Equilibrium Interface Solutions of a Degenerate Singular Cahn-Hilliard Equation

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Abstract—We present an analysis of the equilibrium diffusive interfaces in a model for the interaction of layers of pure polymers. The discussion focuses on the important qualitative features of the solutions of the nonlinear singular Cahn-Hilliard equation with degenerate mobility for the Flory-Huggins-de Gennes free energy model. The spatial structure of possible equilibrium phase separated solutions are found. Using phase plane analysis, we obtain heteroclinic and homoclinic degenerate weak compact-support solutions that are relevant to finite domain boundary value problems and localized impurities in infinite layers. © 1998 Elsevier Science Ltd. All rights reserved.

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1. INTRODUCTION

We study the structure of a class of equilibrium solutions for problems involving phase-separated polymer mixtures. The behavior in such systems can be described by the Cahn-Hilliard equation, originally proposed to describe binary alloy mixtures. Under appropriate thermodynamic conditions, a mixture of two components, A and B, will spontaneously separate into nearly-pure "pockets" of each component. We address the related problem of describing the spatial structure of solutions formed by interdiffusion of two initially pure phases brought into contact. Following a brief review of Cahn-Hilliard theory, we specialize our study to a model for polymer mixtures and analyze its equilibrium interface solutions using phase plane techniques.

The dynamics of an incompressible, isothermal mixture can be described in terms of the local volume fraction $\phi(x,t)$ of one of the components, say A. Conservation of mass for component A is then given by

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \boldsymbol{J} = 0, \qquad \boldsymbol{J} = -\Lambda(\phi)\nabla\mu, \tag{1}$$

where $0 \leq \phi \leq 1$ and the flux $\boldsymbol{J}$ is defined as the product of the mobility $\Lambda(\phi)$ and the gradient of the chemical potential μ. The chemical potential is related back to the volume fraction ϕ through the Cahn-Hilliard energy functional,

$$\mathcal{F} = \int \mathcal{E}\, d\boldsymbol{x} = \int f(\phi) + \frac{1}{2}\kappa(\phi)|\nabla\phi|^2\, d\boldsymbol{x}, \tag{2}$$

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where $f(\phi)$ is the free energy of mixing for a spatially-homogeneous system and the second term in the integrand gives the weighted contribution due to composition gradients. For systems subject to Dirichlet or Neumann boundary conditions on ϕ, the chemical potential is the functional derivative of the free energy density,

$$\mu \equiv \frac{\delta \mathcal{E}}{\delta \phi} = f'(\phi) - \sqrt{\kappa(\phi)}\, \nabla \cdot \left(\sqrt{\kappa(\phi)}\, \nabla \phi \right). \tag{3}$$

Combining (1) and (3), we obtain the Cahn-Hilliard equation,

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \left(\Lambda(\phi) \nabla \left[f'(\phi) - \sqrt{\kappa(\phi)}\, \nabla \cdot \left(\sqrt{\kappa(\phi)}\, \nabla \phi \right) \right] \right). \tag{4}$$

If $f'(\phi)$ is a strictly increasing function, then the mixture is completely miscible and (4) yields diffusion dominated behavior. If $f'(\phi)$ is a nonmonotone function, then the mixture exhibits phase separation; the formation of sharp interfaces in the solution is connected to a range of negative values for the diffusion coefficient $D(\phi) = \Lambda(\phi) f''(\phi)$ (see [1]). In this case, the higher-order gradient term in (4) is crucial in insuring the regularity of solutions and the existence of equilibrium profiles. There has been extensive research done on the analysis of solutions of the Cahn-Hilliard equation. Most classical studies have considered models in the sharp interface limit, $\|\kappa\| \to 0$, with $f'(\phi)$ given as a cubic, and mobility Λ and κ are held constant [1–4]. Recently, Elliott and Garcke [5,6] have considered effects due to degenerate mobility functions $\Lambda(\phi)$. In this article, we consider the influence of a singular gradient energy weight function $\kappa(\phi)$; such models have been proposed for polymer mixtures [7,8].

2. POLYMER MIXTURES

There is considerable interest in the study of interdiffusion in mixtures of polymer materials [9]. Some of the numerous industrial applications of this research include polymer coating and adhesion processes. We study the structure of equilibrium interfaces that are formed when two initially pure layers ($\phi = 1$ and $\phi = 0$) of different polymers are brought into contact.

The appropriate free energy of mixing for this problem is given by Flory-Huggins theory [7,8] as

$$f(\phi) = \frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln (1-\phi) + \chi \phi (1-\phi), \tag{5}$$

where N_A and N_B are the lengths of the monomer chains in polymers A and B. The parameter χ is called the Flory interaction parameter and gives a measure of the attractive or repulsive interaction between the two polymers. A typical form for the mutual mobility [10] in polymer blends is

$$\Lambda(\phi) = \Lambda_0 \phi (1-\phi), \tag{6}$$

where $\Lambda_0 > 0$ is a constant. These functional forms are also mentioned in [5]. De Gennes notes that the gradient energy contribution for polymer mixtures should be weighted by

$$\kappa(\phi) = \frac{2a^2}{36\phi(1-\phi)}, \tag{7}$$

where a is a characteristic monomer length scale. The energy functional (2) with constitutive relations (5) and (7) is called the Flory-Huggins-de Gennes (FHdG) model in polymer physics.

We now study equilibrium solutions of this model under some simplifying conditions. For spatially homogeneous polymer layers of finite or semi-infinite thickness, we will seek one-dimensional diffusive interface profiles in the direction normal to the layers. In general, equilibrium is reached in equation (1) when the flux is a spatially uniform constant $J = J_0$. One class of problems of physical interest is the case of no flux boundary conditions, $J_0 = 0$. Zero flux may be achieved by

requiring that the chemical potential take a spatially uniform constant value, $\mu = \mu_0$. Specifically, $\mu_0 = 0$ describes symmetric mixtures with $N_A = N_B$. For systems that form localized interfaces, the value of μ_0 is selected by a tangent line construction [5] (see Figure 1) or an equivalent equal area rule [4]; this choice of μ_0 has a particular influence on the structure of the phase plane. In the following sections, we consider the solutions of $\mu(\phi) = \mu_0$ in the phase plane. Later, we will return to make use of the degenerate mobility (6) to construct weak "isolated impurity" solutions in conjunction with our phase plane results.
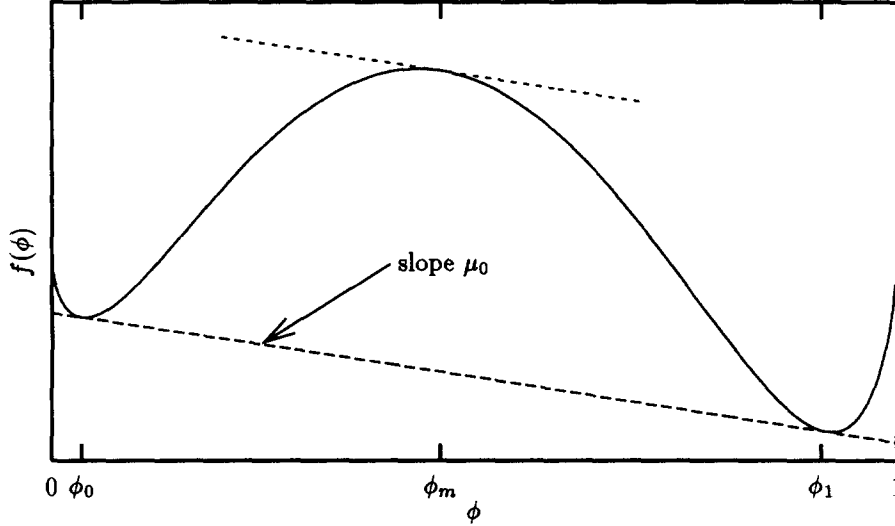

Figure 1. The tangent-line construction for the chemical potential.

3. EQUILIBRIUM SOLUTIONS

To simplify the parameter dependence of the FHdG model, we introduce the following changes of variables:

$$\epsilon = \frac{1}{\chi N}, \qquad N = N_B, \qquad r = \frac{N_B}{N_A}, \qquad \tilde{\mu}_0 = \frac{\mu_0}{\chi}, \qquad \tilde{x} = \frac{\sqrt{\chi}}{a\sqrt{2}}x, \tag{8}$$

$$\kappa(\phi) = \left(\frac{a\sqrt{2}}{l(\phi)}\right)^2, \qquad l(\phi) = 6\sqrt{\phi(1-\phi)}, \tag{9}$$

$$\tilde{f}'(\phi) = 1 - \tilde{\mu}_0 - 2\phi + \epsilon\big(r\ln\phi - \ln(1-\phi) + r - 1\big), \tag{10}$$

where for symmetric mixtures the polymer length ratio is $r = 1$. Note that we have incorporated the chemical potential $\tilde{\mu}_0$ into $\tilde{f}'(\phi)$. Consequently, equation (3), in one dimension, can be written as

$$\frac{1}{l(\phi)}\frac{d}{d\tilde{x}}\left(\frac{1}{l(\phi)}\frac{d\phi}{d\tilde{x}}\right) - \tilde{f}'(\phi) = 0. \tag{11}$$

This second-order nonlinear differential equation can be expressed as the autonomous phase plane system

$$\frac{d\phi}{d\tilde{x}} = l(\phi)\psi, \qquad \frac{d\psi}{d\tilde{x}} = l(\phi)\tilde{f}'(\phi). \tag{12}$$

Using this form, it is clear that the integral curves for the system are given by the Hamiltonian

$$H = \frac{1}{2}\psi^2 - \tilde{f}(\phi), \tag{13}$$

where

$$\tilde{f}(\phi) = \phi(1 - \tilde{\mu}_0 - \phi) + \epsilon\big(r\phi\ln\phi + (1-\phi)\ln(1-\phi)\big), \tag{14}$$

and $\psi^2 = |\nabla\phi/l(\phi)|^2$ corresponds to the gradient energy contribution in (2). Equation (13) shows that the phase plane is symmetric with respect to the line $\psi = 0$ (only the upper half is shown in Figure 2); monotone decreasing solutions $\phi(\tilde{x})$ in the lower half of the phase plane have the same form as the corresponding increasing solutions, since (11) is invariant under reflections $\tilde{x} \to -\tilde{x}$.
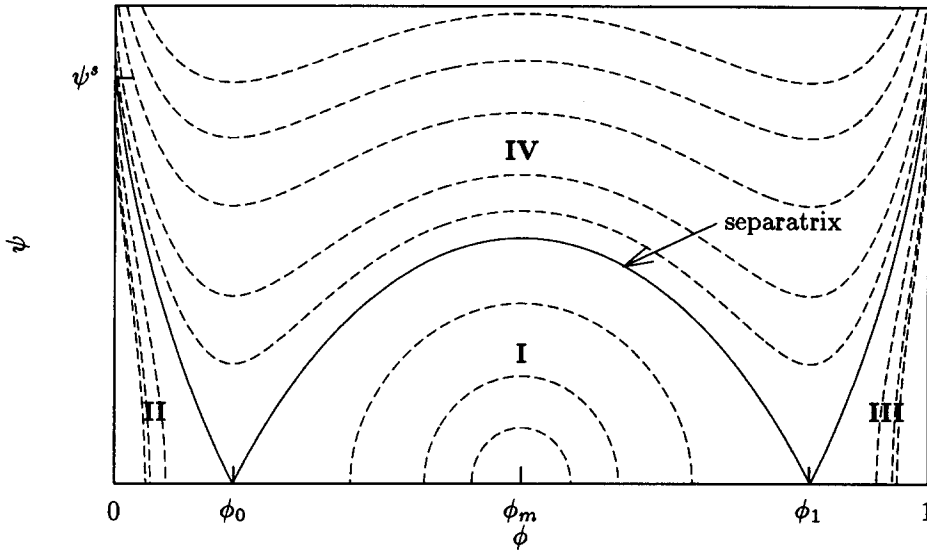

Figure 2. Upper half of the ϕ-ψ phase plane.

Setting the right-hand sides of (12) equal to zero yields the critical points of the system. Since $\tilde{f}(\phi)$ plays the role of the potential function in this problem, for $\psi = 0$ the extrema of $\tilde{f}(\phi)$ are critical points; the minima, ϕ_0 and ϕ_1, are hyperbolic saddle points and the maximum, ϕ_m, is a center point. From the tangent line construction described earlier (see Figure 1), it is clear that the chemical potential is determined by r and ϵ, $\mu_0 = \mu_0(r, \epsilon)$. This definition of μ_0 guarantees that ϕ_0 and ϕ_1 occur at the same value of the Hamiltonian and consequently that a separatrix, representing an interface connecting them, exists. For other applications, such as nucleation, other values of $\tilde{\mu}_0$ yield perturbed forms of this phase plane with some qualitative differences in the classes of solutions. The nonconvex structure of $\tilde{f}$ that yields phase separation and distinct critical points exists for the range of parameters

$$0 < r < 1 + \frac{2}{\epsilon} - 2\sqrt{\frac{2}{\epsilon}}, \qquad 0 < \epsilon < \frac{1}{2}. \tag{15}$$

While ϕ_0, ϕ_1, and ϕ_m depend on r and ϵ, within this parameter range, the qualitative structure of the phase plane does not change. The separatrix divides the plane into four classes of solutions:

(I) periodic oscillations around ϕ_m,

(II) homoclinic-type isolated impurity pockets for $0 \le \phi \le \phi_0$,

(III) similar impurity solutions for $\phi_1 \le \phi \le 1$, and

(IV) heteroclinic-type interface solutions connecting the pure states $\phi = 0$ and $\phi = 1$.

It should be noted that the $l(\phi)$ factors in (12) suggest that the lines $\phi = 0$ and $\phi = 1$ (for all ψ) are also continuous families of critical points; this result is due to the degenerate structure of (12). Trajectories in classes II, III, and IV start and end at $\phi = 0$ or $\phi = 1$; admissible solutions cannot extend outside of this range. Unlike ϕ_0, ϕ_1, and ϕ_m, the uniform constants $\phi = 0$ and $\phi = 1$ are not solutions of equation (11); the logarithmic singularities of $\tilde{f}(\phi)$ at 0 and 1 must be balanced by nonzero gradient contributions. Moreover, unlike linear critical points, trajectories reach $\phi = 0$ and $\phi = 1$ in finite rather than infinite distance. From the first equation in (12), it

is clear that the leading order behavior of a trajectory starting at point $\phi = 0$, $\psi = \psi_0 > 0$ is

$$\phi \sim 9\psi_0^2 (\tilde{x} - \tilde{x}_0)^2, \qquad \text{as } \tilde{x} \to \tilde{x}_0, \tag{16}$$

where $\tilde{x}_0$ is some finite touchdown position; the behavior for $\phi \to 1$ is analogous. Following a brief review of the properties of the separatrix, we will explore the implications of (16) for boundary value problems on finite domains and compact support weak solutions.

4. INTERFACE AND IMPURITY SOLUTIONS

Many studies [9,10] of interface solutions of the Cahn-Hilliard equation focus on the separatrix of (12) in the limit that $\epsilon \to 0$. Physically, this limit corresponds to the study of very long polymer molecules, $N \to \infty$. As $\epsilon \to 0$, the critical points approach the pure states,

$$\phi_0 \sim e^{-\epsilon^{-1}(1-\tilde{\mu}_0+\epsilon(r-1))/r} \to 0, \qquad \phi_1 \sim 1 - e^{-\epsilon^{-1}(1+\tilde{\mu}_0-\epsilon(r-1))} \to 1, \tag{17}$$

and the center point approaches the symmetric solution, independent of r,

$$\phi_m \sim \frac{1}{2} \left(1 - \tilde{\mu}_0 + \epsilon(r-1)(1 - \ln 2) \right) \to \frac{1}{2}, \qquad \tilde{\mu}_0 \to 0. \tag{18}$$

In the phase plane, regions II and III vanish for $\epsilon = 0$ with the separatrix,

$$\phi^s(\tilde{x}) = \frac{e^{6\sqrt{2}\tilde{x}}}{1 + e^{6\sqrt{2}\tilde{x}}}, \tag{19}$$

forming the interface solution from $\phi = 0$ to $\phi = 1$ on the fully infinite domain, $-\infty < \tilde{x} < \infty$. We will now consider the broader classes of solutions that are possible for problems with finite $\epsilon > 0$ and finite domains with no-flux boundary conditions.

We examine solutions that connect to one or both of the pure states $\phi = 0$ and $\phi = 1$. The interface solutions in region IV are heteroclinic connectors while the localized impurity solutions in regions II and III are of homoclinic type. Both classes of solutions have the same local "touchdown" behavior that balance singularities in the gradient and potential terms in (11) as they approach the pure states,

$$\phi \sim 9\psi_0^2(\tilde{x} - \tilde{x}_0)^2 \left(1 + \frac{1}{2}\epsilon r(\tilde{x} - \tilde{x}_0)^2 \ln|\tilde{x} - \tilde{x}_0| \right) \qquad \text{as } \tilde{x} \to \tilde{x}_0, \quad \phi \to 0, \tag{20}$$

$$\phi \sim 1 - 9\psi_1^2(\tilde{x} - \tilde{x}_1)^2 \left(1 + \frac{1}{2}\epsilon(\tilde{x} - \tilde{x}_1)^2 \ln|\tilde{x} - \tilde{x}_1| \right) \qquad \text{as } \tilde{x} \to \tilde{x}_1, \quad \phi \to 1; \tag{21}$$

these solutions, derived from (11) to leading order, can be seen to be extensions of (16). The global structure of these solutions depends on the value of ψ_0 (or ψ_1) relative to the value for the separatrix ψ^s; $\psi_0 < \psi^s$ are region II solutions, $\psi_0 > \psi^s$ are region IV solutions.

Every solution in region IV represents an interface from $\phi = 0$ to $\phi = 1$. Each trajectory, however, has a different width L corresponding to its region of support between the touchdown points, $\tilde{x}_0 < \tilde{x} < \tilde{x}_1$,

$$L = \int_{\tilde{x}_0}^{\tilde{x}_1} d\tilde{x} = \int_0^1 \frac{d\phi}{6\sqrt{2\phi\left(1 - \phi\right)(H - \tilde{f}(\phi))}}, \tag{22}$$

where from (13), $H = \psi_0^2/2$. Solving equation (22) for ψ_0 yields the appropriate interface solution for a finite domain of length L. This relation shows that decreasing the gradient ψ_0 increases the domain size L. This point can also be argued from (2) by minimizing the gradient energy contribution for a fixed domain-size. Solutions with higher gradients may be relevant for some
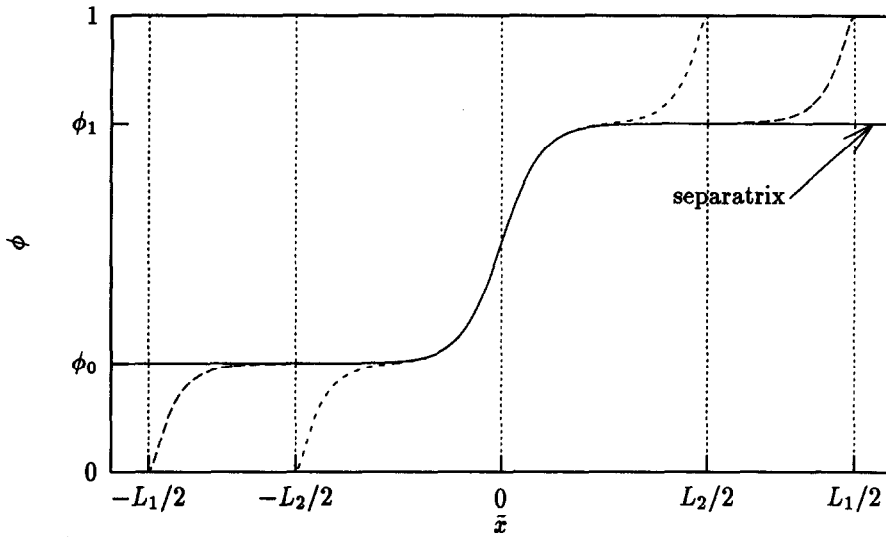
Figure 3. The separatrix and finite-domain interface solutions with $L = L_1, L_2$.
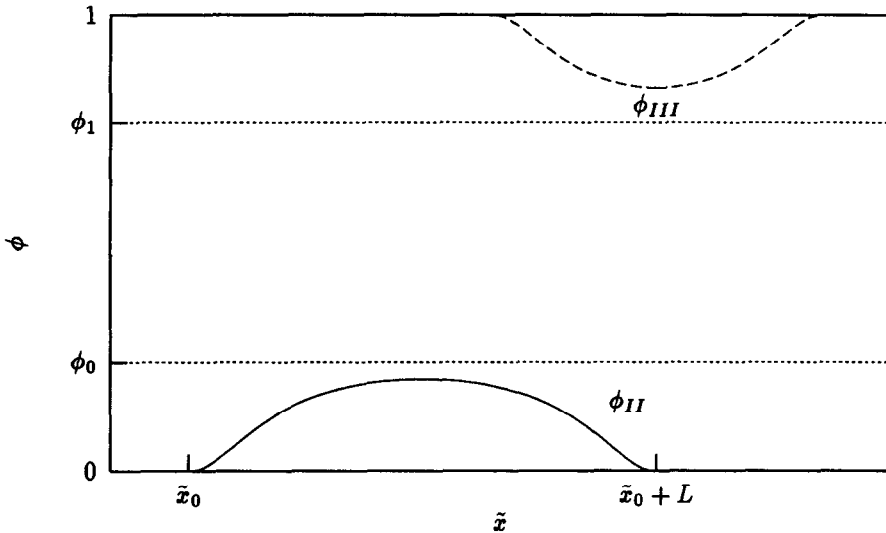

Figure 4. Type II and III impurity solutions.

problems, but they are likely to be unstable since they are energetically unfavorable. As ψ_0 decreases to ψ^s, L becomes very large as the interface approaches the separatrix (see Figure 3). The solutions develop long plateaus at ϕ_0 and ϕ_1 like the separatrix, and have finite tails given by (20),(21) at the edges of the domain that connect them to the pure states (see Figure 3). The limit $L \to \infty$ ($\psi_0 \searrow \psi^s$) appears to be a singular problem, since for $\epsilon > 0$ the separatrix connects ϕ_0 and ϕ_1, not 0 and 1.

We conclude with a brief discussion motivating the existence of isolated impurity solutions (see Figure 4). These homoclinic type solutions in regions II and III have a finite region of support, of width L, and a finite mass, given by (for a region II solution),

$$M = \int_{\tilde{x}_0}^{\tilde{x}_0+L} \phi \, d\tilde{x} = 2 \int_0^{\phi_*} \frac{\phi \, d\phi}{6\sqrt{2\phi \left(1 - \phi\right)(H - \tilde{f}(\phi))}}, \tag{23}$$

where again $H = \psi_0^2/2$ and the maximum value $\phi_* < \phi_0$ satisfies $H = \tilde{f}(\phi_*)$. These solutions can exist as isolated impurities in otherwise pure layers of polymers for systems with degenerate

mobility functions like (6). As a specific example, let us consider a region II impurity solution in an infinite layer of polymer B ($\phi = 0$). Over the region of support of the impurity, the chemical potential of the polymer mixture will be $\tilde{\mu} = \tilde{\mu}_0$, a finite constant. Outside of this region, there is no mixture and ϕ is a uniform constant, so the chemical potential reduces to equation (10), $\tilde{\mu} = \tilde{f}'(\phi)$. To obtain the pure state $\phi = 0$, let $\phi = \beta$ yielding the potential $\tilde{\mu} \sim r\epsilon \ln \beta$ in the limit that $\beta \to 0$. Consequently, the chemical potential is a piecewise constant function, and its gradient is the distribution

$$\nabla \tilde{\mu} \sim (r\epsilon \ln \beta - \tilde{\mu}_0)\big(\delta(\tilde{x} - \tilde{x}_0 - L) - \delta(\tilde{x} - \tilde{x}_0)\big), \qquad \text{as } \beta \to 0, \qquad (24)$$

where $\delta(x)$ is the Dirac delta function. To demonstrate that this impurity solution is a no-flux equilibrium state, we show that $J \to 0$ everywhere. This claim crucially depends on the degenerate form of the mobility (6), $\Lambda(\phi) \to 0$ as $\phi \to 0$, to regularize (24). As $\phi = \beta \to 0$, the flux is

$$J = -\Lambda(\phi)\nabla\tilde{\mu} \sim O(\beta \ln \beta) \to 0, \qquad (25)$$

and converges to zero pointwise everywhere as $\beta \to 0$. This argument is not a rigorous proof of existence, but it is strongly suggestive and consistent with weak convergence to compact support solutions in other degenerate diffusion equations like the porous medium equation [11].

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