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On the Correspondence Between Stored Energy Function and Helmholtz Free Energy Function of Granular Materials

Chung Fang

Institute of Mechanics, AG3,
Darmstadt University of Technology,
Hochschulstr. 1, 64289 Darmstadt, Germany

Abstract: Goodman and Cowin proposed a continuum theory of a dry cohesionless granular material in which the solid volume fraction ν is treated as an independent kinematical field. With their theory the most important phenomenon of granular materials, dilatancy, can well be simulated. The key point of their theory lies in the postulation of the balance of equilibrated force, which is a balance equation proposed for the evolution of ν. In derivation of this equation the existence of the stored energy function ϕ and its specific functional dependence have been assumed, and a variational analysis for ϕ is performed. In the current paper a complete thermodynamic analysis based upon Müller-Liu approach will be given, and the results show that the stored energy function ϕ corresponds to the Helmholtz free energy function Ψ in thermodynamic equilibrium under isothermal condition, which in turn, indicates that the specification of the functional dependence of ϕ in the derivation of the balance of equilibrated force is reasonable.

Keywords: Goodman-Cowin theory; stored energy function; Helmholtz free energy function; granular materials.

1. Introduction

Granular materials are collections of a large number of discrete solid particles with interstices filled with a fluid or a gas. Many theories have been developed to describe the behaviour of flowing granular materials from approaches of molecular dynamics, statistical mechanics or continuum mechanics. The so-called Goodman-Cowin theory is one of the theories based upon continuum mechanics approach, and it has been shown that with this theory the most important phenomenon, dilatancy, can well be simulated (see Goodman and Cowin [5, 6, 7], Wang and Hutter [22]). The most significant point of their theory lies in the postulation of a balance equation, called the balance of equilibrated force, for volume fraction ν, in which the second time derivative of ν is included. Recently, Fang [4] has given a detailed comment on this theory and shown that there exists some logical inconsistency in the derivation of the balance of equilibrated force, and this equation can be physically corrected by a simple dimensional analysis. From his study the modified Goodman-Cowin theory is obtained. A complete thermodynamic analysis has also been performed for the constitutive restrictions of the constitutive variables of the modified theory.

The original derivation of the balance of equilibrated force is based upon a variational

Corresponding e-mail: fang@mechanik.tu-darmstadt.de *Accepted for Publication: Dec. 25, 2003*

analysis (see Cowin and Goodman [3])[a]. In the derivation the existence of the stored energy function ϕ is assumed and its functional dependence in equilibrium is specified, namely, $\phi = \phi(\gamma, \nu, \text{grad}\nu)$, where γ denotes the true mass density of grains. Granular materials are discrete in nature, and due to the different arrangement of grains some kind of energy associated with the distribution of grains should exist in a granular body. Accordingly, in certain sense granular materials can be treated as ordered materials, and the concept of stored energy function ϕ, used by Green & Rivlin [8], Leslie [11], Mindlin [15] and Toupin [19, 20] for their theories of elastic materials, can be equally applied for granular materials. In fact, the counterpart of the stored energy function ϕ used in mechanics is simply the Helmholtz free energy function Ψ used in thermodynamics, and Valanis [21] has indicated that ϕ corresponds to Ψ in thermodynamic equilibrium under isothermal condition, but without any theoretical evidence. However, since the postulated functional dependence of ϕ affects strongly the form of the resulted balance equation of equilibrated force, there remains a question why only γ, ν, gradν are proposed as the independent arguments of the functional dependence of ϕ.

We recall that in the scope of rational thermodynamics the entropy principle is so applied, that the restrictions of constitutive quantities can be obtained[b]. In the current paper a complete thermodynamic analysis based upon Müller-Liu approach is applied to exploitate the entropy inequality[c]. By assuming the Helmholtz free energy Ψ as a constitutive variable, its functional dependence in thermodynamic equilibrium can be identified, which indicates that the stored energy function ϕ corresponds to the Helmholtz free energy Ψ in thermodynamic equilibrium under isothermal condition, and in turn shows that the postulation of $\phi = \phi(\gamma, \nu, \text{grad}\nu)$ is reasonable and enough for the derivation of the balance of equilibrated force.

2. Thermodynamic processes

2.1. Balance equations

Following the original Goodman-Cowin theory the balance equations are given by

- Balance of mass $$(\gamma\nu)^{\cdot} + \gamma\nu \,\text{div}\, \mathbf{v} = 0, \tag{1}$$
- Balance of linear momentum $$\gamma\nu\, \dot{\mathbf{v}} = \text{div}\, \mathbf{t} + \gamma\nu\, \mathbf{b}, \tag{2}$$
- Balance of angular momentum $$\mathbf{t} = \mathbf{t}^{T}, \tag{3}$$
- Balance of equilibrated force $$\gamma\nu\alpha\ddot{\nu} = \text{div}\, \mathbf{h} + \gamma\nu f, \tag{4}$$
- Balance of internal energy $$\gamma\nu\dot{e} = \mathbf{t}\cdot\mathbf{D} + \mathbf{h}\cdot\text{grad}\dot{\nu} - \gamma\nu f\dot{\nu} - \text{div}\mathbf{q} + \gamma\nu r, \tag{5}$$

where γ, $\mathbf{v}$, $\mathbf{t}$, $\mathbf{b}$, α, $\mathbf{h}$, f, e, $\mathbf{D}$, $\mathbf{q}$ and r are the true mass density of grains, velocity, stress tensor, external body force, equilibrated inertia, equilibrated stress vector, equilibrated intrinsic body force, specific internal energy, stretching tensor, heat flux and external energy supply, respectively. Here $(\bullet)^{\cdot}$ denotes the time rate of change of $(\bullet)$ and equals to $\partial(\bullet)/\partial t + \text{grad}(\bullet)\cdot\mathbf{v}$. The balance Eq. (1), Eqs.

(2)-(3) are analogous to the classical balance equations of mass, linear momentum and angular momentum. The balance of equilibrated force is assumed in this simplest form (4) accordingly to Goodman and Cowin [5], and no equilibrated external body force is included since volume fraction ν is an internal variable. The balance of internal energy (5) differs from the traditional statement by the occurrence of the power terms associated with $\dot{\nu}$. Eqs. (1)-(2), Eqs. (4)-(5) should be considered as constraints via Lagrange multipliers in the exploitation of the entropy inequality, while Eq. (4) can be direct achieved by assuming the constitutive class, and the entropy inequality is then investigated to identify the constitutive responses of a granular material, and especially in the current paper, the constitutive response of the free energy Ψ.

2.2. Entropy inequality

There is an additive quantity, the entropy, with specific density η, flux $\mathbf{\Phi}$, supply s and production π, for which we may write an equation of balance in the form

$$\pi = \gamma\nu\dot{\eta} + \mathrm{div}\mathbf{\Phi} - \gamma\nu s. \tag{6}$$

The entropy principle states that the entropy production π is non-negative in all thermodynamic processes, and so the entropy inequality must hold:

$$\gamma\nu\dot{\eta} + \mathrm{div}\mathbf{\Phi} - \gamma\nu s = \pi \geq 0. \tag{7}$$

$$\begin{aligned}\pi = {}& \gamma\nu\dot{\eta} + \mathrm{div}\mathbf{\Phi} - \gamma\nu s - \lambda^{\gamma}(\dot{\gamma}\nu + \gamma\dot{\nu} + \gamma\nu\,\mathrm{div}\mathbf{v}) - \boldsymbol{\lambda}^{\mathbf{v}}\cdot(\gamma\nu\dot{\mathbf{v}} - \mathrm{div}\mathbf{t} - \gamma\nu\mathbf{b}) \\ & - \lambda^{\nu}(\gamma\nu\alpha\ddot{\nu} - \mathrm{div}\mathbf{h} - \gamma\nu f) - \lambda^{e}(\gamma\nu\dot{e} - \mathbf{t}\cdot\mathbf{D} + \mathrm{div}\mathbf{q} - \gamma\nu r - \mathbf{h}\cdot\mathrm{grad}\dot{\nu} + \gamma\nu f\dot{\nu}) \geq 0,\end{aligned} \tag{8}$$

Any process, which satisfies (7), represents a so-called admissible process. Such a process, however, must in addition satisfy the balance Eqs. (1)-(2), Eqs. (4)-(5). Liu [12, 13] has shown that one can account for these balance equations in the entropy inequality (7) by employing Lagrange multipliers as follows and satisfying this new inequality for all (unrestricted) fields. Explicitly, the balance equations appear as constraints on the class of physically-realizable processes, where λ^{γ}, $\boldsymbol{\lambda}^{\mathbf{v}}$, λ^{ν} and λ^{e} represent the corresponding Lagrange multipliers.

Introducing the free energy

$$\Psi = e - \theta\eta, \tag{9}$$

and introducing the assumption $\lambda^{e} = 1/\theta$ **d** , where θ is the empirical temperature, and substituting them into (8) yields for the entropy inequality in the for

$$\begin{aligned}\pi = {}& \frac{\gamma\nu}{\theta}(\dot{e} - \dot{\theta}\eta - \dot{\Psi}) + \mathrm{div}\mathbf{\Phi} - \gamma\nu s - \lambda^{\gamma}(\dot{\gamma}\nu + \gamma\dot{\nu} + \gamma\nu\,\mathrm{div}\mathbf{v}) - \boldsymbol{\lambda}^{\mathbf{v}}\cdot(\gamma\nu\dot{\mathbf{v}} - \mathrm{div}\mathbf{t} - \gamma\nu\mathbf{b}) \\ & - \lambda^{\nu}(\gamma\nu\alpha\ddot{\nu} - \mathrm{div}\mathbf{h} - \gamma\nu f) - \frac{1}{\theta}(\gamma\nu\dot{e} - \mathbf{t}\cdot\mathbf{D} + \mathrm{div}\mathbf{q} - \gamma\nu r - \mathbf{h}\cdot\mathrm{grad}\dot{\nu} + \gamma\nu f\dot{\nu}) \geq 0.\end{aligned} \tag{10}$$

In deducing it, we assume that the material behaviour is independent of the supplies; so the sum of all external source terms in (10) must vanish, implying that

$$-\gamma\nu s + \boldsymbol{\lambda}^{\mathbf{v}}\cdot\gamma\nu\mathbf{b} + \frac{\gamma\nu}{\theta}r = 0, \tag{11}$$

which serves as an equation determining the entropy supply in terms of other supply terms and is more general than the classical selection via the contribution of **b**. The entropy and its flux as well as the Lagrange multipliers must be considered as auxiliary quantities. Entropy inequality (10) will be used to investigate the constitutive postulates in the next subsection.

2.3. Constitutive assumptions and restrictions

Based upon Wang & Hutter's [22] postulation of the constitutive responses of a granular body, the constitutive class

$$C = \hat{C}(\nu_0, \nu, grad\ \nu, \dot{\nu}, \gamma_0, \gamma, grad\ \gamma, \dot{\gamma}, \theta, grad\ \theta, \mathbf{v}, \mathrm{grad}\ \mathbf{v}) \tag{12}$$

is proposed for the material quantities

$$\mathrm{C} = \{\Psi, \eta, \mathbf{t}, \mathbf{h}, \mathrm{f}, \mathbf{q}, \mathbf{\Phi}\}. \tag{13}$$

It is noted that the constitutive class (12) is the most general one for a dry cohesionless granular material since for the true mass density of grains γ, its value of a reference configuration γ_0, its gradient and its time rate of change are additionally considered as independent arguments. Invoking the principle of material objectivity expression (12) reduces to

$$\mathrm{C} = \hat{\mathrm{C}}(\nu_0, \nu, \mathrm{grad}\ \nu, \dot{\nu}, \gamma_0, \gamma, \mathrm{grad}\ \gamma, \dot{\gamma}, \theta, \mathrm{grad}\ \theta, \mathbf{D}), \tag{14}$$

with which the requirement of the balance of angular momentum is automatically satisfied.

If the functional dependence of Ψ, $\mathbf{t}$, $\mathbf{h}$, $\mathbf{q}$ and $\mathbf{\Phi}$ in (13) is incorporated into the entropy inequality (10) by use of the chain rule of differentiation and using the identities

$$\begin{aligned}(\mathrm{grad}\nu)^{\cdot} &= \mathrm{grad}\dot{\nu} - (\mathrm{grad}\nu)(\mathrm{grad}\mathbf{v}),\\ (\mathrm{grad}\gamma)^{\cdot} &= \mathrm{grad}\dot{\gamma} - (\mathrm{grad}\gamma)(\mathrm{grad}\mathbf{v}),\end{aligned} \tag{15}$$

then the entropy inequality (10) become

$$\begin{aligned}
\pi = {} & \left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\nu} - \lambda^{\gamma}\gamma - \frac{\gamma\nu}{\theta}\mathrm{f}\right\}\dot{\nu} + \left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\dot{\nu}} - \lambda^{\nu}\gamma\nu\alpha\right\}\ddot{\nu} + \left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\gamma} - \lambda^{\gamma}\nu\right\}\dot{\gamma} + \left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\dot{\gamma}}\right\}\ddot{\gamma}\\
& + \left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\theta} - \frac{\gamma\nu}{\theta}\eta\right\}\dot{\theta} + \left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\,\mathrm{grad}\ \theta}\right\}\cdot(\mathrm{grad}\ \theta)^{\cdot} + \left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\mathbf{D}}\right\}\cdot\dot{\mathbf{D}}\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\nu_0} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\nu_0} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\nu_0} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\nu_0}\right\}\cdot(\mathrm{grad}\ \nu_0)\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\gamma_0} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\gamma_0} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\gamma_0} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\gamma_0}\right\}\cdot(\mathrm{grad}\ \gamma_0)\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\nu} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\nu} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\nu} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\nu}\right\}\cdot(\mathrm{grad}\ \nu) + \left\{\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\,\mathrm{grad}\ \nu}\otimes\mathrm{grad}\ \nu\right\}\cdot\mathrm{grad}\ \mathbf{v}\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\gamma} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\gamma} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\gamma} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\gamma}\right\}\cdot(\mathrm{grad}\ \gamma) + \left\{\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\,\mathrm{grad}\ \gamma}\otimes\mathrm{grad}\ \gamma\right\}\cdot\mathrm{grad}\ \mathbf{v}\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\dot{\nu}} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\dot{\nu}} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\dot{\nu}} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\dot{\nu}} + \frac{1}{\theta}\mathbf{h} - \frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\,\mathrm{grad}\ \nu}\right\}\cdot(\mathrm{grad}\ \dot{\nu})\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\dot{\gamma}} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\dot{\gamma}} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\dot{\nu}} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\dot{\gamma}} - \frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\,\mathrm{grad}\ \gamma}\right\}\cdot(\mathrm{grad}\ \dot{\gamma})\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\,\mathrm{grad}\ \nu} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\,\mathrm{grad}\ \nu} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\,\mathrm{grad}\ \nu} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\,\mathrm{grad}\ \nu}\right\}\cdot\mathrm{grad}\ (\mathrm{grad}\ \nu)\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\,\mathrm{grad}\ \gamma} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\,\mathrm{grad}\ \gamma} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\,\mathrm{grad}\ \gamma} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\,\mathrm{grad}\ \gamma}\right\}\cdot\mathrm{grad}\ (\mathrm{grad}\ \gamma)\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\,\mathrm{grad}\ \theta} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\,\mathrm{grad}\ \theta} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\,\mathrm{grad}\ \theta} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\,\mathrm{grad}\ \theta}\right\}\cdot\mathrm{grad}\ (\mathrm{grad}\ \theta)\\
& + \left\{\frac{\partial\mathbf{\Phi}}{\partial\theta} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\theta} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\theta} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\theta}\right\}\cdot(\mathrm{grad}\ \theta) + \left\{\frac{\partial\mathbf{\Phi}}{\partial\mathbf{D}} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\mathbf{t}}{\partial\mathbf{D}} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\mathbf{D}} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\mathbf{D}}\right\}\cdot(\mathrm{grad}\ \mathbf{D})\\
& - \lambda^{\gamma}\gamma\nu\ \mathrm{div}\ \mathbf{v} + \lambda^{\nu}\gamma\nu\ \mathrm{f} + \frac{1}{\theta}\mathbf{t}\cdot\mathbf{D} - \boldsymbol{\lambda}^{v}\cdot\gamma\nu\,\dot{\mathbf{v}} \geq 0.
\end{aligned} \tag{16}$$

Let $\mathbf{x}$ be given by $\mathbf{x} = \{\dot{\mathbf{v}}, \ddot{\nu}, \ddot{\gamma}, \dot{\theta}, (\mathrm{grad}\theta)^{\cdot}, \dot{\mathbf{D}}, \mathrm{grad}\nu_0, \mathrm{grad}\dot{\nu}, \mathrm{grad}(\mathrm{grad}\nu), \mathrm{grad}\gamma_0, \mathrm{grad}\dot{\gamma}, \mathrm{grad}(\mathrm{grad}\gamma), \mathrm{grad}(\mathrm{grad}\theta), \mathrm{grad}\mathbf{D}\}$. It is now straightforward to see that the inequality (16) has the form

$$\mathbf{a} \cdot \mathbf{x} + \mathrm{b} \geq 0, \tag{17}$$

where the vector $\mathbf{a}$ and the scalar b are functions of the variables listed in (14), but not of $\mathbf{x}$, and the vector $\mathbf{x}$ depends on time and space derivatives of these quantities. Accordingly (17) is linear in $\mathbf{x}$, and since these variables can take any values, it would be possible to violate (17) unless

$$\mathbf{a} = \mathbf{0} \quad \text{and} \quad \mathrm{b} \geq 0, \tag{18}$$

where $(18)_1$ leads to the so-called Liu identities and $(18)_2$ gives rise to the residual entropy inequality. Explicitly, the entropy inequality must hold for all independent variations of $\mathbf{x}$. These variables appear linearly in (16), and thus their coefficients must vanish. It then follows that the Lagrange multipliers $\boldsymbol{\lambda}^{v}$ and λ^{ν} are given by

$$\boldsymbol{\lambda}^{v} = \mathbf{0}, \qquad \lambda^{\nu} = -\frac{1}{\alpha\theta}\frac{\partial\Psi}{\partial\dot{\nu}}, \tag{19}$$

whilst the specific entropy density becomes

$$\eta = -\frac{\partial\Psi}{\partial\theta}. \tag{20}$$

Moreover, the free energy must obey the relations

$$\frac{\partial\Psi}{\partial\mathrm{grad}\theta} = \mathbf{0}, \qquad \frac{\partial\Psi}{\partial\mathbf{D}} = \mathbf{0}, \qquad \frac{\partial\Psi}{\partial\dot{\gamma}} = 0, \tag{21}$$

and the equilibrated stress vector $\mathbf{h}$ (with $\boldsymbol{\lambda}^{v} = \mathbf{0}$) obtains

$$\mathbf{h} = \gamma\nu\frac{\partial\Psi}{\partial\mathrm{grad}\nu} - \theta\left\{\frac{\partial\mathbf{\Phi}}{\partial\dot{\nu}} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\dot{\nu}} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\dot{\nu}}\right\}, \tag{22}$$

whilst the relations (with $\boldsymbol{\lambda}^{v} = \mathbf{0}$)

$$\frac{\partial\mathbf{\Phi}}{\partial\nu_0} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\nu_0} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\nu_0} = \mathbf{0}, \qquad \frac{\partial\mathbf{\Phi}}{\partial\gamma_0} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\gamma_0} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\gamma_0} = \mathbf{0}, \tag{23}$$

$$\frac{\partial\mathbf{\Phi}}{\partial\mathbf{D}} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\mathbf{D}} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\mathbf{D}} = \mathbf{0}, \qquad \frac{\partial\mathbf{\Phi}}{\partial\dot{\gamma}} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\dot{\gamma}} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\dot{\gamma}} = \frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\mathrm{grad}\,\gamma}, \tag{24}$$

$$\mathrm{sym}\left\{\frac{\partial\mathbf{\Phi}}{\partial\mathrm{grad}\,\nu} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\mathrm{grad}\,\nu} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\mathrm{grad}\,\nu}\right\} = \mathbf{0}, \tag{25}$$

$$\mathrm{sym}\left\{\frac{\partial\mathbf{\Phi}}{\partial\mathrm{grad}\,\theta} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\mathrm{grad}\,\theta} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\mathrm{grad}\,\theta}\right\} = \mathbf{0}, \tag{26}$$

$$\mathrm{sym}\left\{\frac{\partial\mathbf{\Phi}}{\partial\mathrm{grad}\,\gamma} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\mathrm{grad}\,\gamma} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\mathrm{grad}\,\gamma}\right\} = \mathbf{0}, \tag{27}$$

must hold among $\mathbf{\Phi}$, $\mathbf{h}$, $\mathbf{q}$, where sym{$\mathbf{A}$} denotes the symmetric part of a tensor $\mathbf{A}$. Eqs. (19)-(27) correspond to the condition $\mathbf{a} = \mathbf{0}$ in (18) and are known as Liu identities.

To simply the ensuring analysis, it is assumed here that the free energy Ψ is not a function of the time rate of change of ν. Under this assumption the emerging constitutive relations are in correspondence with those of Goodman and Cowin [5,6] which were gained by use of the classical Coleman-Noll approach. With $\Psi \neq \hat{\Psi}(\cdot, \dot{\nu})$, there follows

$$\lambda^{\nu} = -\frac{1}{\alpha\theta}\frac{\partial\Psi}{\partial\dot{\nu}} = 0. \tag{28}$$

Furthermore, with this assumption and condition (21) the functional dependence of Ψ reduces to

$$\Psi = \hat{\Psi}(\nu_0, \nu, \gamma_0, \gamma, \theta, \mathrm{grad}\nu, \mathrm{grad}\gamma). \qquad (29)$$

If we assume that Ψ is an isotropic scalar function, then from (29) it must have the form

$$\Psi = \hat{\Psi}(\nu_0, \nu, \gamma_0, \gamma, \theta, \mathrm{grad}\nu \cdot \mathrm{grad}\nu, \mathrm{grad}\nu \cdot \mathrm{grad}\gamma, \mathrm{grad}\gamma \cdot \mathrm{grad}\gamma). \qquad (30)$$

In the next step we define the extra entropy flux vector **k** via the formula

$$\mathbf{\Phi} = \frac{\mathbf{q}}{\theta} - \boldsymbol{\lambda}^{v}\mathbf{t} - \lambda^{v}\mathbf{h} + \mathbf{k}, \qquad (31)$$

which, with $\boldsymbol{\lambda}^{v} = \mathbf{0}$, $\lambda^{v} = 0$, reduces to

$$\mathbf{\Phi} = \frac{\mathbf{q}}{\theta} + \mathbf{k}. \qquad (32)$$

Substituting (32) into (23)-(27) gives rise to the following identities for **k**

$$\frac{\partial \mathbf{k}}{\partial \nu_0} = \mathbf{0}, \quad \frac{\partial \mathbf{k}}{\partial \gamma_0} = \mathbf{0}, \quad \frac{\partial \mathbf{k}}{\partial \mathbf{D}} = \mathbf{0}, \quad \frac{\partial \mathbf{k}}{\partial \dot{\gamma}} = \frac{\gamma\nu}{\theta}\frac{\partial \Psi}{\partial grad\gamma},$$
$$sym\{\frac{\partial \mathbf{k}}{\partial grad\nu}\} = \mathbf{0}, \quad sym\{\frac{\partial \mathbf{k}}{\partial grad\gamma}\} = \mathbf{0}, \quad sym\{\frac{\partial \mathbf{k}}{\partial grad\theta}\} = \mathbf{0}. \qquad (33)$$

From $(33)_1$-$(33)_3$ the functional dependence of **k** is identified as

$$\mathbf{k} = \hat{\mathbf{k}}(\nu, \dot{\nu}, \mathrm{grad}\nu, \gamma, \dot{\gamma}, \mathrm{grad}\gamma, \theta, \mathrm{grad}\theta). \qquad (34)$$

Integrating $(33)_{5,6,7}$ with each other results in

$$\begin{aligned} \mathbf{k} &= \mathbf{A}_1 \cdot \mathrm{grad}\nu + \mathbf{B}_1 \cdot \mathrm{grad}\gamma + \mathbf{C}_1 \cdot (\mathrm{grad}\nu \otimes \mathrm{grad}\gamma) + \mathbf{d}_1(\nu, \dot{\nu}, \gamma, \dot{\gamma}, \theta, \mathrm{grad}\theta), \\ &= \mathbf{A}_2 \cdot \mathrm{grad}\nu + \mathbf{B}_2 \cdot \mathrm{grad}\theta + \mathbf{C}_2 \cdot (\mathrm{grad}\nu \otimes \mathrm{grad}\theta) + \mathbf{d}_2(\nu, \dot{\nu}, \gamma, \dot{\gamma}, \theta, \mathrm{grad}\gamma), \\ &= \mathbf{A}_3 \cdot \mathrm{grad}\gamma + \mathbf{B}_3 \cdot \mathrm{grad}\theta + \mathbf{C}_3 \cdot (\mathrm{grad}\gamma \otimes \mathrm{grad}\theta) + \mathbf{d}_3(\nu, \dot{\nu}, \gamma, \dot{\gamma}, \theta, \mathrm{grad}\nu), \end{aligned} \qquad (35)$$

where $\otimes$ denotes dyadic product. $\mathbf{A}_i$, $\mathbf{B}_i$ (i=1-3) are 2^{nd}-order skw-symmetric tensors, $\mathbf{C}_i$ (i=1-3) are 3^{rd}-order skew-symmetric tensor and $\mathbf{d}_i$ (i=1-3) are vector functions. $\mathbf{A}_1$, $\mathbf{B}_1$ and $\mathbf{C}_1$ are not functions of gradν and gradγ, $\mathbf{A}_2$, $\mathbf{B}_2$ and $\mathbf{C}_2$ are not functions of gradν and gradθ, while $\mathbf{A}_3$, $\mathbf{B}_3$ and $\mathbf{C}_3$ are not functions of gradγ and gradθ. Since, moreover, the vector **k** must be isotropic, then it follows immediately that $\mathbf{A}_i = \mathbf{B}_i = \mathbf{0}$ (i=1-3) and $\mathbf{C}_i = \mathbf{0}$ (i=1-3) because there are no isotropic skew-symmetric second and third order tensors; thus

$$\mathbf{k} = \mathbf{d}_1(\nu, \dot{\nu}, \gamma, \dot{\gamma}, \theta, \mathrm{grad}\theta) = \mathbf{d}_2(\nu, \dot{\nu}, \gamma, \dot{\gamma}, \theta, \mathrm{grad}\gamma) = \mathbf{d}_3(\nu, \dot{\nu}, \gamma, \dot{\gamma}, \theta, \mathrm{grad}\nu) = \mathbf{d}(\nu, \dot{\nu}, \gamma, \dot{\gamma}, \theta) = \mathbf{0}, \qquad (36)$$

since there is no isotropic vector function of only scalar function arguments. Thus, the entropy flux takes its traditional form i.e., $\mathbf{\Phi} = \mathbf{q}/\theta$ is obtained. This result will not follow, when the Helmholtz free energy depends upon $\dot{\nu}$. Indeed, in that case λ^{v} is nontrivially determined by the free energy and so the entropy flux must deviate in direction from that of the heat flux by a contribution proportional to **h**, the equilibrated stress vector. Substituting (36) into $(33)_4$ yields

$$\frac{\partial \Psi}{\partial \mathrm{grad}\gamma} = \mathbf{0}, \qquad (37)$$

thus, another restriction of the functional dependence of Ψ is obtained. With (37) and (29) now the functional dependence of Ψ can be identified as

$$\Psi = \hat{\Psi}(\nu_0, \gamma_0, \nu, \gamma, \theta, \mathrm{grad}\nu \cdot \mathrm{grad}\nu). \qquad (38)$$

Further restrictions on Ψ will be given by investigating the residual entropy inequality in thermodynamic equilibrium. With (32) and (36) the expression (22) for the equilibrated stress vector $\mathbf{h}$ can now be identified as

$$\mathbf{h} = \gamma\nu \frac{\partial \Psi}{\partial \mathrm{grad}\nu}. \qquad (39)$$

With this, the Liu-identities are now fully exploitated. Next we investigate the residual entropy inequality. The residual entropy inequality, corresponding to $(18)_2$, or $b \geq 0$, is given by (with $\boldsymbol{\lambda}^{\mathrm{v}} = \mathbf{0}$)

$$\begin{aligned}\pi' = &\left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\nu} - \lambda^{\gamma}\gamma - \frac{\gamma\nu}{\theta}f\right\}\dot{\nu} + \left\{-\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\gamma} - \lambda^{\gamma}\nu\right\}\dot{\gamma} - \lambda^{\gamma}\gamma\nu\,\mathrm{div}\mathbf{v} + \lambda^{\nu}\gamma\nu f + \frac{1}{\theta}\mathbf{t}\cdot\mathbf{D} \\ &+ \left\{\frac{\partial\mathbf{\Phi}}{\partial\nu} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\nu} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\nu}\right\}\cdot(\mathrm{grad}\nu) + \left\{\frac{\gamma\nu}{\theta}\frac{\partial\Psi}{\partial\mathrm{grad}\nu}\otimes\mathrm{grad}\nu\right\}\cdot\mathrm{grad}\mathbf{v} \\ &+ \left\{\frac{\partial\mathbf{\Phi}}{\partial\theta} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\theta} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\theta}\right\}\cdot(\mathrm{grad}\theta) + \left\{\frac{\partial\mathbf{\Phi}}{\partial\gamma} + \lambda^{\nu}\frac{\partial\mathbf{h}}{\partial\gamma} - \frac{1}{\theta}\frac{\partial\mathbf{q}}{\partial\gamma}\right\}\cdot(\mathrm{grad}\gamma) \geq 0.\end{aligned} \qquad (40)$$

Substituting (28), (32), (36), (38) and (39) into (40) results in the new form of the residual entropy inequality

$$\begin{aligned}\theta\pi' = &\{-\beta - \theta\lambda^{\gamma}\gamma - \gamma\nu f\}\dot{\nu} + \{-\gamma\nu\frac{\partial\Psi}{\partial\gamma} - \theta\lambda^{\gamma}\nu\}\dot{\gamma} \\ &- \frac{\mathbf{q}\cdot grad\,\theta}{\theta} + \{\mathbf{t} + \mathbf{h}\otimes grad\nu - \theta\lambda^{\gamma}\gamma\nu\mathbf{I}\}\cdot\mathbf{D} \geq 0,\end{aligned} \qquad (41)$$

where the definition

$$\beta = \gamma\nu\frac{\partial\Psi}{\partial\nu}, \qquad \text{configuration pressure}, \qquad (42)$$

has been introduced, and $\mathbf{I}$ denotes the unit tensor. It should be noted that in (41) the Lagrange multiplier λ^{γ} is not yet determined by the free energy Ψ.

2.4. Thermodynamic equilibrium

Further restrictions on the constitutive relations can be obtained from the residual entropy inequality (41) in the context of thermodynamic equilibrium, which is characterized in the current local formulation by vanishing the entropy production, i.e., $\theta\pi' = 0$. Inequality (41) can be represented as

$$\begin{aligned}&\theta\pi' = \mathbf{X}(\mathbf{Y})\cdot\mathbf{Y} \geq 0, \\ &\mathbf{X} = (-\beta - \theta\gamma\lambda^{\gamma} - \gamma\nu f, -\gamma\nu\frac{\partial\Psi}{\partial\gamma} - \theta\lambda^{\gamma}\nu, \frac{-\mathbf{q}}{\theta}, \mathbf{t} - \theta\gamma\nu\lambda^{\gamma}\mathbf{I} + \mathbf{h}\otimes\mathrm{grad}\nu), \\ &\mathbf{Y} = (\dot{\nu}, \dot{\gamma}, \mathrm{grad}\theta, \mathbf{D}).\end{aligned} \qquad (43)$$

Thus, we define thermodynamic equilibrium as those states, in which the independent dynamic variables $\mathbf{Y}$ all vanish. Besides, $\theta\pi'$ also possesses its minimum value, namely 0, in thermodynamic equilibrium. Necessary conditions for this minimum are that

$$\left.\frac{\partial(\theta\pi')}{\partial Y_i}\right|_{\mathbf{Y}=0} = 0, \qquad Y_i \in \mathbf{Y},$$

$$\left.\frac{\partial^2(\theta\pi')}{\partial Y_i \partial Y_j}\right|_{\mathbf{Y}=0} \text{ is positive semi-definite}, \quad Y_i, Y_j \in \mathbf{Y}. \tag{44}$$

$(44)_1$ restricts the equilibrium forms of the dependent constitutive fields, while $(44)_2$ constrains the signs of material functions in it. Here we will only deal with the first condition. It yields the equilibrium values of the equilibrated intrinsic body force f, the heat flux **q,** the stress **t** and the Lagrange multiplier λ^γ

$$f\big|_E = \frac{-\beta - \theta\lambda^\gamma\gamma}{\gamma\nu}, \quad \mathbf{q}\big|_E = \mathbf{0}, \quad \mathbf{t}\big|_E = \theta\gamma\nu\lambda^\gamma\mathbf{I} - \mathbf{h}\otimes grad\nu, \quad \lambda^\gamma = -\frac{\gamma}{\theta}\frac{\partial\Psi}{\partial\gamma}, \tag{45}$$

where the subindex E indicates that the indexed quantity is evaluated in thermodynamic equilibrium. Here it is noted that according to the definition of thermodynamic equilibrium and expression (38), the functional dependence of the free energy Ψ is the same either in thermodynamic equilibrium or in non-equilibrium. Consequently when Ψ is known, the Lagrange multiplier λ^γ can be directly determined by $(45)_4$ and can be interpreted as thermodynamic pressure. Besides, in (38) ν_0 and γ_0 are material constants, and furthermore for the case of thermodynamic equilibrium under isothermal condition the functional dependence of Ψ on temperature θ can be removed, consequently in this case the functional dependence of Ψ can be identified as

$$\Psi = \hat{\Psi}(\nu_0,\ \gamma_0,\ \nu,\ \gamma,\ grad\nu \cdot grad\nu), \tag{46}$$

with which the statement that the stored energy function ϕ corresponds to the Helmholtz free energy function Ψ in thermodynamic equilibrium under isothermal condition has been proved to be true.

3. Conclusions

In the current paper the statement that the stored energy function ϕ corresponds to the Helmholtz free energy function Ψ in thermodynamic equilibrium under isothermal condition has been proved to be true. This result shows that the postulated functional dependence of the stored energy function ϕ proposed by Cowin and Goodman [3] for the derivation of the balance of equilibrated force is enough and reasonable. There is no need to propose a more general functional dependence of ϕ since from the current thermodynamic analysis it is seen that the inclusion of other independent argument outside γ, ν and gradν has no influence upon the final constitutive form of the free energy Ψ, which in turn, the stored energy ϕ. From the gradient theory of internal variables proposed by Valanis [21] it is also understood that the balance of equilibrated force of Goodman-Cowin theory can be regarded as the "1st order gradient theory of ν" of Valanis since outside γ and ν only gradν is considered as an independent argument of the functional dependence of ϕ.

A complete thermodynamic analysis is also performed in the current paper and the constitutive responses in thermodynamic equilibrium of the stress tensor **t**, the equilibrated intrinsic body force f and the heat flux vector **q** have been obtained. In deducing these additional requirement that $\dot{\gamma}$ must vanish is introduced for the definition of thermodynamic equilibrium. This is so because $\dot{\gamma}$ is introduced as additional independent argument of the constitutive class, if it is not introduced, thermodynamic equilibrium can then be defined by conventional ways, but in this case the Lagrange multiplier λ^{γ} can not be determined directly from the free energy Ψ and should be regarded as an undetermined field quantity.

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Symbol list

b = external body force
c = constitutive class
d = symmetric part of velocity gradient
e = specific internal energy,
f = equilibrated intrinsic body force
h = equilibrated stress vector
k = extra entropy flux vector
q = heat flux vector
r = specific external energy supply
s = specific external entropy supply
t = stress tensor
v = velocity
w = equilibrated external body force
α = equilibrated inertia
β = configuration pressure
γ = true mass density of grains
γ_0 = reference true mass density of grains
ν = volume fraction
ν_0 = reference volume fraction
η = specific entropy density
π' = residual entropy production
Ψ = helmholtz free energy
ϕ = stored energy function
θ = empirical temperature
π = entropy production
Φ = entropy flux vector
λ^{γ} = lagrange multiplier corresponding to the balance of mass
$\lambda^{\mathbf{v}}$ = lagrange multiplier corresponding to the balance of linear momentum
λ^{ν} = lagrange multiplier corresponding to the balance of equilibrated force
λ^{e} = lagrange multiplier corresponding to the balance of internal energy

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