Thermodynamics of higher gradient van der Waals fluids and the modelling of GUVs.

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Abstract

Biological structures, such as Giant Unilamellar Vesicles (GUVs) and others, exhibit configurations where line boundaries occur; in some cases, at a finer scale with respect to their size, such lines are shown to exhibit non-smoothness. Higher gradient van der Waals fluids may be viewed as very crude models for structures resembling such a feature, whose compatibility with the thermodynamics is here investigated.

The occurrence of (possibly piecewise smooth) lines, formed by the boundaries between adjacent surfaces, each of which such that the traces of the volume changes (and so of the densities) or the normal component of the derivative of the energy with respect to the gradient of the volume change, is found to be compatible with thermodynamics through the Coleman and Noll’s procedure.

Henceforth, a corresponding jump of the surface tension is predicted. In particular, this is interpreted to give the local magnitude of the line tension field.

Key words: Higher gradient van der Waals fluids, Thermodynamics, Biological structures, Giant Unilamellar Vesicles, GUVs

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1 Introduction

The thermodynamics of compressible elastic fluids exhibiting capillarity is examined in this paper. Although this is a classical topic in Continuum Mechanics, the aim of the present analysis is twofold; one is to support a bifurcation analysis, recently worked out in [DH], and the second is to check whether or not line forces and line tensions directly connect with the surface tension arising in zones of the fluids in different phases. For instance, this is what it seems to happen in Giant Unilamellar Vesicles, GUVs, which are lipid multilayers mostly shaped initially as spheres (see e.g. [BWH], [Z] and references cited therein). Under either changes of temperature or on (osmotic) pressure these GUVs turn out to exhibit different material and geometrical phases. Although such objects appear to be thin with respect their initial diameter, some rough indications about their behavior may be obtained by a fully three dimensional energetics, such as the one considered in this paper.

Striking formal analogies with this energy are also obtained in [DPPZ],[DPPZ2].

A free energy for van der Waals higher gradient elastic fluids was first introduced in [V] and re-analyzed by several authors (see e.g. [Ai1], [Ai2], [AS1], [AS2], [AMcFW], [FK], [SE] among many others) both in statics and dynamics. Higher gradient van der Waals energetics was the sum of a non-convex function of the density and a term proportional to the square of the spatial gradient of the density.

Sixty-five years later a similar approach was rediscovered by Cahn and Hilliard [CH]. In any case, starting with van der Waals himself, most, if not all, analyses of the theory have been restricted to one-dimensional settings, viz., the density variation across a “flat” interface is a function of one spatial variable, e.g., [V], [CH], [CGS], [DS]. Indeed, the difficulty in analyzing van der Waals’ model in space-dimensions larger than one has been acknowledged in [G], [GPV].

In a previous work [DH], a class of such problems in three spatial dimensions was formulated (see also [SD]) in the presence of piecewise smooth boundaries. There, an energy dependent on the local measure of the volume change (basically equivalent to the local mass density) and on its (spatial) gradient was assumed to be double well in the former variable and strictly convex in the latter. Stationary points of the energy were sought with respect to deformation induced variations in the volume change and Euler-Lagrange equations of equilibrium in the spatial description were derived. The existence of homogeneous solutions of the obtained boundary value problem were proved and the onset of bifurcated two-phase configuration about such homogeneous states was studied.
Thermodynamic consistency with the Second Law of the constitutive equations inferred in [DH] was not included there: this check is indeed the aim of the present paper.

Issues concerning the thermodynamics of higher gradient van der Waals fluids have been extensively discussed in the literature, (see e.g. [A], [deS], [DS], [GPV], [PL], [SD], [SE], etc.) although there is no mention about the possible nucleation of neither one dimensional domains (lines) nor associated line tensions. Something along these lines was investigated for solids in [PPG] \(^1\).

In particular, some aspects of the problem of thermodynamics for second order van der Waals fluids remain still open (see also [SR] for a different treatment). Indeed, the thermodynamic restrictions allowing for determining compatible stress-like entities arising at one dimensional (e.g. "line-like") boundaries is of interest (see e.g. [NV]) especially to the extend to formulating boundary value problems, possibly leading to bifurcation [DH].

This issue is very important because it arises in the observed configurations of biological systems, such as Giant Unilamellar Vesicles (see e.g. [Z] and references cited therein), called also GUVs. Detailed images at a sufficiently fine scale may show some roughness of the boundary between zones where lipids are in different phases [BWH]. In this paper we formulate the thermodynamics of higher gradients van der Waals fluids in a piecewise-smooth geometrical context, so that this feature may be taken into account. In particular, we consider situations in which the boundary of the configuration body is equal to the measure of a countable union of \( C^1 \) surfaces.

In this treatment, the simplest form of the external power pairing the terms arising from the rate of change of energy is assumed. Actions external to a given arbitrary part of the body are singled out in (i) contact forces acting through the boundary, exerting power against the velocity at that site, and (ii) non-classical "interstitial" (see e.g. [DS]) forces, acting against the rate of change of the local volume measure \( J \) (or, equivalently, against the rate of change of density of the fluid). In this way, no dissipation arises in such materials and both the Cauchy stress and the surface tension turn out to be constitutively determined by the energetics.

In the present paper we obtain:

- the constitutive equation for the higher-gradient (often called "non-local")

\[^1\] There \( W(F, \nabla_X F, \nabla_X \nabla_X F) \), where \( F \) represents the deformation gradient, is assumed instead of (15): in the particular case of a cubic domain, our formulation would come out as a particularization of the formulation developed in [PPG]. Here, as it will be seen in the sequel, no vertex forces are recovered because of the absence of the third gradient of the deformation.
Cauchy stress;

- the presence of surface tension due to the higher gradient dependence of the energy, we derive a constitutive equation for such field;

- the presence of discontinuous edge interstitial surface tension (i.e. the trace of the surface tension on lines) at the "internal" line boundaries where adjacent normals may jump;

- the consequent jump on:

  – the "surface tractions";

  – the "line tension", i.e. the tangential field right on the line boundaries mentioned above.

These equations have an impact on the bifurcation problem for higher gradient van der Waals fluids investigated in [DH].

The outline of the paper is as follows.

In Section 2, the geometry of the problem is described. In particular the jump set of the normal field defined on the boundary of a given region, the motion, a time-parametrized family of orientation preserving ($C^1$) diffeomorphisms, and the associate measure of change in volume $J$ are introduced.

In Section 3, the thermodynamics of higher gradients van der Waals fluids is explored. First of all, the rate of change of energy on an arbitrary part of the body is evaluated. The bulk part of it is easily determined, whereas the surface part of it requires lengthy considerations.

In particular, a known (see e.g. [LT] and many others) non-simple constitutive equation for the Cauchy stress and an explicit expression for the surface tension field are determined; the latter is here shown to enter in both surface and line boundary terms, leading to a discontinuous edge interstitial traction field. Furthermore, line tensions do not explicitly appear in the Second Law of Thermodynamics, although they may be conjectured to be the tangential component of the jump of the trace of surface tension fields arising at the line boundaries. This seems to be exactly what happens in GUVs whenever different material and geometrical phases are induced either thermally or mechanically.
2 Preliminaries and geometry

Some few technical issues will be introduced in this section.

Let $B_t \subset \mathbb{R}^3$ be a Lipschitz open bounded region with finite perimeter, representing either the configuration at time $t$, called here current configuration, occupied by the body under consideration or the control volume based upon which the motion of a fluid may be studied. Such regions are obviously Lebesgue measurable. The Lebesgue measure of a given set $\circ$ may be denoted by $\mathcal{L}^n(\circ)$, where $n$ is the dimension of the set.

Let $P_t \subset B_t$ be an arbitrary part with the same properties of $B_t$ (in particular this is an open Lebesgue-measurable set). Assume that the boundary $\partial P_t$ is a countable union of $C^1$ surfaces, i.e.

$$\partial P_t := \bigcup_j (\partial P_t)_j.$$  \hspace{1cm} (1)

Hence, because $P_t$ has finite perimeter, it is known that (see e.g. [VH]) the Lebesgue measure of its boundary $\mathcal{L}^2(\partial P_t)$ is finite and

$$\mathcal{L}^2(\partial P_t) = \mathcal{L}^2(\bigcup_j (\partial P_t)_j) = \sum_j \mathcal{L}^2((\partial P_t)_j).$$  \hspace{1cm} (2)

The outward normal $n$ at $z \in \partial P_t$ does exist, although this may not be unique. In particular, $n(\circ)$ is unique at every point in the interior of each $(\partial P_t)_j$ and admits discontinuities in a subset $J_n$ such that

$$J_n \subseteq \bigcup_{h,k,h \neq k} \left((\partial P_t)_h \cap (\partial P_t)_k\right), \quad \mathcal{L}^1(J_n) < \infty,$$  \hspace{1cm} (3)

i.e. there must be at least two surfaces $(\partial P_t)_r$ and $(\partial P_t)_s$ such that

$$n_s(z) \cdot n_r(z) \neq 1$$  \hspace{1cm} (4)

whenever $z \in (\partial P_t)_r \cap (\partial P_t)_s$. The fact that the surfaces $(\partial P_t)_r$ and $(\partial P_t)_s$ are $C^1$, implies the existence of a neighborhood $N_z$ of $z$ of $\mathcal{L}^1(N_z) \neq 0$ where the same property holds, i.e. $z$ is not an isolated point.

The subset $J_n$ may be improper if, for example, the boundary $\partial P_t$ is formed by the mantle of a cylinder of height $h$, circular and constant cross section of radius $r$ and rectilinear axes, closed on its boundary by the surfaces of two identical hemispheres of the same radius. In this case there is no discontinuity set of the normal field $n(\circ)$ although $\bigcap_k (\partial P_t)_k = \{C_r(0,0,-h/2), C_r(0,0,h/2)\}$, where $C_r(x_1^C, x_2^C, x_3^C) := \{(x_1, x_2, x_3)|((x_1 - x_1^C)^2 + (x_2 - x_2^C)^2 = r^2}\}$ denotes a circle of radius $r$ centered at $(x_1^C, x_2^C, x_3^C)$ and $(x_1, x_2, x_3)$ is a cartesian coordinate system centered at the centroid of the region included in such $\partial P_t$.  

Jump tensors of the field \( n(\circ) \) relative to each of the two normals may be introduced as follows

\[
J(n(z))|^{nr} := (n_r(z) - n_s(z)) \otimes n_r(z),
\]

(5)

\[
J(n(z))|^{ns} := (n_s(z) - n_r(z)) \otimes n_s(z).
\]

(6)

We note that if

\[
\hat{J}(n(z))|^{nr} := tr J(n(z))|^{nr} = 1 - n_s(z) \cdot n_r(z)
\]

(7)

then

\[
\hat{J}(n(z))|^{nr} = \hat{J}(n(z))|^{ns}
\]

(8)

and that the jump set of the normal field \( J_n \) defined by (3) is such that

\[
J_n = \bigcup_i \gamma_i,
\]

(9)

where \( \{\gamma_i\}_{i \in \mathbb{N}} \) is a countable set of closed lines \( \gamma_i \) such that \( L^1(\gamma_i) < \infty \) for all \( i \in \mathbb{N} \). In particular \( \gamma_i = \bigcup_r \gamma^r_i \), \( L^1(\gamma^r_i \cap \gamma^r_{i+1}) = L^1(\gamma^r_i \cap \gamma^s_i) = 0, \ r \neq s \), i.e. each \( \gamma_i \) is formed by a finite union of \( C^1 \) curves \( \gamma^r_i \), which in the sequel shall be called arches, and the intersection among subsequent arches is a point and there is no intersection among arches which are not subsequent. This is the case of observed configurations in Giant Unilamellar Vescicles (see e.g. [BWH]).

Whenever \( \mathcal{B}_t \) represents the current configuration of a given body, we may denote with \( \mathcal{B}_0 \subset \mathbb{R}^3 \) the corresponding initial configuration, which could also be taken as an underlying reference configuration. Hence, \( y : \mathcal{B}_0 \times [0, \, T] \rightarrow \mathbb{R}^3 \), a one parameter family of orientation preserving piecewise \( C^1 \) diffeomorphism, may denote the motion from \( \mathcal{B}_0 \), whereas \( T \) denotes the time duration of the motion. Let \( x := y(X, \, t) \in \mathcal{B} \) be a point in the current configuration; the point \( X \in \mathcal{B}_0 \) is such that \( X = y^{-1}(x) \).

Let \( t \in (0, \, T) \) be fixed. If we introduce the following tensor field

\[
F(X, \, t) := \nabla_X y(X, \, t),
\]

(10)

we shall call it the (material) deformation gradient at \( X \). Henceforth, the change in volume at \( x \in \mathcal{B} \) may be written as follows:

\[
\hat{J}(X, \, t) := det(F(X, \, t))
\]

(11)

\[
J := \hat{J}(x, \, t) := \hat{J}(y^{-1}(x, \, t)),
\]

(12)

\[
\{J\}_m := \hat{J}(X, \, t) = \hat{J}(y(X, \, t)),
\]

(13)

where \( \{\circ\}_m \) denotes the material description of ”\( \circ \)”.
3 Thermodynamics

Let us assume that the local form of the continuity equation does hold throughout $B_t$, i.e.

$$\rho(x, t)J(x, t) = \rho_0(y^{-1}(x, t)),$$

where $\rho(x, t)$ is the current mass density of the fluid at $x$ and $\rho_0(y^{-1}(x, t))$ is the corresponding referential density.

Let

$$W(J, \nabla J)$$

be the Helmholtz free energy density per unit mass. This may be assumed to be a smooth double well potential in $J$ and a smooth and convex function of its gradient: in this case we shall call the corresponding material element a van der Waals higher gradient elastic fluid.

Recall that with $\mathcal{P}_t \subset B_t$ such that (1) holds, we denote an open arbitrary part of $B_t$ with the same properties of this set; for further developments we may also introduce $\mathcal{P}_0 := y^{-1}(\mathcal{P}_t, t) \in B_0$, the counter-image of $\mathcal{P}_t$ under $y(\circ, t)$.

3.1 Rate of change of energy

The rate of change of energy on $\mathcal{P}_t$ reads as follows:

$$\frac{d}{dt} \mathcal{E}(J; \mathcal{P}_t) = \frac{d}{dt} \int_{\mathcal{P}_t} \rho W(J, \nabla J) d\mathcal{L}^3$$

$$= \frac{d}{dt} \int_{\mathcal{P}_0} \rho_0 \{W(J, \nabla J)\}_m d\mathcal{L}_0^3$$

$$= \int_{\mathcal{P}_0} \rho_0 \frac{d}{dt} \{W(J, \nabla J)\}_m d\mathcal{L}_0^3$$

$$= \frac{d}{dt} \mathcal{E}(\{\circ\}_m; \mathcal{P}_0),$$

where $\{\circ\}_m$ means material description of $\circ$. Hence, rewriting (16) in the spatial form we have:

$$\frac{d}{dt} \mathcal{E}(\mathcal{P}_t) = \int_{\mathcal{P}_t} \rho \frac{d}{dt} W(J, \nabla J) d\mathcal{L}^3$$

$$= \int_{\mathcal{P}_t} \rho (W_1 \dot{J} + W_2 \cdot (\nabla J)) d\mathcal{L}^3,$$

where
\[ W_1 := \partial W / \partial J \quad \text{(18)} \]
\[ W_2 := \partial W / \partial \nabla J, \quad \text{(19)} \]

Because:
\[ \nabla J = \nabla (\dot{J}) - (\nabla v)^T \nabla J, \]

we get:
\[ \frac{d}{dt} \mathcal{E}(P_t) = \int_{P_t} \rho (W_1 \dot{J} + W_2 \cdot (\nabla \dot{J} - (\nabla v)^T \nabla J)) \, d\mathcal{L}^3; \quad \text{(20)} \]

the integration by parts of the second integral yields:
\[ \int_{P_t} \rho W_2 \nabla \dot{J} d\mathcal{L}^3 = \int_{\partial P_t} \rho \dot{J} W_2 \cdot n \, d\mathcal{L}^2 - \int_{P_t} \dot{J} \text{div} (\rho W_2 I) \, d\mathcal{L}^3, \quad \text{(21)} \]

so that the rate of change in energy can be rewritten as follows:

\[ \frac{d}{dt} \mathcal{E}(P_t) = \int_{P_t} \rho J \left[ (W_1 - \text{div} (\rho W_2)) I - \frac{\nabla J \otimes W_2}{J} \right] \cdot \nabla v \, d\mathcal{L}^3 + \]
\[ + \int_{\partial P_t} \rho J (W_2 \cdot n) \, \text{div} v \, d\mathcal{L}^2, \quad \text{(22)} \]

where
\[ \dot{J} = J \text{ div } v \quad \text{(23)} \]

applies. Obviously, the integrand in (21) is understood in the sense of the flux of the trace of \( \rho J W_2 \) right on the set \( \partial P_t \), i.e. the boundary of the region under consideration.

It is worth noting that the rate of change of the energy has to be worked out in details because of this surface term. The latter may be rewritten as follows by virtue of (23):

\[ \int_{\partial P_t} n \cdot W_2 \rho \dot{J} \, d\mathcal{L}^2 = \int_{\partial P_t} n \cdot W_2 \rho J \, \text{div} v \, d\mathcal{L}^2. \quad \text{(24)} \]

We recall that (1) holds and we note that, away from sites included in \( J_n \) (see e.g. (3) and (9) for its inclusion and its definition respectively), we may write:

\[ \text{div}(\mathbf{v}) = \text{div}_\Sigma (\mathbf{v}) + (\mathbf{v})_m, \quad \text{(25)} \]

where
\[ (\mathbf{v})_m := \mathbf{v}_m \cdot n := (\nabla \mathbf{v}) n \cdot n \quad \text{(26)} \]

and
\[ \text{div}_\Sigma (\mathbf{v}) := I_\Sigma \cdot \nabla_\Sigma \mathbf{v}, \quad \text{(27)} \]

where
\[ I_\Sigma := a_u \otimes a_u^e; \quad \text{(28)} \]
here \( \{ a_\alpha \}_{\alpha=1,2} \) is a covariant basis of the tangent space at a generic point of the boundary \( \partial \mathcal{P}_t \) and \( \{ a^\alpha \}_{\alpha=1,2} \) is the corresponding dual basis, \( \nabla_\Sigma(\circ) := \circ \otimes a^\alpha \) is the surface gradient operator.

Hence, (25) into (24) and the divergence theorem yield

\[
\int_{\partial \mathcal{P}_t} \mathbf{n} \cdot W_{,2} \rho \, J \, d\mathcal{L}^2 = \int_{\partial \mathcal{P}_t} \mathbf{n} \cdot W_{,2} \rho 
abla \Sigma(\mathbf{v}) + \\
+ \int_{\partial \mathcal{P}_t} (\mathbf{n} \cdot W_{,2} \rho \, J) \mathbf{n} \cdot \mathbf{v} \, n \, d\mathcal{L}^2 = \\
= \int_{\partial \mathcal{P}_t} \nabla \Sigma(\mathbf{v} \cdot \mathbf{n} \cdot W_{,2} \rho \, J) \, d\mathcal{L}^2 + \\
- \int_{\partial \mathcal{P}_t} \mathbf{v} \cdot \nabla \Sigma(\rho \, J \, \mathbf{n} \cdot W_{,2}) \, d\mathcal{L}^2 + \\
+ \int_{\partial \mathcal{P}_t} (\rho \, J \, \mathbf{n} \otimes W_{,2}) \cdot \mathbf{v} \, n \, d\mathcal{L}^2. \\
\]

We are now in the position to evaluate the term

\[
\int_{\partial \mathcal{P}_t} \nabla \Sigma(\mathbf{v} \cdot \mathbf{n} \cdot W_{,2} \rho \, J) \, d\mathcal{L}^2 \\
\]

in (29). Indeed, by virtue of (1) and by the (surface) divergence theorem [DrH], the first term in (29) may finally be rewritten as follows:

\[
\sum_j \int_{(\partial \mathcal{P}_t)_j} \nabla \Sigma(\mathbf{v}(\mathbf{z}) \cdot \mathbf{n}_j(\mathbf{z}) \cdot \nabla \tilde{J}(\mathbf{z}) \rho(\mathbf{z}) \tilde{J}(\mathbf{z})) \, d\mathcal{L}^2(\mathbf{z}) = \\
= \sum_j \int_{\cup_{i} \gamma_i^j} \mathbf{m}_i^j(\mathbf{z}) \cdot (\rho(\mathbf{z}) \tilde{J}(\mathbf{z}) \mathbf{v}(\mathbf{z}) \cdot \nabla \tilde{J}(\mathbf{z}) \cdot \mathbf{n}_i^j(\mathbf{z})) \, d\mathcal{L}^1(\mathbf{z}) + \\
- \sum_j \int_{(\partial \mathcal{P}_t)_j} 2 \, H(\mathbf{z}) \mathbf{v}(\mathbf{z}) \cdot \mathbf{n}_j(\mathbf{z}) \left( \rho(\mathbf{z}) \tilde{J}(\mathbf{z}) \right) \, d\mathcal{L}^2(\mathbf{z}),
\]

where \( H(\mathbf{z}) := -\frac{1}{2} tr \nabla_\Sigma \mathbf{n} \) is the mean curvature of \( (\partial \mathcal{P}_t)_j \) at \( \mathbf{z} \) and where \( \partial(\partial \mathcal{P}_t)_j = \bigcup_i \gamma_i^j \), has been introduced; here \( \mathbf{n}_j(\mathbf{z}) \) denotes the normal at \( \mathbf{z} \in (\partial \mathcal{P}_t)_j \), \( \mathbf{n}_i^j(\mathbf{z}) \) denotes the trace to the boundary \( \gamma_i^j \) of the normal \( \mathbf{n}_j \) on the surface \( (\partial \mathcal{P}_t)_j \) at \( \mathbf{z} \in \gamma_i^j \cap (\partial \mathcal{P}_t)_i \) , \( \mathbf{m}_i^j(\mathbf{z}) := \mathbf{n}_i^j(\mathbf{z}) \wedge \mathbf{\tau}_r(\mathbf{z}) \) is a unit vector normal to the curve \( \gamma_i \) at \( \mathbf{z} \) and \( \mathbf{\tau}_r(\mathbf{z}) \) is the unit tangent vector to \( \gamma_i^j \) at the same point \( \mathbf{z} \).

This agrees with (A.4) in [PPG] and with the more general patchwork divergence formula (24) in [DrH], where the first term involving a non-discontinuous integrand vanishes because none of the curves \( (\partial \mathcal{P}_t)_j \) has such a feature. Indeed, \( (\partial \mathcal{P}_t)_j \) is supported by closed curves where at least one of the fields among \( \mathbf{n}_i^j \), and so \( \mathbf{m}_i^j, \nabla \tilde{J}, \nabla \tilde{J} \cdot \mathbf{n}_i^j \), may jump.
Hence, (31) in (29) yields:

\[
\sum_j \int_{(\partial P_t)_j} n_j \cdot W_{2, \rho} \; \rho \; J \; dL^2 = \sum_j \int_{\bigcup_r \gamma^j_r} m^j_r \cdot \left( \rho \; J \; v \cdot W_{2, \rho} \cdot n^j_r \right) \; dL^1
\]

\[
- \sum_j \int_{(\partial P_t)_j} v \cdot (\nabla \Sigma (\rho \; J \; n \cdot W_{2, \rho}) + n_j \; (2 \; H \; n_j \cdot W_{2, \rho} \; \rho \; J)) \; dL^2
\]

\[
+ \sum_j \int_{(\partial P_t)_j} (\rho \; J \; n_j \otimes n_j \; W_{2, \rho}) \cdot v \cdot n \; dL^2
\]

\[
= \sum_j \int_{\bigcup_r \gamma^j_r} m^j_r \cdot \left( \rho \; J \; v \cdot W_{2, \rho} \cdot n^j_r \right) \; dL^1
\]

\[
- \sum_j \int_{(\partial P_t)_j} v \cdot (\nabla \Sigma (\rho \; J \; n_j \cdot W_{2, \rho}) - n_j \; (\rho \; J \; n_j \otimes W_{2, \rho} \cdot \nabla \Sigma n_j)) \; dL^2
\]

\[
+ \sum_j \int_{(\partial P_t)_j} (\rho \; J \; n_j \otimes n_j \; W_{2, \rho}) \cdot v \cdot n \; dL^2;
\] (32)

from now on the dependence upon \( z \) will be omitted if the meaning of the corresponding formulas will not be affected.

Because

\[
L^1 \left( \bigcup_r \gamma^j_r \right) = \sum_r L^1 \left( \gamma^j_r \right),
\] (33)

relation (31) yields

\[
\sum_j \int_{(\partial P_t)_j} (\text{div}_\Sigma (v \cdot n_j \cdot \nabla J \; \rho \; J) + v \cdot n_j \; (\rho \; J \; n_j \otimes W_{2, \rho} \cdot \nabla \Sigma n_j)) \; dL^2 =
\]

\[
= \sum_j \sum_r \int_{\gamma^j_r} m^j_r \cdot \left( \rho \; J \; v \cdot \nabla \tilde{J} \cdot n^j_r \right) \; dL^1,
\] (34)

In order to explicitly evaluate (34), it is worth noting that each \( \gamma^j_r \in \bigcup_j \partial(\partial P_t)_j \) may be traced twice.

Indeed, for a given surface \( \partial(\partial P_t)_k \) and for a given arch \( \gamma^h_r \subseteq \partial(\partial P_t)_k \), such that \( L^2 (\partial(\partial P_t)_k) < \infty \) and \( L^1 (\gamma^h_r) < \infty \), there exists a "neighboring" surface \( \partial(\partial P_t)_k \) such that we also have \( \gamma^h_r \subseteq \partial(\partial P_t)_k \).

Henceforth, suppose for instance that the arch \( \gamma^h_r \) is traced, say, counterclockwise whenever the line integral on \( \partial(\partial P_t)_k \), the perimeter of \( \partial(\partial P_t)_k \), is evaluated; then the (oriented) measure of any "small" traced arch at \( z \in \gamma^h_r \) is \( \tau_r(z) \; dL^1 \), where \( \tau_r(z) \) is the unit tangent vector at such \( z \).

Furthermore the same arch \( \gamma^h_r \) turns out to be traced clockwise whenever the line integral over \( \partial(\partial P_t)_k \), the perimeter of \( \partial(\partial P_t)_k \), is computed. In the latter case the (oriented) measure of any "small" traced arch at \( z \in \gamma^h_r \subseteq \partial(\partial P_t)_k \) is instead \( - \tau_r(z) \; dL^1 \); here we may set
\[ m^-(z) := m^k_r = n^k_r \wedge (-\tau_r(z)) \]  
\[ n^-(z) := n^k_r. \]  
(35)

In the former case we have,

\[ m^+(z) := m^h_r = n^h_r \wedge \tau_r(z) \]  
\[ n^+(z) := n^h_r. \]  
(37)

For such \( z \) we then have \( n^+(z) \neq n^-(z) \), so that the normal field \( n : \partial P_t \to \mathbb{R}^3, |n| = 1 \) does jump\(^2\). We recall that the jump set of the normal field introduced in (3) is denoted by \( J_n \) and verifies (9).

It is now convenient to introduce the following set

\[ \Gamma_t(P_t) := \bigcup_j \partial \partial P_t j = \bigcup_j \gamma^j_t \]  
(39)

and label the \( s^{th} \) element of such a set as \( \gamma_s(t) \). Obviously such \( \gamma_s(t) \) coincides one of the \( \gamma^j_t \in \bigcup_j \partial \partial P_t j \); nevertheless, the advantage here is that there is no need to keep track of the particular \( \partial \partial P_t j \) from which the arch \( \gamma_s(t) \) was generated\(^3\).

It is worth noting that \( J_n \subseteq \Gamma_t(P_t) \); whenever \( J_n \subset \Gamma_t(P_t) \) the domain of integration of the term on the right-hand side of (34) may be partitioned as

\[ \Gamma_t(P_t) = J_n \cup (\Gamma_t(P_t)/J_n). \]

Non-zero contribution to the right-hand side of (34) is obtained whenever jumps in either both fields \( n, n \cdot W, 2 \) or \( n \) alone occur\(^4\); we denote the corresponding jump set with \( J_{\{n, W, 2\}} \). If this is the case, the refinement of the partition of the domain of integration of the term on the right-hand side of (34) turns out to be as follows:

\[ \Gamma_t(P_t) = J_{\{n, W, 2\}} \cup \Gamma_t(P_t)/(J_n \cup J_{W, 2}), \]

where

\[ J_{\{n, W, 2\}} := (J_n \cap J_{W, 2}) \cup (J_n/J_n \cap J_{W, 2}) \cup (J_{W, 2}/J_n \cap J_{W, 2})). \]

\(^2\) One could actually evaluate the jump between normals to two adjacent neighboring surfaces by specializing (5, 6, 8), i.e. \( J\left( n(z) \right) \left| n^+ := (n^+(z) - n^-(z)) \otimes n^+(z), \right. \)
\( J\left( n(z) \right) \left| n^- := (n^-(z) - n^+(z)) \otimes n^-(z) \right. \) and \( J\left( n(z) \right) \left| n^+ := t \cdot J\left( n(z) \right) \right. \)
\( 1 - n^+(z) \cdot n^-(z) = |J\left( n(z) \right)|^2. \)

\(^3\) This arch is generated by \( \partial \partial P_t j \) through its boundary \( \partial \partial \partial P_t j \).

\(^4\) Another case may be whenever the referential density field is assumed to be discontinuous, which is not the case in this treatment.
We note that
\[ J_{\{n,W,2\}} = \bigcup_s \gamma_s(t), \]
where \( \mathcal{L}^1(\gamma_s(t)) < \infty \).

Hence, the right-hand side of (34) takes the form:

\[
\sum_j \sum_r \int_{\gamma_j^r} m_j^r(z) \cdot \left( \rho(z) \tilde{J}(z) \, v(z) \, W_{2}(z) \cdot n_j^r(z) \right) d\mathcal{L}^1(z) \\
= \int_{\bigcup_s \gamma_s(t)} \int_s \left( \rho(z) \tilde{J}(z) \, m(z) \cdot v(z) \, W_{2}(z) \cdot n(z) \right) d\mathcal{L}^1(z); \quad (40)
\]

here
\[ z = \hat{z}(s), \quad s \in [0, \mathcal{L}_1(\gamma_{1/2}^r)] \]
denotes the parametric equation of the arch \( \gamma_{1/2}^r \) traced counterclockwise, i.e. the parametric equation of \( \gamma_s(t) \), and the quantity
\[ \int_s (\circ) := (\circ)^+ - (\circ)^- \]
denotes the jump of \( \circ \) across \( \gamma_s(t) \) where, analogy with the notation introduced above, \((\circ)^\pm\) denote the traces\(^5\) of the field \( \circ \) on each of the two sides of \( \gamma_s(t) \).

Thus, from (40) we get:

\[
\sum_j \sum_r \int_{\gamma_j^r} m_j^r(z) \cdot \left( \rho(z) \tilde{J}(z) \, v(z) \, W_{2}(z) \cdot n_j^r(z) \right) d\mathcal{L}^1(z) \\
= \int_{\bigcup_s \gamma_s(t)} \int_s \left( \rho(z) \tilde{J}(z) \, m(z) \otimes n(z) \, W_{2}(z) \cdot v(z) \right) d\mathcal{L}^1(z). \quad (41)
\]

We may summarize (34, 41) to saying that

\[
\sum_j \int_{(\partial \mathcal{D}_j)} \left( \text{div}_\Sigma (v \cdot n_j \cdot \nabla J \rho J) + v \cdot n_j (\rho J n_j \otimes W_{2} \cdot \nabla \Sigma n_j) \right) d\mathcal{L}^2 = \\
= \left\{ \begin{array}{ll}
0 & \text{if } \mathcal{L}^1 \left( J_{\{n,W,2\}} \right) = 0, \\
\int_{\bigcup_s \gamma_s(t)} \int_s (\rho J m \otimes n W_{2} \cdot v) \ d\mathcal{L}^1 & \text{if } \mathcal{L}^1 \left( J_{\{n,W,2\}} \right) \neq 0.
\end{array} \right. \quad (42)
\]

\(^5\) Indeed, because \( \gamma_{1/2}^r = \gamma_s(t) \) is traced both counterclockwise and clockwise in the sum (40) the integrand of the right-hand side in it effectively becomes \( \rho_0 v \cdot (m^+ (n^+ \cdot W_{2}) - m^- (n^- \cdot W_{2})) \).
Since
\[ L^1 \left( J_{\{n,W_2\}} \right) = L^1 \left( \bigcup_s \gamma_s(t) \right) = \sum_s L^1 \left( \gamma_s(t) \right), \tag{43} \]
we have
\[ \int_{\bigcup_s \gamma_s(t)} \int_s (\rho J n \otimes n W_2 \cdot v) \, dL^1 = \sum_s \int_{\gamma_s(t)} \int_s (\rho J n \otimes n W_2 \cdot v) \, dL^1 \]
and if we set:
\[ \left\langle \int_{\bigcup_s \gamma_s(t)} \int_s (\rho J n \otimes n W_2 \cdot v) \, dL^1 \right\rangle := \begin{cases} 0 & \text{if } \sum_s L^1 (\gamma_s(t)) = 0, \\ \sum_s \int_{\gamma_s(t)} \int_s (\rho J n \otimes n W_2 \cdot v) \, dL^1 & \text{if } \sum_s L^1 (\gamma_s(t)) \neq 0, \end{cases} \tag{44} \]
and
\[ \sum_j \int_{(\partial \Omega) j} \left( \text{div}_\Sigma (v n_j \cdot \nabla J \rho J) + v \cdot n_j (\rho J n_j \otimes W_2 \cdot \nabla \Sigma n_j) \right) \, dL^2 = \left\langle \int_{\bigcup_s \gamma_s(t)} \int_s (\rho J n \otimes n W_2 \cdot v) \, dL^1 \right\rangle. \tag{45} \]
Now, (29) in (22) yields:
\[ \frac{d}{dt} \mathcal{E}(P_t) = \sum_j \int_{(P_t) j} \rho J \left[ (W_{1} - \text{div}(\rho W_{2})) I - \frac{\nabla J \otimes W_{2}}{J} \right] \cdot \nabla v \, dL^3 \\
- \sum_j \int_{(\partial \Omega) j} v \cdot (\nabla \Sigma (\rho J n_j \otimes W_2) - n_j (\rho J n_j \otimes W_2 \cdot \nabla \Sigma n_j)) \, dL^2 \\
+ \sum_j \int_{(\partial \Omega) j} (\rho J n_j \otimes n_j W_2) \cdot v_n \, dL^2 \\
+ \left\langle \int_{\bigcup_s \gamma_s(t)} \int_s (\rho J n \otimes n W_2 \cdot v) \, dL^1 \right\rangle. \tag{46} \]

### 3.2 Power and its partition

We are now in the position to state and explore the Second Law of Thermodynamics by (i) assuming a partition of the power and (ii) applying the Coleman and Noll’s procedure.
The Second Law reads as follows:

$$\frac{d}{dt} E(P_t) \leq P(P_t), \quad (47)$$

where $P(P_t)$ is the power expended by the mechanical agents external to the part $P_t$: it is worth recalling that $P_t = \bigcup_j (P_t)_j$.

In the absence of body forces, the working done by those agents is here assumed to be done through the boundary $\partial P_t = \bigcup_j (\partial P_t)_j$: this obviously does also include $J_{(n, \omega, 2)} = \bigcup_s \gamma_s(t)$.

In particular, the structure of the rate of change of energy (22) and relations (24, 29, 34, 45, 44) suggest that the mechanical agents performing power may be the following:

1. The traction $t(x, t; n) := T(x, t)n(x, t)$, $x \in \bigcup_j (\partial P_t)_j$, which exerts power against the velocity $v(x, t)$, $x \in \bigcup_j (\partial P_t)_j$;

2. The "surface traction" $T(x, t)$, $x \in \bigcup_j (\partial P_t)_j$ at the boundary of the part $P_t$, which exert power against $J|_{\partial P_t}$, the (trace of) the rate of change of $J$ at the boundary of $P_t$.

The term (ii) may be view as the interstitial working in the sense of [DS], explained also in [DeSep1]. Roughly speaking, since mass continuity holds (see e.g. (14)) this working may be viewed as the power expended by the surface traction against the rate of change of (surface) mass density.

Hence, the power is chosen to have the following form:

$$P(P_t) := P^t(\partial P_t) + P^T(\partial P_t) \quad (48)$$

where, by (39), $\Gamma_t(P_t) := \bigcup_j \partial (\partial P_t)_j$.

Here

$$P^t(P_t) := \sum_j \int_{(\partial P_t)_j} Tn \cdot v d\mathcal{L}^2 \quad (49)$$

$$P^T(P_t) := \sum_j \int_{(\partial P_t)_j} T \cdot J d\mathcal{L}^2 = \sum_j \int_{(\partial P_t)_j} J^T \div v d\mathcal{L}^2 \quad (50)$$

It is worth noting that the choice (49) implies that at each boundary $(\partial P_t)_j$ there is a hydrostatic field $\mathbf{T}^I$ expending power against the velocity gradient.

---

6 A possible alternative might be to assume that the configurational fields acting in the bulk may contribute to the expenditure of the power.
ent. Hence, recalling (28), each term on the right-hand side of (49) may be rewritten as follows:

\[
\int_{\partial P_l} J T I \cdot \nabla v \, d\mathcal{L}^2 = \int_{\partial P_l} J T (I \Sigma + n_j \otimes n_j) \cdot \nabla v \, d\mathcal{L}^2
\]

\[\begin{align*}
= & \int_{\partial P_l} J T I \Sigma \cdot \nabla \Sigma v \, d\mathcal{L}^2 \\
+ & \int_{\partial P_l} J T n_j \cdot v \cdot n \, d\mathcal{L}^2.
\end{align*}\]

(51)

(52)

This present form of external power appears to be only apparently inconsistent with the form deduced in [PPG] equation (4.2) restricted to a second order non-simple material. In particular, besides (49), which is present in the equation just mentioned, the second term is fully consistent with such relation, whereas neither line contact terms explicitly appear in (48) nor surface interactions exerting power against the surface gradient of the velocity are present in [PPG]-(4.2).

In the sequel this apparent inconsistency will be automatically reconciled.

Indeed, putting the terms (51, 52) back together, steps analog to the ones allowing for the transformation of (42) (appearing in (29) in 45) yield:

\[
\sum_j \int_{\partial P_l} J T \, div v \, d\mathcal{L}^2 =
\]

\[\begin{align*}
= & -\sum_j \int_{\partial P_l} v \cdot (\nabla \Sigma (J T) - n_j (I \cdot \nabla \Sigma n_j) T J) \, d\mathcal{L}^2 + \\
+ & \sum_j \int_{\partial P_l} J T n_j \cdot v \cdot n \, d\mathcal{L}^2 + \\
+ & \left\langle \int_{\bigcup_s \gamma_s(t)} (v \cdot m) J T \, d\mathcal{L}^1 \right\rangle.
\end{align*}\]

(53)

It clearly appears that surface term expending power against the trace of the velocity at points in the given \((\partial P_l)_j\) is consistent with the second item in [PPG]-4(5)^7. Moreover, line terms, i.e. the third integral on the right-hand side of (53), do automatically arise and this is because of the apparently inconsistent term (51). Here we then see that line forces spontaneously arise thanks to the traces of the surface traction field on line boundaries between surfaces in which either geometrically discontinuities are present or the surface traction field itself does jump.

\[\footnote{It is worth noting that this term matters whenever the surface-like boundaries are not flat} \]
Henceforth, we shall see that discontinuous line forces come from the expected discontinuity of the surface traction fields across line boundaries between surface zones in which either geometric discontinuities are present, i.e. \( n \) jumps, or material properties do abruptly change across such line boundaries.

### 3.3 Thermodynamic Restrictions

Gauss-Green formula applied to the integral in (49) yields

\[
P^t(P) = \sum_j \int_{(P_t)_j} \text{div}(T \cdot v) \, d\mathcal{L}^3 = \sum_j \int_{(P_t)_j} (v \cdot \text{div}T + T \cdot \nabla v) d\mathcal{L}^3,
\]

(54)

Now, relations (29, 30, 45, 44, 48, 49, 50, 50) and (54) into inequality (22) imply:

\[
\sum_j \int_{(P_t)_j} \rho J \left[ (W_{i1} - \text{div}(\rho W_{i2})) \right] \cdot \nabla \mathbf{v} \, d\mathcal{L}^3 + \\
- \sum_j \int_{\partial(P_t)_j} \mathbf{v} \cdot (\nabla \Sigma (\rho J \cdot n_j \cdot W_{i2}) - n_j (\rho J n_j \otimes W_{i2} \cdot \nabla n_j)) \, d\mathcal{L}^2 + \\
+ \sum_j \int_{\partial(P_t)_j} (\rho J n_j \otimes n_j W_{i2}) \cdot v \cdot n \, d\mathcal{L}^2 + \\
+ \left\langle \int_{\bigcup_{s(t)}} (\rho J m \otimes n W_{i2} \cdot v) \, d\mathcal{L}^1 \right\rangle \leq \\
\leq \sum_j \int_{(P_t)_j} (v \cdot \text{div}T + T \cdot \nabla v) \, d\mathcal{L}^3 + \\
- \sum_j \int_{\partial(P_t)_j} \mathbf{v} \cdot (\nabla \Sigma (J T) - n_j (I \cdot \nabla \Sigma n_j) T J) \, d\mathcal{L}^2 + \\
+ \sum_j \int_{\partial(P_t)_j} J T n_j \cdot v \cdot n \, d\mathcal{L}^2 + \\
+ \left\langle \int_{\bigcup_{s(t)}} (\mathbf{v} \cdot m J T) \, d\mathcal{L}^1 \right\rangle
\]

(55)

Localization of this inequality and Coleman-Noll’s procedure lead to the conclusions summarized as follows:

**i.1** for the test function \( v \) in \((P_t)_j\) we obtain

\[
\text{div}T = 0;
\]

**i.2** for the test function

\[
v^{n_j} := (I - n_j \otimes n_j)v
\]
in \((\partial P_t)_j\) we obtain
\[ T = \rho W_{i2} \cdot n; \]
i.3 for the test function \(W\) in \((P_t)_j\)we obtain
\[ \text{skw} \{ \rho \nabla J \otimes W \} = 0; \]
i.4 for the test function \(D\) in \((P_t)_j\)we obtain
\[ T = \rho J \left[ (W_{i1} - \text{div}(\rho W_{i2})) I - \frac{\text{sym}(\nabla J \otimes W \cdot J)}{J} \right], \]
where
\[ D := \text{sym} \nabla v \]
\[ W := \text{skw} \nabla v \]
denote the local stretching and the spin respectively.

The terms left out from the analysis come from the line integrals on set \(\gamma_s(t)\), i.e.
\[ \left\langle \int_{\gamma_s(t)} (\mathbf{m} T - \rho J \mathbf{m} \otimes n W_{i2} \cdot v) \ d\mathcal{L}^1 \right\rangle \geq 0. \tag{56} \]
which involves the trace \(v|_{\gamma_s(t)}\) of the test function.

In the relation above, the only components of the trace of the test function arising from each side, here labelled as \((\partial P_t)^+\) and \((\partial P_t)^-\) (sharing the given point on \(\gamma_s(t)\)) are \(v^\pm|_{\gamma_s(t)} := v|_{\gamma_s(t)} \cdot m^\pm \equiv (I - \tau \otimes \tau) v|_{\gamma_s(t)} \cdot m^\pm\), where \(m^\pm := n^\pm \wedge \tau\).

Test functions are smooth, and so continuous in the given domain; their trace on the boundary of a given domain may also be smooth. One way to localize (56) is to choose a narrow bump function, e.g. a mollifier, say \(z \mapsto \exp\left(-\frac{|z-x|^2}{\varepsilon^2}\right)^{m^+ + m^-}, z \in \gamma_s(t),\) centered at a point \(x\) of a given arch on \(\gamma_s(t)\). Whenever \(\varepsilon \to 0\), the integral on \(\gamma_s(t)\) in (55) localizes as follows:
\[ \int_{\gamma_s(t)} (J (T - \rho W_{i2} \cdot n)) v|_{\gamma_s(t)} = 0, \tag{57} \]
where \(v^+ = v^- =: v|_{\gamma_s(t)}\) is arbitrary and \(o|_{\gamma_s(t)}\) denotes the trace of \(o\) on \(\gamma_s(t)\).

Henceforth, the quantity
\[ J|_{\gamma_s(t)} (T|_{\gamma_s(t)} \]
must be discontinuous across \(\gamma_s(t)\).
Furthermore, such a discontinuity may be explicitly evaluated through the equation:

\[ \int_s (J \mathcal{T}) |_{\gamma_s(t)} = \int_s (\rho J W_2 \cdot \mathbf{n}) |_{\gamma_s(t)}. \]  

(58)

It is worth noting that whenever the trace of \( J \) across the given line boundary \( \gamma_s(t) \) does not jump, relation (i.3) is obtainable by computing the jump of the trace of the surface tension \( J \mathcal{T} \), constitutively determined by (i.2). This confirms the conjecture announced at the end of the previous subsection.

The field \( \mathcal{T} \), whose constitutive equation is given by (i.2), has the meaning of a surface traction: this may be relevant at the boundary whenever \( |W_2 \cdot \mathbf{n}| \) may be large. For example, if a Cahn-Hilliard energy is assumed [CH], [DH], i.e. if

\[ W(J, \nabla J) = \bar{W}(J) + \varepsilon |\nabla J|^2, \]

we have \( |W_2 \cdot \mathbf{n}| = |\varepsilon \nabla J \cdot \mathbf{n}| \). It may be inferred, by (14), that this term would be relevant wherever the normal component of the density gradient at a point on the boundary in a given phase becomes meaningful.

More generally, even in the presence of jumps in \( J \), the quantity \( \int_s (J \mathcal{T} \mathbf{m}) \) represents the jump of the "edge interstitial tractions", say

\[ J_{\bar{h}} \mathbf{m}_{\bar{h}} \mathcal{T}_{\bar{h}} - J_{\bar{k}} \mathbf{m}_{\bar{k}} \mathcal{T}_{\bar{k}}, \]

where the indexes \( \bar{h} \) and \( \bar{k} \) label the two neighboring sides of the given point in \( \gamma_s(t) \in J_{(\mathbf{n},W_2)} \subseteq \Gamma_t \), and \( \mathbf{m}_{\bar{h}} := \mathbf{n}_{\bar{h}} \wedge \tau, \mathbf{m}_{\bar{k}} := \mathbf{n}_{\bar{k}} \wedge \tau \) to \( \gamma_s(t) \), where \( \mathbf{n}_{\bar{h}}, \mathbf{n}_{\bar{k}} \) denote the traces of the normals to \( \partial(P_{\bar{h}}), \partial(P_{\bar{k}}) \) at a point of the common boundary \( \gamma_s(t) \).

Furthermore, the tangential vector field

\[ \tau \int_s (J \mathcal{T}) |_{\gamma_s(t)} = \tau \left( J_{\bar{h}} \mathcal{T}_{\bar{h}} - J_{\bar{k}} \mathcal{T}_{\bar{k}} \right) \]

resulting from (58) may resemble the so called line tension at \( \gamma_s(t) \): in this present formulation line tensions do not explicitly enter the Second Law of Thermodynamics, although they may be calculated as above. Such a field seem to have a great importance when it comes to considering the various shapes that Giant Unilamellar Vesicles do exhibit [Z].

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