbb{R}^n = E_1 \oplus E_2$. The spectrum of $\mathscr{T}_1 = \mathscr{T}|E_1$ lies outside the radius ρ , while the spectrum of $\mathscr{T}_2 = \mathscr{T}|E_2$ lies inside.

THEOREM HPS. Let $F: \mathbb{R}^n \to \mathbb{R}^n$ be a C^r map, $r \ge 1$, F(0) = 0 with $DF(0): \mathbb{R}^n \to \mathbb{R}^n \rho$ -pseudo hyperbolic. Then the sets W_1, W_2 defined by

$$W_1 = \bigcap_{n \ge 0} F^n S_1 \qquad S_1 = \{(x, y) \in E_1 E_2; |x| \ge |y|\},$$
$$W_2 = \bigcap_{n \le 0} F^n S_2 \qquad S_2 = \{(x, y) \in E_1 E_2; |y| \ge |x|\},$$

are the graphs of C^1 maps $E_1 \rightarrow E_2$, $E_2 \rightarrow E_1$. They are characterized by

 $z \in W_1 \Leftrightarrow$ there exist inverse images $F^{-1}z$ such that $|F^n z|/\rho^n \to 0$ as $n \to -\infty$,

 $z \in W_2 \Leftrightarrow |F^n z|/\rho^n \to 0 \text{ as } n \to +\infty.$

If
$$\|\mathcal{T}_1^{-1}\|^j \|\mathcal{T}_2\| < 1, 1 \le j \le r$$
, then W_1 is C' and if $\|\mathcal{T}_1\|^{-1} \|\mathcal{T}_2\|^j < 1, 1 \le j \le r$, then W_2 is C'.

The manifolds W_1, W_2 depend continuously on F in the C' sense.

We now return to the proof of Lemma 1. If F corresponds to the Poincaré map $P_{t_0}^0$ then spectrum of DF(0) is given by (2.13) with $\epsilon = 0$. So DF(0) is ρ -pseudo hyperbolic for both $\rho_2 < \rho < 1$ and $1 < \rho < \rho_1$. By smoothness results for ordinary differential equations, F is C' for any finite $r \ge 0$. For $\rho_2 < \rho < 1$, W_1 corresponds to the homoclinic orbit $z_0(t)$ and for $1 < \rho < \rho_1$, W_2 also corresponds to $z_0(t)$. The map $P_{t_0}^{\epsilon}$ is a C' perturbation of F and Lemma 1 follows from the continuous dependence of W_1, W_2 on ϵ as given by the HPS Theorem. \Box

LEMMA 2. Corresponding to the characteristic multipliers ρ_1 , ρ_3 , and ρ_4 , there is for $\epsilon > 0$ a unique invariant manifold $W^s(p_{\epsilon}(t_0))$ for $P_{t_0}^{\epsilon}$, the stable manifold of $p_{\epsilon}(t_0)$, which is tangent to the eigenspace of ρ_1 , ρ_3 , ρ_4 at $p_{\epsilon}(t_0)$. If $z \in W^s(p_{\epsilon}(t_0))$, then $\lim_{n \to \infty} (P_{t_0}^{\epsilon})^n z = p_{\epsilon}(t_0)$.

As $\epsilon \to 0$, $W^{s}(p_{\epsilon}(t_{0}))$ converges C^{r} (in a neighborhood of $\{z_{0}(t); -\infty < t < t^{*}\}$) to a manifold $W^{sc}(p_{0}(t_{0}))$, a center stable manifold for $P_{t_{0}}^{0}$, for any fixed $r, 1 \le r < \infty$; $W^{sc}(p_{0}(t_{0}))$ is an invariant manifold for $P_{t_{0}}^{0}$ corresponding to the eigenvalues $\rho_{1}(0)$, $\rho_{3}(0)$, and $\rho_{4}(0)$.

Proof. The existence of $W^{s}(p_{\epsilon}(t_{0}))$ follows from Hirsch, Pugh, and Shub [14] as in Lemma 1. To prove the convergence statement as $\epsilon \to 0$, we consider as in bifurcation theory (cf. Carr [3, Sect. 1.4]) the suspended system

$$\hat{P}_{t_0}(z,\epsilon) = \left(P^{\epsilon}_{t_0}(z),\epsilon\right)$$

in (z, ϵ) -space. By the results of Section 5A of Hirsch, Pugh, and Shub [14], the suspended system has a C' center manifold $W^{s,c}$ through $(p_0(t_0), 0)$. This contains the orbit $z_0(t)$, $-\infty < t \le t^*$. Since $W^{s,c}$ contains all the local recurrent and stable orbits, it also contains $(p_{\epsilon}(t_0), \epsilon)$ and $(W^{s}(p_{\epsilon}(t_0)), \epsilon)$. Now the three manifold $W^{s}(p_{\epsilon}(t_0))$ contains $W^{ss}(p_{\epsilon}(t_0))$ which, by Lemma 1, converges to $\{z_0(t)\}$ as $\epsilon \to 0$. Near such points, $(W^{s}(p_{\epsilon}(t_0)), \epsilon)$ belongs to $W^{s,c}$ and since $W^{s,c}$ is C' in all variables, and $W^{s}(p_{\epsilon}(t_0))$ must converge C' to the center stable manifold at $\epsilon = 0$. \Box

Remark. It follows that in regions where one knows *a priori* that the stable manifold of the approximating system persists, the center stable manifold of the limiting system must be unique. Compare Hirsch, Pugh, and Shub [14, Theorem 5A.3] and Fenichel [8].

LEMMA 3. Let

$$M(t_0) \stackrel{\text{def}}{=} \int_{-\infty}^{\infty} \Omega \big[f_0(z_0(t-t_0)), f_1(z_0(t-t_0), t) \big] dt$$

where $\Omega[u, v] = u^T J v$, $u, v \in \mathbb{R}^4$, and

$$J = \begin{bmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{bmatrix}.$$

Suppose that $M(t_0)$ has a simple zero as a function of t_0 . Then for $\epsilon > 0$ sufficiently small the unstable manifold $W^u(p_{\epsilon}(t_0))$ and the stable manifold $W^s(p_{\epsilon}(t_0))$ intersect transversally. $M(t_0)$ is called the Mel'nikov function.

Proof. We sketch a proof similar to Lemma 4 in Holmes and Marsden [18].

Choose a point $z_0(0)$ on the homoclinic orbit for the $\epsilon = 0$ unperturbed system, $\dot{z} = f_0(z)$. Choose a codimension one hyperplane H orthogonal to the homoclinic orbit through $z_0(0)$. Since the curves $W^{ss}(p_{\epsilon}(t_0))$ and $W^u(p_{\epsilon}(t_0))$ are C' close to $z_0(0)$, they intersect H in unique points $z_{\epsilon}^{ss}(t_0, t_0)$ and $z_{\epsilon}^u(t_0, t_0)$ (see Fig. 3). The line through the point $z_{\epsilon}^u(t_0, t_0)$ in the direction of the vector $Jf_0(z_0(0))$ (which lies in $\Sigma \cap H$ since H is orthogonal to $f_0(z_0(0))$ and Σ is symplectic) meets $W^s(p_{\epsilon}(t_0))$ in a unique point, since $W^s(p_{\epsilon}(t_0))$ is C' close to $W^{s,c}(p_0(t_0))$ by Lemma 2 and the persistence of transversality. Call this point $z_{\epsilon}^{s}(t_0, t_0)$.

Define $z_{\epsilon}^{s}(t, t_{0}), z_{\epsilon}^{u}(t, t_{0})$ to be the solutions of (2.7) passing through $z_{\epsilon}^{s}(t_{0}, t_{0}), z_{\epsilon}^{u}(t_{0}, t_{0})$ at $t = t_{0}$, respectively. We note that $z_{\epsilon}^{s}(t_{0}, t_{0}) = z_{0}(0) + v_{\epsilon}v_{s} + O(\epsilon^{2}), z_{\epsilon}^{u} = z_{0}(0) + \epsilon v_{u} + O(\epsilon^{2})$ for fixed vectors v_{s}, v_{u} and $z_{\epsilon}^{s}(t, t_{0})$

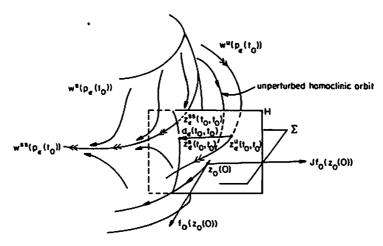


FIGURE 3

 $= z_0(t - t_0) + \epsilon z_1^{\mathfrak{s}}(t, t_0) + O(\epsilon^2), \quad z_{\epsilon}^{\mathfrak{u}}(t, t_0) = z_0(t - t_0) + \epsilon z_1^{\mathfrak{u}}(t, t_0) + O(\epsilon^2)$ where both $z_1^{\mathfrak{s}}, z_1^{\mathfrak{u}}$ satisfy the variational equation

$$\frac{d}{dt}z_1^{s}(t,t_0) = dF_0(z_0(t-t_0)) \cdot z_1^{s}(t,t_0) + f_1(z_0(t-t_0),t),$$

and $z_1^{s}(t_0, t_0) = v_s, z_1^{u}(t_0, t_0) = v_u$.

Let $d_{\epsilon}(t, t_0) = z_{\epsilon}^{s}(t, t_0) - z_{\epsilon}^{u}(t, t_0)$. The vector $d_{\epsilon}(t_0, t_0)$ is parallel to $Jf_0(z_0(0))$ by construction. Thus the oriented length of $d_{\epsilon}(t_0, t_0)$ is given by

$$\Delta_{\epsilon} \stackrel{\text{def}}{=} d_{\epsilon}(t_0, t_0) \cdot Jf_0(z_0(0)) = \Omega[f(z_0(0)), d_{\epsilon}(t_0, t_0)].$$

If $\Delta_{\epsilon}(t_0)$ has a zero, then $W^{s}(p_{\epsilon}(t_0))$ and $W^{u}(p_{\epsilon}(t_0))$ intersect. If the zero is simple, then the intersection is transverse; this follows by noting that changing t_0 can be done by moving the base point $z_0(0)$ along the homoclinic orbit.

To effectively compute $\Delta_{\epsilon}(t_0)$ we note that

$$\Omega\left[f_0(z_0(t-t_0)), d_{\epsilon}(t,t_0)\right]$$

= $\Omega\left[f_0(z_0(t-t_0)), \epsilon z_1^{s}(t,t_0) - \epsilon z_1^{u}(t,t_0)\right] - O(\epsilon^2),$

so that

$$\frac{d}{dt}\Omega[f_0(z_0(t-t_0)), z_1^s(t, t_0)] = \Omega[f_0(z_0(t-t_0)), f_1(z_0(t-t_0), t)],$$

$$\frac{d}{dt}\Omega[f_0(z_0(t-t_0)), z_1^u(t, t_0)] = \Omega[f_0(z_0(t-t_0)), f_1(z_0(t-t_0), t)],$$

Now integrate the first equation from t_0 to $+\infty$, the second from $-\infty$ to t_0 . We then find

$$\Delta_{\epsilon}(t_0) = -\epsilon \int_{-\infty}^{\infty} \Omega \big[f_0(z_0(t-t_0)), f_1(z_0(t-t_0), t) \big] dt + O(\epsilon^2)$$

and the lemma follows. \Box

That $W^{s}(p_{\epsilon}(t_{0}))$ and $W^{u}(p_{\epsilon}(t_{0}))$ intersect transversally implies the existence of a horseshoe now will follow from the following extension of Smale [32].

THEOREM S (Holmes and Marsden [18, p. 151]). If the diffeomorphism $P_{t_0}^{\epsilon} : \mathbb{R}^4 \to \mathbb{R}^4$ possesses a hyperbolic saddle point $p_{\epsilon}(t_0)$ and an associated transverse homoclinic point $h \in W_{\epsilon}^{u}(p_{\epsilon}(t_0)) \cap W_{\epsilon}^{s}(p_{\epsilon}(t_0))$, with $W_{\epsilon}^{u}(p_{\epsilon}(t_0))$ of dimension 1 and $W_{\epsilon}^{s}(p_{\epsilon}(t_0))$ of codimension 1, then some power of $P_{t_0}^{\epsilon}$ possesses an invariant zero dimensional hyperbolic set Λ homeomorphic to a Cantor set on which a power of $P_{t_0}^{\epsilon}$ is conjugate to a shift on two symbols.

148

COROLLARY S (Holmes and Marsden [18, p. 152]). A power of $P_{t_0}^{\epsilon}$ restricted to Λ possesses a dense set of periodic points of arbitrarily high period and there is a nonperiodic orbit dense in Λ .

In the spirit of Li and Yorke [24] we shall consider (i) the existence of an infinite number of periodic points of different periods and (ii) the existence of an infinite collection of points which are asymptotically aperiodic (as described in Corollary S) to be an indication of chaos. Furthermore, we note that the λ -Lemma of Palis (see, e.g., Palis and de Melo [30] or Newhouse [28, Sect. 2]) implies that the stable and unstable manifolds accumulate on themselves. In addition, the shadowing lemma of Anosov and Bowen (see, e.g., Newhouse [28, Sect. 3]) shows that, roughly speaking, an approximate orbit is shadowed by a true orbit.

Now for (2.6) a direct calculation using residues shows that

$$M(t_0) = (\gamma \omega \sin \omega t_0) J + 8q\mu_0 K$$

where

$$J \stackrel{\text{det}}{=} 4p_{\theta}(w_0, \theta_0) (-p_{www}(w_0, \theta_0))^{1/2} + \frac{4}{3} (-p_{www}(w_0, \theta_0))^{-1/2} (\omega^2 + a^2) \frac{\pi \exp(-\omega \pi/2a)}{(1 + \exp(-\pi \omega/a))}$$

and

$$K \stackrel{\text{def}}{=} \frac{a^3}{3p_{www}(w_0, \theta_0)}$$

Hence $M(t_0)$ will have a simple zero as a function of t_0 if

$$\left|\frac{8q\mu_0 K}{\gamma\omega J}\right| \le 1. \tag{2.14}$$

We can now state the following theorem.

THEOREM 1. If (H.1), (H.2), and (2.14) hold, where J and K are as defined above, then for $\epsilon > 0$ sufficiently small the stable and unstable manifolds of (2.6) intersect transversally. Furthermore, the conclusions of Theorem S and Corollary S hold so that there exists "temporal chaos."

For example, (2.14) shows that if $\mu_0 q$ is sufficiently small, $M(t_0)$ will have a simple zero.

Unfortunately, we cannot easily extend our results beyond the two-mode case since even at n = 3 the six-vector $(z_0(t), 0, 0)$ is not a solution of the

unperturbed Hamiltonian system. Thus the obvious candidate for a homoclinic orbit fails. The existence of homoclinic orbits for higher mode approximations to the original partial differential equation or for the infinite-dimensional problem itself remains an open problem.

3. SPATIAL CHAOS IN EQUILIBRIUM CONFIGURATIONS

In this section we consider the effects of small spatially periodic thermal variations on the equilibrium configuration of a van der Waals fluid. We once again constitute the stress (now Cauchy stress) according to the van der Waals-Korteweg theory as

$$\tau = -p(w,\theta) - Aw'' \tag{3.1}$$

where p is as given in (0.1), w(x) is the specific volume, $\theta(x)$ is the absolute temperature, A > 0 is a constant, and ' = d/dx. In the absence of body forces the balance of linear momentum is $\tau' = 0$ which upon integration yields $\tau = B = \text{constant} (B \text{ is the stress at } |x| = \infty)$. Substitution into (3.1) yields

$$Aw'' + p(w,\theta) = B, \qquad -\infty < x < \infty. \tag{3.2}$$

Hence for solutions possessing limits as $|x| \to \infty$, B represents the ambient pressure at the "ends" of the tube.

Denote by w_m^- , w_m^+ the values of w that determine the Maxwell equal area construction, i.e.,

$$\int_{w_m^-}^{w_m^-} \{ p(w,\theta_0) - p(w_m^-,\theta_0) \} dw = 0$$
 (3.3)

(see Fig. 5).

Equation (3.2) describes a one-degree-of-freedom Hamiltonian system with independent variable x.

For any fixed $\theta = \theta_0 < \theta_{crit}$ (3.2) will yield three different types of portraits in the w - w' phase plane. These are given as follows:

Case 1. The constant B is such that $p(w_m, \theta_0) < B < p(\beta, \theta_0)$. In this case the w - w' phase portrait of (3.2) for B fixed is shown in Fig. 4 while the values w_1, w_2, w_3 so that $p(w_1, \theta_0) = p(w_2, \theta_0) = p(w_3, \theta_0) = B$ are shown in Fig. 5.

Case 2. The constant B is such that $p(\alpha, \theta_0) < B < p(w_m^+, \theta_0)$. Again in this case the w - w' phase portrait is shown in Fig. 6 while the values w_1, w_2, w_3 so that $p(w_1, \theta_0) = p(w_2, \theta_0) = p(w_3, \theta_0) = B$ are shown in Fig. 7.

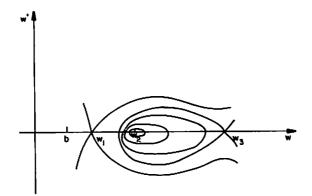


FIG. 4. The w - w' phase plane for Case 1.

Case 3. Here B is the Maxwell stress $B = p(w_m^+, \theta_0) = p(w_m^-, \theta_0)$. In this case the w - w' phase portrait is shown in Fig. 8 while the values w_1, w_2, w_3 such that $w_1 = w_m^-$, $w_3 = w_m^+$, and $p(w_1, \theta_0) = p(w_2, \theta_0) = p(w_3, \theta_0) = B$, are shown in Fig. 9.

In all three cases w_1, w_3 are saddles and w_2 is a center with respect to the differential equation (3.2).

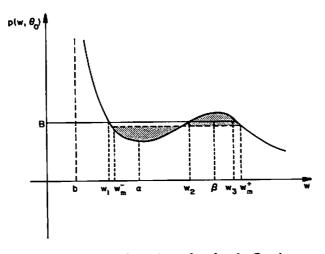


FIG. 5. The $p(w, \theta_0)$ isotherm, $\theta_0 < \theta_{cnt}$, for Case 1.

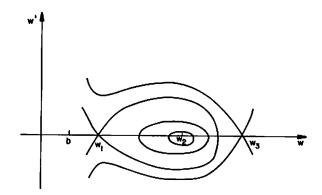


FIG. 6. The w - w' phase plane for Case 2.

If we consider the van der Waals-Landau-Ginsburg potential (see Widom [35])

$$\int_{-\infty}^{\infty} \left\{ \frac{Aw'^2}{2} - \int_{w_1}^{w} p(s,\theta_0) \, ds + B(w-w_1) \right\} \, dx \stackrel{\text{def}}{=} \Phi(w),$$

the following is true: In Case 1, $w(x) = w_1$ is the absolute minimizer of Φ , $w(x) = w_2$ is unstable in that the second variation of Φ is positive there, $w(x) = w_3$ is a local (metastable) minimum. Case 2 is the same as Case 1 if we reverse w_1 and w_3 . In Case 3 the solutions $w(x) = w_1$ and $w(x) = w_3$ both minimize Φ , and $w(x) = w_2$ is unstable. Also in Case 1 there is a

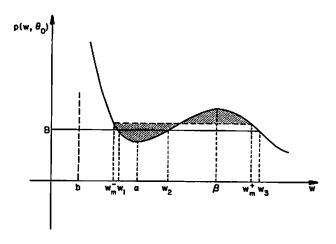


FIG. 7. The $p(w, \theta_0)$ isotherm, $\theta_0 < \theta_{crit}$, for Case 2.

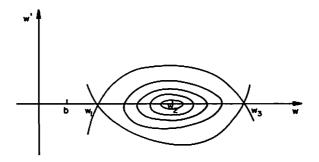


FIG. 8. The w - w' phase plane for Case 3.

homoclinic orbit W(x) connecting the metastable state w_3 to itself, i.e., $W(x) \rightarrow w_3$ as $x \rightarrow \pm \infty$, $W'(x) \rightarrow 0$ as $x \rightarrow \pm \infty$. A similar homoclinic orbit exists in Case 2. In Case 3 there is a heteroclinic orbit Z(x)connecting the states w_1 and w_3 , i.e., $Z(x) \rightarrow w_1$ as $x \rightarrow -\infty$, $Z(x) \rightarrow w_3$ as $x \rightarrow +\infty$, $Z'(x) \rightarrow 0$ as $x \rightarrow \pm \infty$; Z(x) is the van der Waals solution representing the interfacial transition from one phase to a second coexisting phase.

Now we consider the effect of a small spatially periodic perturbation in the absolute temperature of the form

$$\theta(x) = \theta_0 + \epsilon \cos qx.$$

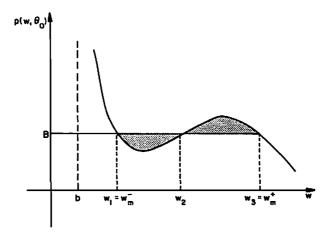


FIG. 9. The $p(w, \theta_0)$ isotherm for $\theta_0 < \theta_{crit}$, for Case 3.

According to the van der Waals equation of state (0.1),

$$p(w,\theta) = p(w,\theta_0) + \frac{\epsilon R \cos qx}{w-b}$$
(3.4)

and (3.2) takes the form

$$Aw'' + p(w, \theta_0) + \frac{\epsilon R \cos qx}{w - b} = B.$$
(3.5)

But this equation is a perturbed Hamiltonian system of the type considered by Holmes [16, 17]. In fact, Lemma 2 of Section 2 immediately applies where we replace \mathbb{R}^4 by \mathbb{R}^2 . (In this one-degree-of-freedom case we have no higher modes to consider so standard Mel'nikov theory applies.) The Mel'nikov function in all three cases is of the form

$$M(x_0) = \int_{-\infty}^{\infty} \frac{Y'(x - x_0) \cos qx}{(Y(x - x_0) - b)} \, dx$$

where Y(x) denotes either the homoclinic or heteroclinic orbit. So we see immediately that

$$M(x_0) = -RL\cos qx_0 + RN\sin qx_0$$

where

$$L = \int_{-\infty}^{\infty} \frac{Y'(x)\cos qx}{(Y(x)-b)} dx, \qquad N = \int_{-\infty}^{\infty} \frac{Y'(x)\sin qx}{(Y(x)-b)} dx.$$

If $L \neq 0$, $N \neq 0$, $M(x_0)$ has a simple zero at $qx_0 = \arctan(L/N)$; if N = 0, $L \neq 0$, $M(x_0)$ has a simple zero at $qx_0 = (2m + 1)\pi/2$, m any integer; and if L = 0, $N \neq 0$, $M(x_0)$ has a simple zero at $qx_0 = m\pi$, m any integer. Hence $M(x_0)$ always possesses simple zeros and in Cases 1 and 2 the perturbed system (3.5) has transversal intersections of the stable and unstable manifolds given by the Poincaré iterates $P_{x_0}^{\epsilon}$. In Case 3 the transversal intersection will be of Poincaré iterates of a stable manifold originating near w_1 . In all three cases Theorem S and Corollary S apply when ϵ is sufficiently small. In fact the earlier Mel'nikov theory as given in Guckenheimer and Holmes [12], Greenspan and Holmes [10], and Holmes [16] yields the transverse intersection and Smale's [32] theorem proves the existence of horseshoes. We summarize in the following theorem.

THEOREM 2. Consider the equilibrium configurations of a van der Waals fluid undergoing thermal variations $\theta(x) = \theta_0 + \epsilon \cos qx$, $\theta_0 < \theta_{crit}$. Then for an applied stress B, $p(\alpha, \theta_0) < B < p(\beta, \theta_0)$, an equilibrium configuration will exhibit spatial chaos in the sense of possessing horseshoes. We also note that the results of Greenspan and Holmes [10] show that the periodic orbits surrounding the center undergo subharmonic bifurcations with the addition of the perturbation and that these subharmonic bifurcations accumulate in a complex way in the horseshoe chaos found near the homoclinic orbit by Mel'nikov's method in Theorem 2.

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One possible implication of the above result falls within the realm of the classical theory of interfaces. According to the 1893 van der Waals theory (and many others since), the heteroclinic orbit Z(x) represents the profile of the specific volume joining coexisting phases. We see from the above result on the existence of horseshoes that small spatially periodic perturbations in temperature drastically change the interface profile Z(x). Specifically, for large values of |x| the solution of (3.5) can have chaotic behavior. The physical meaning (if any) of W(x) is less obvious. Aifantis and Serrin [1] have termed such solutions "thin films" as their profile in x resembles a thin film. In any case we see that small spatially periodic perturbations in temperature destroy the film solution and the perturbed solution exhibits spatial chaos.

4. APPLICATION TO THE ERICKSEN BAR

Consider the extension of a one-dimensional isotropic thermo-viscoelastic bar. Assume the bar is of length $2\pi/q$ and unit density in its deformed reference configuration, $0 \le X \le 2\pi/q$. We let x(X, t) denote the point in the deformed configuration which was originally at X at time t = 0.

As a model for a "shape memory" material, Ericksen [6] suggested choosing the Piola-Kirchoff stress of the form

$$\sigma = -p(x_{\chi},\theta) + p(1,\theta)$$

where p has a graph similar to the one shown in Fig. 1, i.e., p satisfies (0.2). If we assume the total stress is the sum of σ , a small viscoelastic contribution proportional to x_{tX} , and a higher gradient term proportional to x_{tXX} , we recover (1.5) from the balance of linear momentum. Also if we deform the bar so that its deformed length is $2\pi w_0/q$ (a "hard" loading device), then the integral constraint on $w(X, t) = x_X(X, t)$ is recovered. Hence the results of Section 2 are directly applicable to Ericksen's bar. Specifically we can state the following theorem.

THEOREM 3. Consider the thermo-viscoelastic constitutive relation $\tau = -p(x_X, \theta) + p(1, \theta) + \epsilon \mu_0 x_{Xt} - A x_{XXX}$ for a material in a "hard" loading device, i.e., fixed length $2\pi w_0/q$, undergoing thermal variations $\theta(X, t) = \theta_0 + \epsilon \gamma \cos wqt \cos qX$, $\theta_0 < \theta_{crit}$, w_0 such that $p_{ww}(w_0, \theta_0) = 0$. Then if (H.1), (H.2), and (2.14) hold and if $\epsilon > 0$ is sufficiently small, the two-degrees-of-

freedom approximation to the balance of linear momentum given by (2.6) possesses temporal chaos in the sense of having horseshoes.

Similarly, the results of Section 3 are applicable to an infinite bar with a prescribed stress B as $|X| \rightarrow \infty$.

THEOREM 4. Consider the equilibrium configurations of the material described in Theorem 3 undergoing thermal variations $\theta(X) = \theta_0 + \epsilon \cos qX$, $\theta_0 < \theta_{crit}$. Then for $p(\alpha, \theta_0) < B < p(\beta, \theta_0)$, an equilibrium configuration will possess spatial chaos in the sense of having horseshoes.

Finally we make three observations regarding Ericksen's bar. First, unlike the van der Waals fluid, there is little doubt about the validity of the continuum mechanical balance laws in describing the evolution of the bar. Secondly we note that Dr. L. Zapas [36] of the National Bureau of Standards has observed a spatially distributed "sickening" of certain polymeric materials at what he believes is the load yielding coexistence of phases. Such a sickening may be related to the spatial chaos predicted at the coexistence Maxwell load. Finally, we note the role of stabilizing higher gradient terms in elasticity has been considered by Ball, Currie, and Olver [2] and Coleman [4].

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