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The Equations of Ostwald Ripening for Dilute Systems

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We consider a dilute mixture in 3D of a finite number of particles initially close to spherical, but of varying sizes, and representing one of the phases evolving according to the quasistatic dynamics. Under the scaling hypotheses that (1) typical size/typical distance and (2) deviation from sphericity/typical size are small, we associate centers and radii to each particle for the whole evolution and derive rigorously a set of ODEs fo the radii which we relate to the Lifschitz–Slyosov–Wagner theory of coarsening.

KEY WORDS: Quasi-static Stefan; Ostwald ripening; Mullins–Sekerka; stability of spherical shape.

1. INTRODUCTION

We consider a system of two phases and evolving by diffusion. The canonical example is a uniform mixture of a binary alloy quenched at a temperature between the liquidus and the solidus lines. At first there is separation in two phases. This can occur via two distinct mechanisms known as *spinodal decomposition* and *nucleation*. During these stages a large number of small particles representing one of the phases is generated.

In this work we are not concerned with these initial stages, but rather with a later stage, called *Ostwald ripening*. Alternatively this stage is known as *coarsening* or *aging*. This stage is characterized by a decrease of the interfacial area. Accordingly there is a reduction of particles and the large particles grow at the expense of the smaller ones.(1) The driving force of

This paper is dedicated to Prof. John Cahn on the occasion of his 70th birthday. We express our admiration and our warmest thanks to him for being a source of inspiration to us all these years.

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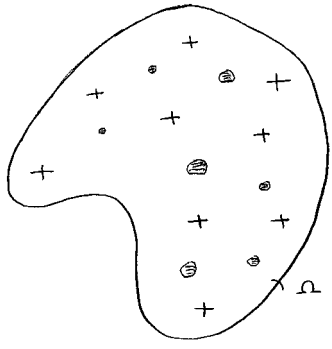

Fig. 1. Particles representing the $\ominus$ phase swimming in the $\oplus$ phase.

this process is the Gibbs–Thomson condition which states that the chemical potential on the interface is proportional to its mean curvature.

In this paper we consider an initially dilute mixture of a finite number of particles in three space dimensions (Fig. 1). These particles do not interact directly, and in particular they are too far to collide. However, they exchange mass with their surroundings in such a way so that the volume of each phase is preserved and at the same time the *total* surface area of the interface between the two phases is decreasing. Three is physically the appropriate dimension. We do expect some differences in two dimensions (cf. Zhu *et al.*[33]).

We take the particles initially close to spherical but of varying size. Under the scaling hypotheses

$$\frac{\text{distance between typical particles}}{\text{size of typical particle}} = O\left(\frac{1}{\varepsilon}\right)$$

$$\frac{\text{size of typical particle}}{\text{deviation from sphericity}} = O\left(\frac{1}{\varepsilon}\right)$$

$0 < \varepsilon \ll 1$, we show that we can associate to each particle a center $\xi_i(t)$, a radius $\rho_i(t)$, and a function $r_i(u, t)$, defined over the unit sphere that is measuring the deviation from sphericity of the ith particle. We then establish rigorously the O.D.E.'s[3]

$$\begin{aligned} &\dot{\rho}_i = \left(\frac{1}{\bar{\rho}} - \frac{1}{\rho_i}\right)\frac{1}{\rho_i}, \qquad i = 1,..., n \\ &\bar{\rho} := \frac{1}{n}\sum_{i=1}^{n} \rho_i \end{aligned} \tag{1}$$

[3] These equations were brought to our attention by P. Bates and P. Fife in 1992.

and the global in time estimates

$$\begin{aligned} \dot{\xi}_i &= O(\varepsilon) \\ r_i &= O(\varepsilon) \end{aligned} \tag{2}$$

We also establish that during the whole evolution, the particles stay approximately spherical, and their radii satisfy, *to principal order in* ε, Eqs. (1). The decoupling (to principal order) of Eqs. (1) from the equations of the centers is mainly due to the fact that the motion of the centers is slower by an order of magnitude.

In this work we do not derive explicit equations for the centers ξ_i.[4] Such a task would amount to determining higher order terms in the asymptotic expansion of the solution. We expect the ξ equations to be strongly coupled with Eqs. (1) (cf. example (4.5) in Zhu *et al.*[33]).

Equations (1) predict that at any given time the radius of a given particle decreases or increases depending on whether its size is below or above the average radius $\bar{\rho}$. The smallest particle always shrinks, while the largest always expands. Particles keep disappearing until finally we are left with a single one. We validate the equations all the way to the end.

The equilibrium states of Eqs. (1) are equal sphere configurations, $\rho_1 = \rho_2 = \cdots = \rho_n$. As we show in ref. 20 they correspond to unstable equilibrium configurations of the original evolution system. Equations (1) happen to respect the initial order of sizes, $\rho_1 < \rho_2 < \cdots < \rho_n$.

Most importantly Eqs. (1) preserve the total volume of each phase and reduce the total perimeter,

$$\begin{aligned} \frac{d}{dt} \sum_{i=1}^{n} \rho_i^3 &= 0 \\ \frac{d}{dt} \sum_{i=1}^{n} \rho_i^2 &\leqslant 0 \end{aligned} \tag{3}$$

in accordance with the diffusion law they are derived from.

The first who analyzed succesfully in a quantitative way the time asymptotic behavior of the particle size distribution in three dimensions were Lifschitz and Slyosov, in a celebrated paper[3] in 1961, and independently Wagner.[18] The analysis in these works is based on assumptions and approximations that are reasonable for dilute systems with a large number of particles. Effective equations for the growth of a spherical particle coupled with an external field representing the effect of the rest of the particles are

[4] We have done this recently in work in progress where also we obtain the next term in the ρ-equations.

derived. This is done under the explicit hypotheses that the particles are exact spheres and that their centers stay fixed in time. The results concern the long time behavior of the particle radius distribution $n(R, t)\, dR$ ($:=$ number of particles with radi in $[R, R+dR]$).

Specifically the LSW theory provides the equation

$$\frac{\partial n(R, t)}{\partial t} + \frac{\partial}{\partial R}\left(\frac{dR}{dt} n(R, t)\right) = 0 \tag{4}$$

with

$$\frac{dR}{dt} = \left(\frac{1}{\bar{R}(t)} - \frac{1}{R(t)}\right)\frac{1}{R(t)} \tag{5}$$

(cf. (1)), and where $\bar{R}$ stands for average size

$$\bar{R}(t) = \frac{\int Rn(R, t)\, dR}{\int n(R, t)\, dR} \tag{6}$$

A self-similar solution then is obtained, which is thought to be representing the typical dynamics of the system for large times. On the basis of this solution temporal laws for the average size $\bar{R}(t)$, the supersaturation $\theta_\infty(t)$, and the total number of particles $N(t)$, are derived,

$$\begin{aligned} \bar{R}(t) &= (\bar{R}^3(0) + ct)^{1/3} \\ \theta_\infty &= (\bar{R}(0) + ct)^{-1/3} \\ N(t) &= \bar{c}(\bar{R}^3(0) + ct)^{-1} \end{aligned} \tag{7}$$

Self-similarity amounts to the statement that after normalizing with respect to $\bar{R}(t)$, all systems, independedependently of the initial configuration, ultimately behave identically, exhibiting a very special distribution of sizes, maximized at a special value. For an examination of similarity see the recent work of Niethammer and Pego.[39]

Since then the LSW has been subjected to an amount of criticism and has been modified to account better for experiments. We refer to Penrose *et al.*[34, 35] and especially to Voorhees *et al.*,[37, 38] for the more recent developments.

LSW is a mean field theory, and provides the effective Eq. (5). Recently Niethammer[6] gave a rigorous derivation of Eqs. (4) and (5) utilizing homogenization techniques under the restrictive hypotheses that the particles are spherical and the centers are fixed. Working with exact spheres requires modification of the dynamical law. We hope that the results of the present paper which dismiss with these hypotheses will also make possible a more general derivation of Eqs. (4) and (5).[23]

The reader can easily check that Eqs. (1) have scale invariance compatible with the $t^{1/3}$ law, that is if $\rho(t) = (\rho_1(t), ..., \rho_n(t))$ is a solution, then so is $\lambda^{-1/3}\rho(\lambda t)$ for $\lambda > 0$. We notice the related fact that the equation

$$\dot{\rho} = -\frac{1}{\rho^2} \tag{8}$$

that describes approximately the evolution of a particle near its extinction admits the solution

$$\rho(t) = (\rho(0) - \tfrac{1}{3}t)^{1/3} \tag{9}$$

In the present paper we derive Eqs. (1) under the dynamics considered in the original Lifschitz–Slyosov–Wagner theory:

$$\begin{aligned} \Delta u &= 0 && \text{off } \Gamma \\ u &= H && \text{on } \Gamma \qquad (10) \\ \frac{\partial u}{\partial v} &= 0 && \text{on } \partial\Omega \end{aligned}$$

$$V = -\left\| \frac{\partial u}{\partial n} \right\| \qquad \text{on } \Gamma \tag{11}$$

Here $\Gamma = \bigcup_{i=1}^{n} \Gamma_i$, is the union of the boundaries of the n particles, H is the mean curvature, V is the normal velocity, and $\|\partial u/\partial n\|$ is the jump of the derivative of u in the normal direction to Γ. Ω is a bounded, smooth domain in $\mathbf{R}^3$.

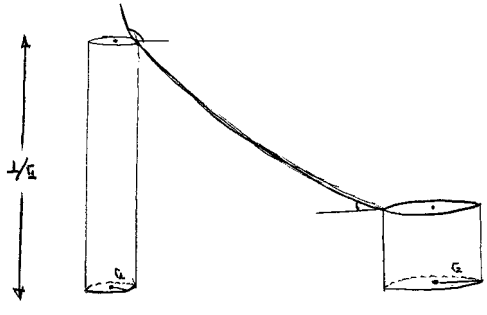

Fig. 2. A schematic representation of the potential u generated by two unequal spherical particles of radii r_1, r_2. The height represents the (mean) curvature of each particle. The harmonic extension in the interior of each sphere is constant.

Equation (11) is the sharp interface limit of the celebrated Cahn–Hilliard equation (refs. 8 and 9, Pego,[10] Alikakos, Bates, and Chen[11]). In this physical context u stands for the chemical potential and $u = H$ is the Gibbs–Thomson relation.

Equation (11) is the quasistatic approximation of the two-phase Stefan problem with surface tension where the diffusivity is taken infinite and so the diffusion equation has been replaced by Laplace's equation. In the solidification context (10), (11) is known as the Mullins–Sekerka equation, and first appeared in ref. 12. The quasistatic approximation in the solidification context is reasonable if the sensible heat is negligible in relation to the latent heat (Alexiades and Solomon[13]). Naturally this model overestimates the motion of the interface.

Equations (10) and (11) define a volume preserving, perimeter shortening law. This follows from the following formal calculations: Let $\mathrm{Per}(\Gamma(t))$, $\mathrm{Vol}(\Omega^-(t))$ stand for the perimeter and enclosed volume respectively. Then by calculus

$$\begin{aligned} \frac{d}{dt}\mathrm{Per}(\Gamma(t)) &= 2\int_\Gamma HV = -2\int_\Gamma u\left(\frac{\partial u_{\mathrm{int}}}{\partial n} - \frac{\partial u_{\mathrm{ext}}}{\partial n}\right) = -2\int_\Omega |\nabla u|^2 \\ \frac{d}{dt}\mathrm{Vol}(\Omega^-(t)) &= \int_\Gamma V = -\int_\Gamma \left(\frac{\partial u_{\mathrm{int}}}{\partial n} - \frac{\partial u_{\mathrm{ext}}}{\partial n}\right) = 0 \end{aligned} \tag{12}$$

where u_{int}, u_{ext} stand for interior and exterior harmonic extensions of H. These calculations presuppose well-posedness of Eqs. (10) and (11). In this direction there is the work of Chen *et al.*[14] on local existence of classical solutions following earlier work in 2 dimensions by Chen[15] (cf. Constantine and Pugh[16]). More recently, Escher and Simonett[19] have introduced an alternative approach to the local existence theory. Global exsitence of weak solutions representing the interface through and beyond topological changes is due to Soner[36] and Chen.[18]

From Eq. (12) we see that $(d/dt)\,\mathrm{Per}(\Gamma(t)) \equiv 0$ if and only if u is a constant, and therefore the only equilibria not intersecting the boundary of Ω are necessarily the union of *spheres of equal radii*. In the following discussion we focus our attention on the class of solutions not intersecting $\partial\Omega$, and of a fixed initial volume $|\Omega^-(0)|$, and we take $\Omega \subset \mathrm{R}^3$, a bounded, smooth, open set.

In explaining our main result it is natural to begin by considering the one particle case. A single sphere is clearly an equilibrium. Reflecting for a moment one can see that there is a 3-parameter family of such equilibria (and hence each one of them has a 3-dimensional center manifold). Chen[15] (and Constantine and Pugh[16] for a related problem) showed that

such equilibria are stable. Escher and Simonett[17] extended and refined these local stability results.

The situation is drastically different when we switch to more than one particle. To begin with, a two-sphere equilibrium has an 1-dimensional unstable manifold corresponding to the shrinking/expanding motion preserving the total volume, and a 6-dimensional center manifold corresponding to the 3 plus 3 independent translations of each sphere. We refer the reader to Alikakos and Fusco,[5] for precise general statements. A configuration of two, unequal, spheres is not an equilibrium configuration and generally it is far from it.

What however poses as the greatest difficulty in justifying rigorously Eqs. (1) is the fact that the radial class, for two or more particles, is not preserved under Eqs. (10), (11), as such an initial condition is immediately distorted.

The present problem under the stability hypotheses above can still be viewed as a perturbation problem. The perturbation parameter is ε; it measures simultaneously size to distance, and distortion to size (Fig. 3). The reference problem for studying any given particle is a nonequilibrium problem, on $\mathbf{R}^n$, a spherical particle coupled with an isotropic external field representing the effect of the remaining particles, and corresponds to the effective Eq. (5).

We now present some of the ideas along with some notation preparing the ground for the main result.

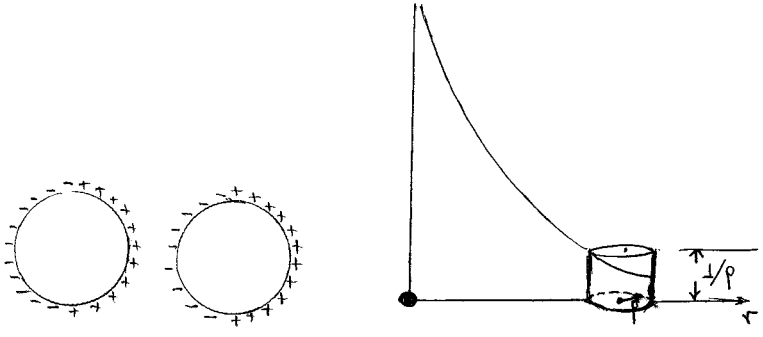

Fig. 3. The Distortion Factor. In Fig. 3a we present an electrostatic analogy suggesting the distortion away from the spherical shape of two, slightly unequal spheres. If the spheres are equal, no charge is needed to generate the constant potential. In Fig. 3b we quantify the distortion. The point charge at the origin represents the anisotropic effect of the external field generated by the remaining particles. The distortion is proportional to $(1/r)-(1/(\rho+r))=(\rho/(r(r+\rho)))=O(\varepsilon^2)$ (according to our scaling assumptions). It can be detected at the linear level by studying the principal eigenfunction of the linearized operator.

• Our strategy is to focus attention on one particle at a time, and reduce the problem to a single particle plus an external field representing the effect of the rest of the particles.

• Equations (10), (11) is an evolution equation, somewhat in disguise. For advancing Γ one first computes H, and then apply to it a Dirichlet–Neumann type of operator, which roughly amounts to one more derivative, and so three[5] derivatives in all, that gives V, the normal velocity. Thus the underlying operator is a 3rd order, pseudodifferential operator. The *linearization* of this operator about a general Γ_0 has the form

$$A = TL \tag{13}$$

where T is a Dirichlet–Neumann type operator, and L is the classical Jacobi operator on the sphere,

$$L = \Delta S^2_\rho + \frac{2}{\rho^2} I \tag{14}$$

where Δ_{Γ_0} is the Laplace–Beltrami operator on S^2_ρ.

• The spectrum of A, in the class of conservative perturbations plays a significant role. Notice that in this case L becomes a shift of the Laplace–Beltrami on the sphere and so the spherical harmonics are easily utilized.

• The definition of a *co-ordinate system* and in particular of *a center* is an important ingredient. Given a particle, close to spherical, we associate to it in a unique manner a sphere, and view the particle as a small perturbation of that sphere. In particular if the interface is already spherical, the procedure associates the same sphere. Thus to each such interface we give a center and a radius. The key fact about the co-ordinate system that singles it out comes from the way we intend to utilize it, which is for studying the global stability properties of the spherical shape. Given a sufficiently smooth Γ close to the sphere $S^2(\bar{\xi}; \bar{\rho})$, we prove that there are unique $\xi \in \mathbf{R}^3$, $\rho \in \mathbf{R}^+$, $r(\cdot) \in C^{3+\alpha}(S^2)$ such that

$$\Gamma = \{x \mid x = \xi + \rho[1 + r(u)]\, u, u \in S^2(0; 1)\} \tag{15}$$

[5] This explains to some extent the structure of Eqs. (10) and (12). Notice that the motion by mean curvature corresponds to $\dot{\rho} = -1/\rho$, while Eqs. (10) and (12), relate to $\dot{\rho} = -1/\rho^2$, the derivative of the curvature. This also explains the $t^{1/3}$ scaling law (see Eq. (9)).

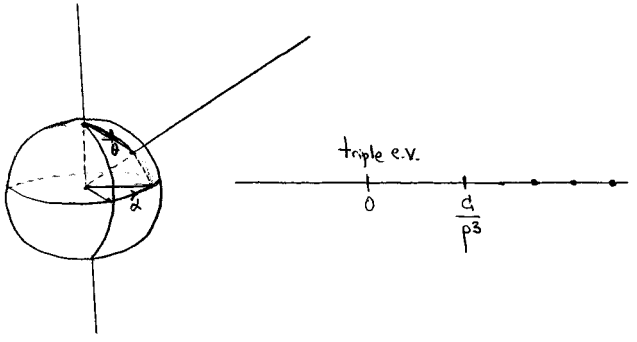

Fig. 4. The spectrum of A on S_ρ: $\lambda_1 = \lambda_2 = \lambda_3 = 0$ is a triple eigenvalue, with $\lambda_4 \geqslant C/\rho^3$. The zero eigenfunctions which correspond to the three independent translations are given by the spherical harmonics of degree one, $\eta_j = (u, e_j)$, $|u| = 1$, $j = 1, 2, 3$ where $(\ ,\ )$ is the Euclidean inner product, $\eta_1 = \cos\alpha \sin\theta$, $\eta_2 = \sin\alpha \sin\theta$, $\eta_3 = \cos\theta$.

with

$$\int_{S^2(\xi, 1)} r(u)\, d\sigma(u) = 0$$

$$\int_{S^2(\xi, 1)} r(u)\, \eta_i(u)\, d\sigma(u) = 0, \qquad i = 1, 2, 3 \tag{16}$$

where η_i are the eigenfunctions of A corresponding to the zero eigenvalue and coincide with the spherical harmonics of degree one, as discussed in Fig. 4. Notice that Eq. (16) consists of four constraints matching exactly the four parameters $\xi = (\xi_1, \xi_2, \xi_3)$, ρ. Notice also how ρ is factored out in Eq. (15) so as to be appropriate near the extinction of the particle.

A similar co-ordinate system was introduced in Alikakos *et al.*[23] for two dimensions and in Bellettini and Fusco[22] for three dimensions. Independently a similar notion of center has been employed by Huisken and Yau[24] and especially in the related work of Ye's.[25]

We will describe the evolution of initial interfaces of the form $\Gamma_i(0)$, where (Fig. 5)

$$\Gamma_i(t) := \xi(t) + \rho_i(t)[1 + \varepsilon r_i(u, t)]\, u, \qquad u \in S^2, \qquad i = 1, \ldots, n \tag{17}$$

Our intention is to decompose the motion into a motion for the centers $\xi_i(t)$, for the radii $\rho_i(t)$ and for the distortions $r_i(u, t)$. The co-ordinate

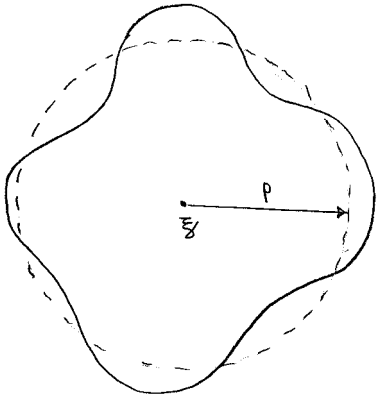

Fig. 5. The co-ordinate system.

system we introduced provides a decomposition of the linearized problem into the normal modes ξ, ρ and r. It turns out that it decomposes the nonlinear motion as well, *globally* in time.

2. THE MAIN RESULT. STATEMENT AND SKETCH OF PROOF

Theorem. Let $\Omega = \Omega_\varepsilon$ have diameter $O(1/\varepsilon)$. Let the initial n-particle system be given by $\Gamma_i(0)$ as in Eq. (17), with

$$\begin{aligned} d(\Gamma_i(0), \Gamma_j(0)) &\geqslant \frac{C}{\varepsilon}, \qquad i \neq j \\ d(\Gamma_i(0), \partial\Omega_\varepsilon) &\geqslant \frac{C}{\varepsilon}, \qquad i = 1,..., n \end{aligned} \tag{18}$$

C some fixed, positive constant. Then Eqs. (10) and (11), for $\varepsilon < \varepsilon_0$ is equivalent to a system of evolution equations for ρ_i, ξ_i and r_i satisfying

$$\begin{aligned} \dot{\rho}_i &= \left(\frac{1}{\bar{\rho}} - \frac{1}{\rho_i}\right)\frac{1}{\rho_i} + O(\varepsilon) \\ \dot{\xi}_i &= O(\varepsilon) \\ \|r_i\|_{C^{3+\alpha}(\Omega_\varepsilon)} &= O(1), \qquad i = 1,..., n \geqslant 2 \end{aligned} \tag{19}$$

where $\rho_1(t) \to 0$ as $t \to T$ and the estimates hold uniformly for $t \in [0, T]$, T the time of extinction of the smallest particle for which the following estimate holds:

$$\frac{1}{3}(\min_j \rho_j(0))^3 \leqslant T \leqslant \frac{1}{3}(\min_j \rho_j(0))^3 \frac{n((3/4\pi)\,\mathrm{Vol}(0))^{1/3}}{\max_j \rho_j(0) - \min_j \rho_j(0)} \tag{20}$$

$$\mathrm{Vol}(0) = \frac{4}{3}\pi \sum_{j=1}^{n} \rho_j^3(0) \tag{21}$$

Remarks. 1. The statement of the theorem above could be improved in two ways. First the optimal estimate for the distortion is $O(\varepsilon^2)$ and therefore we expect

$$\|r_i\| = O(\varepsilon)$$

This improved estimate would imply that the ξ equations are independent or r, to principal order, and hence that the system for ρ, ξ and r would have triangular structure. Second the $\lim_{t \to T} r_1(t, u) = 0$ would establish that the particle shrinks like a sphere.

2. Globalizing the solution by removing and continuing is not always legitimate. In our situation it can be done due to the results in Chen.[18] We refer the reader to ref. 5.

In the following we present a sketch of the argument indicating briefly the analytical difficulties and referring to Alikakos and Fusco[5] for details.

Sketch of the Proof.

Step 1. The Potential theoretic Reduction on the Interface. The evolution system (10, 12) can be reformulated as a problem that lives entirely on Γ. This reduction, in principle, is known for Stefan probems (see also Chen *et al.*[33]). For the problem at hand

$$\int_\Gamma g(x, y)\, V(y)\, dy - \frac{1}{|\Gamma|} \int_\Gamma \int_\Gamma g(x, y)\, V(y)\, dy\, dx$$

$$= H(x) - \bar{H}, \qquad x \in \Gamma \tag{22}$$

where $g(x, y)$ is the Green's function

$$\Delta_y g(x, y) = \delta_x(y) - \frac{1}{|\Omega|}$$

$$\frac{\partial g}{\partial n_y} = 0 \qquad \text{on } \partial\Omega \tag{23}$$

$$\bar{H} := \frac{1}{|\Gamma|} \int_\Gamma H(y)\, dy, \qquad |\Gamma| := \text{surface area of } \Gamma$$

Notice that g is independent of $\Gamma = \Gamma(t)$.

Equation (22) can be written abstractly in the form

$$S(V) = H - \bar{H} \tag{24}$$

where S is the linear operator defined by the left hand side of Eq. (22).[6]

S is invertible in the class of functions with zero average

$$V = S^{-1}(H - \bar{H}). \tag{25}$$

Step 2. The Reduction To a single Particle plus a Field. Pick i and fix it and consider $x \in \Gamma_i$. Utilizing Eq. (18) and the estimate

$$|g(x, y)| \leqslant \frac{C}{|x - y|}$$

we obtain

$$\begin{aligned} \int_{\Gamma_i} g(x, y)\, V_i(y)\, dy &= \bar{V} + H_i(x) - \bar{H} - \sum_{j \neq i} \int_{\Gamma_i} g(x, y)\, V_i(y)\, dy \\ &= \bar{V} + H_i(x) - \bar{H} + O(\varepsilon), \qquad x \in \Gamma_i \end{aligned} \tag{26}$$

where

$$\begin{aligned} V_i &= V|_{\Gamma_i} \\ \bar{V} &:= \frac{1}{|\Gamma|} \int_\Gamma \int_\Gamma g(x, y)\, V(y)\, dy\, dx \end{aligned} \tag{27}$$

[6] Compare with the simpler, second order evolution law $V = H - \bar{H}$.[26, 2] Notice that for this the pattern of exact spheres is invariant.

Estimate (26) is needed in an appropriate $C^{k+\alpha}(\Gamma_i)$ norm uniformly in time. It is based on a (hard) estimate on r (cf. (29)) below) which we will revisit later.

Step 3. Replacement of $g(x, y)$ with the Newtonian Potential. We replace $g(x, y)$ in Eq. (26) with $N(x-y) = -(\omega_3/(|x-y|))$. The estimate is not particularly hard provided Eq. (29) is given. It amounts to removing the boundary $\partial\Omega$.

Step 4. Reduction on the Sphere $S^2(\xi^i; \rho_i)$. Assuming the estimate

$$\|r_i\|_{C^{3+\alpha}(\Gamma)} < C \tag{29}$$

holding up to $t = T$ we can replace in Eq. (28) Γ_i with $S^2(\xi^i, \rho_i)$ at the expense of changing slighty V_i to $\hat{V}_i$:

$$\int_{S^2(\xi^i, \rho_i)} N(x-y)\, \hat{V}_i\, dy = \bar{V} + H(x) - \bar{H} + O(\varepsilon), \qquad x \in S^2(\xi^i, \rho_i) \tag{30}$$

Step 5. Linearization of the Mean Curvature about the Sphere. For $x \in \Gamma_i$ we have the estimate

$$H(x) - \bar{H} = \frac{1}{\rho_i} - \frac{\sum \rho_k}{\sum \rho_k^2} + \frac{\varepsilon}{\rho_i} Lr_i + O(\varepsilon^2) \tag{31}$$

where L is the Jacobi operator on the sphere $S^2(\xi^i, \rho_i)$.

Step 6. The first Approximation. From Eq. (31) we see that replacing $H(x) - \bar{H}$ in (30) with its linear approximation will affect $\hat{V}_i$ only by a small amount. Thus $\hat{V}_i - \hat{\hat{V}}_i = O(\varepsilon)$, where $\hat{\hat{V}}_i$ is obtained by solving

$$\int_{S^2(\xi^i; \rho_i)} N(x-y)\, \hat{\hat{V}}_i(y)\, dy = \bar{V} + \frac{1}{\rho_i} - \frac{\sum \rho_k}{\sum \rho_k^2} + \frac{\varepsilon}{\rho_i} Lr_i, \quad x \in S^2(\xi^i; \rho_i) \tag{32}$$

The advantage of all this is that we can now calculate $\hat{\hat{V}}_i$ by hand in terms of spherical harmonics. It amounts to calculating the harmonic extensions $u^i(x)$ of the Dirichlet Data on the right of Eq. (32). Utilizing the special nature of r_i (orthogonality to first four spherical harmonics) plays a role in this and in the following calculation. We find

$$\hat{\hat{V}}_i(x) = -\left\{\left[\frac{1}{\rho_i} - \frac{\sum \rho_k}{\rho_k^2}\right] + \bar{V}\right\} \frac{1}{\rho_i} + \frac{\varepsilon}{\rho_i} T_0 Lr_i \tag{33}$$

Here T_0 stands for the Dirichlet–Neumann type operator on the sphere and with Ω replaced by R^3.

Step 7. Conclusion. Under the estimate (29), the following approximations are legitimate

$$\dot{\rho}_i \simeq \text{average of } V_i \simeq \text{average of } \hat{\hat{V}}_i = \left\{ \left[\frac{1}{\rho_i} - \frac{\sum \rho_k}{\rho_k^2} \right] + \bar{V} \right\} \frac{1}{\rho_i} \tag{34}$$

where we used that

$$\int_{S^2(\xi^i;\, \rho_i)} T_0 L r_i = 0$$

Finally to calculate $\bar{V} = \bar{V}(t)$ we employ the conservation which holds approximately at the level of ρ-equations: From

$$\frac{d}{dt} \sum_k \rho_k^3 = 0 \tag{35}$$

and

$$\dot{\rho}_i = -\left\{ \left[\frac{1}{\rho_i} - \frac{\sum \rho_k}{\sum \rho_k^2} \right] + \bar{V} \right\} \frac{1}{\rho_i} \tag{36}$$

we obtain

$$\bar{V} = -\frac{\sum \rho_k [(1/\rho_k) - \bar{H}]}{\sum \rho_k} \tag{37}$$

and substituting in Eq. (36) we obtain Eqs. (1) and so the main part of the theorem. ▮

COMMENTS

1. In ref. 5, for making rigorous many of the estimations above we use systematically Miranda's elliptic regularity. The following is a sample result which we employ throughout:

Let Ω be bounded in R^n, $\partial\Omega \in C^{1,\lambda}$. Consider the interior and exterior problem

$$\begin{aligned} \Delta u &= 0 \quad \text{in } \Omega, & \Delta u &= 0 \quad \text{in } \Omega^c \\ u &= g \quad \text{on } \partial\Omega, & u &= g \quad \text{on } \partial\Omega \end{aligned}$$

Then we have the estimate

$$\{\|u\|_{C^{1,\lambda}(\bar{\Omega})}, \|u\|_{C^{1,\lambda}(\Omega^c)}\} \leqslant C \|g\|_{C^{1,\lambda}(\partial\Omega)}$$

C independent of g.

All the elliptic theory we need (including the result above) can be found in Miranda's paper[27] on Newtonian potentials which is a further development of Agmon, Douglis, Nirenberg.[28]

2. The estimate on $\|r\|_{C^{3,\lambda}}$ is a major analytical step. For this purpose we employ the semigroup formulation of (10), (11), following Escher and Simonett[17] that utilizes the maximal regularity theory of Da Prato and Grisvard.[29–32] In this direction we profited a lot from several discussions with G. Simonett and from a careful reading of Chen *et al.*[14]

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