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Non-local Thermoelasticity Based on Equilibrium Statistical Thermodynamics

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Abstract The purpose of this work is the formulation of energetic constitutive relations for thermoelasticity of non-simple materials based on atomistic considerations and equilibrium statistical thermodynamics (EST). In particular, both (unrestricted) canonical, and (restricted) quasi-harmonic, formulations are considered. In the canonical case, (spatial) non-locality results from relaxation of the assumption that atoms subject to continuum deformation change position uniformly and affinely. In the quasi-harmonic case, the analogous assumption on mean atomic position (i.e., Cauchy-Born) is relaxed. Two types of spatial non-locality, i.e., strong and weak, are considered. In the former case, atomic position (or mean position) is a functional of the deformation gradient $\boldsymbol{F}$, while in the latter, this functional is approximated by a function of $\boldsymbol{F}$ and its higher-order gradients $\nabla^1\boldsymbol{F}, \ldots, \nabla^n\boldsymbol{F}$. On this basis, canonical and quasi-harmonic non-local model relations are obtained for the thermoelastic free energy, entropy, internal energy, and stress. In addition, such relations are formulated for thermoelastic material properties (e.g., stiffness).

In the second part of the work, basic relations from the continuum thermodynamics of (non-polar) simple materials are generalized to higher-order deformation gradient (i.e., weakly non-local) continua and applied to energetic thermoelasticity. The corresponding formulation is based in particular on (i) Euclidean frame-indifference of the energy balance and (ii) the dissipation principle. As in the standard case, necessary for (i) is linear momen-

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tum balance and the symmetry of the (generalized) Kirchhoff stress (i.e., angular momentum balance). In the context of (ii), the free energy density determines in particular the first Piola-Kirchhoff stress $\boldsymbol{P}$, the higher-order stress measures $\boldsymbol{P}_1, \ldots, \boldsymbol{P}_n$ conjugate to $\nabla^1\boldsymbol{F}, \ldots, \nabla^n\boldsymbol{F}$, as well as the generalized Kirchhoff stress. Modeling the phenomenological free energy on the corresponding (weakly non-local) canonical free energy yields EST-based constitutive forms for the entropy, all stress measures, and thermoelastic material properties. Alternatively, one can model the former energy as an approximation to the latter. An example of this for the second-order ($n = 2$) case is discussed both theoretically and computationally in the last part of the work.

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1 Introduction

The formulation of continuum constitutive relations based on discrete *ab initio* and/or atomistic considerations and methods rather than on continuum phenomenology alone has been pursued for many classes of materials in the literature. In the case of solids crystals, for example, Wallace [30, Chaps. 2–3] formulated zero-temperature hyperelasticity for simple materials based on an interatomic potential (see also, e.g., [23, §8.1.2]). This treatment was extended to finite temperature and energetic thermoelasticity (i.e., without heat conduction and viscosity) for simple materials by Wallace [30, Chaps. 4–5] and more recently [31] in the context of (quantum) phonon thermodynamics (see also, e.g., [23, §8.1.3]). Among other things, the establishment of (quantum) density functional theory for the quantitative determination of material properties (for a detailed review, see, e.g., [23, Chaps. 4–5]), as well as continuum modeling of nanoscopic systems and processes, has maintained interest in the formulation of continuum constitutive models based on *ab initio* and/or atomistic considerations. For example, a quantitative elastic stored energy model for simple materials was recently formulated in [24] based on atomistic considerations and quantum density functional theory (DFT) in terms of material-symmetry-adapted strain tensor components and determined the corresponding elastic stiffnesses.

One purpose of the current work is the generalization of such formulations for energetic thermoelasticity to non-simple materials in the context of equilibrium statistical thermodynamics (EST). As detailed in what follows, this results in general in strongly non-local (SNL) constitutive relations, i.e., relations which are functionals of the deformation gradient $\boldsymbol{F}$. Also treated in this work is the weakly non-local (WNL) approximation of these, i.e., functions of the deformation gradient $\boldsymbol{F}$ and its higher-order gradients $\nabla^1\boldsymbol{F}, \ldots, \nabla^n\boldsymbol{F}$. Both non-local formulations represent broad non-local generalizations of existing treatments (e.g., [23, §§8.1.2–8.1.3]).

To employ such constitutive relations in the continuum modeling of non-simple materials, a formulation of corresponding basic field and balance relations is required. To this end, a second purpose of the current work is the phenomenological formulation of such relations for higher-order deformation gradient (i.e., WNL) continua in the context of continuum thermodynamics (e.g., [29]). Since the pioneering works of Mindlin (e.g., [14, 15]) or Toupin (e.g., [26]), a number of extensions and generalizations have been pursued. For example,

direct generalization of the formulation of [14] to geometrically non-linear isothermal gradient hyperelasticity has been carried out in [10]. In contrast to the variational formulation common in these works, a direct formulation is pursued in the current work in the context of the Euclidean frame-indifference of the energy balance (e.g., [9]). As such, the current work represents a generalization of the second-order case in [20] to arbitrary order. Since the focus in this work is on energetic thermoelasticity and EST, additional kinetic / dissipative constitutive relations (e.g., in the second-order case: [20]) are not considered here.

The current work begins in Sect. 2 with the constitutive formulation of energetic thermoelasticity in SNL form based on the (unrestricted) canonical ensemble and corresponding ensemble averaging. The corresponding WNL canonical formulation is given in Sect. 3. SNL and WNL constitutive formulation based on the quasi-harmonic (QH) approximation to the canonical ensemble is carried out in Sect. 4. This is followed in Sect. 5 by the phenomenological formulation of balance and field relations for higher-order deformation gradient continua based on continuum thermodynamics. This is then applied to the case of energetic thermoelasticity in the context of the dissipation principle, resulting i corresponding energetic thermoelastic constitutive relations, e.g., for stress. More detailed relations for these and related material properties (e.g., elastic stiffness) are obtained in Sect. 6 with the help of the free energy models from EST. Lastly, as a computational example, the EST-based WNL free energy is compared in Sect. 7 to second-order (i.e., $n = 2$) with its approximation via higher-order deformation gradient thermoelasticity in strain-gradient form. The work ends with a summary and discussion in Sect. 8. For completeness, reduced forms of the interatomic potential in the EST-based formulations are summarized in Appendix A in the context of material frame-indifference (e.g., [27, 29]). Corresponding material frame-indifference, reduced forms for the free energy density in higher-order deformation gradient thermoelasticity are discussed in Appendix B. Finally, the boundary-value problem for higher-order deformation gradient thermoelasticity is briefly summarized in Appendix C in variational form.

In this work, Euclidean vectors are represented by lower-case bold italic characters $\boldsymbol{a}, \ldots, \boldsymbol{z}$, second-order Euclidean tensors by upper-case bold italic characters $\boldsymbol{A}, \ldots, \boldsymbol{Z}$, and calligraphic characters $\mathcal{A}, \ldots, \mathcal{Z}$ for Euclidean tensors of arbitrary order. The notation $\mathcal{A} \cdot \mathcal{B}$ is used for the scalar product of arbitrary tensors. Given this product on vectors, $(\boldsymbol{a} \otimes \boldsymbol{b})\boldsymbol{c} := (\boldsymbol{b} \cdot \boldsymbol{c})\boldsymbol{a}$ defines the tensor product $\boldsymbol{a} \otimes \boldsymbol{b}$ of $\boldsymbol{a}$ and $\boldsymbol{b}$, and $\boldsymbol{A}^{\mathrm{T}}\boldsymbol{a} \cdot \boldsymbol{b} := \boldsymbol{a} \cdot \boldsymbol{A}\boldsymbol{b}$ the transpose $\boldsymbol{A}^{\mathrm{T}}$ of $\boldsymbol{A}$. Let $\operatorname{sym} \boldsymbol{A} := \frac{1}{2}(\boldsymbol{A} + \boldsymbol{A}^{\mathrm{T}})$ represent the symmetric part, and $\operatorname{skw} \boldsymbol{A} := \frac{1}{2}(\boldsymbol{A} - \boldsymbol{A}^{\mathrm{T}})$ the skew-symmetric part, of $\boldsymbol{A}$ in what follows. Unless otherwise stated, upper-case subscripted slanted sans-serif characters $\boldsymbol{A}_i, \boldsymbol{B}_i, \ldots$ represent tensorial and non-tensorial quantities of order $i + 2$ for $i \geqslant 0$ in this work. In particular, $\boldsymbol{A}_0$ is then second-order. For $i \geqslant 1$, any $\boldsymbol{A}_i$ satisfying $(\boldsymbol{A}_i \boldsymbol{b})\boldsymbol{a} = (\boldsymbol{A}_i \boldsymbol{a})\boldsymbol{b}$ is referred to as symmetric in what follows. Further concepts and notation will be introduced as needed along the way.

2 Strongly Non-local Canonical Formulation

As stated above, the current formulation is restricted to the simplest case of unary solids, primitive unit cells, and purely bulk relations (i.e., periodic system). In the corresponding canonical ensemble for a system of N of mass points at temperature θ, let $\boldsymbol{r}_a$ represent the position of mass point a ($a = 1, \ldots, N$) and $\boldsymbol{p}_a = m_a \dot{\boldsymbol{r}}_a$ its momentum. As usual, the system Hamiltonian $H(\boldsymbol{r}, \boldsymbol{p}) = K(\boldsymbol{p}) + U(\boldsymbol{r})$ consists of kinetic K and potential U parts, with $\boldsymbol{r} := (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ and $\boldsymbol{p} := (\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N)$. Given these, the partition function and free

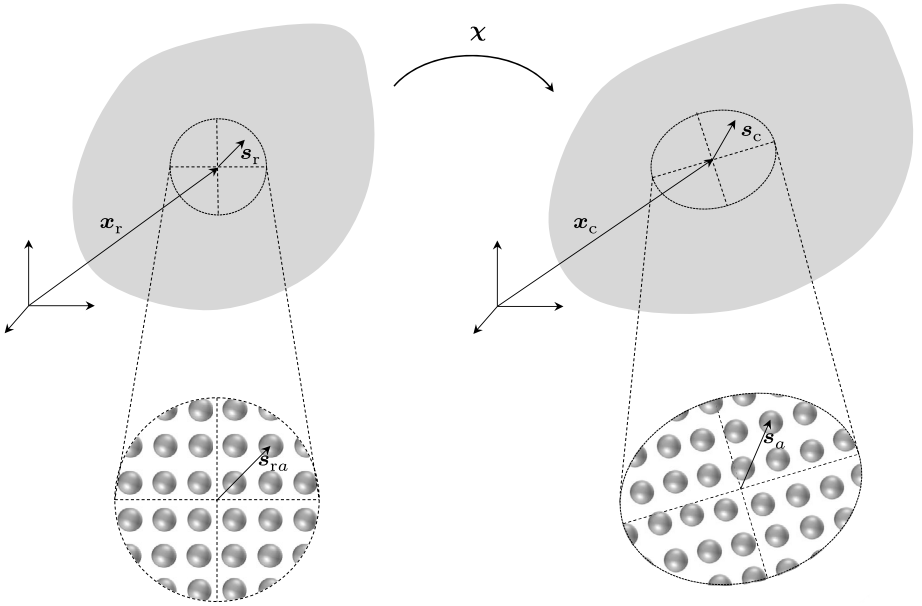

Fig. 1 $\boldsymbol{\chi}$ maps the position $\boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}}$ of any point in a neighborhood of the reference position $\boldsymbol{x}_{\mathrm{r}}$ of a material element to $\boldsymbol{x}_{\mathrm{c}} + \boldsymbol{s}_{\mathrm{c}} = \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}})$ in a neighborhood of its current position $\boldsymbol{x}_{\mathrm{c}} = \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}})$. In the context of (3), this is the case in particular for $\boldsymbol{r}_{\mathrm{r}a} = \boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}a}$ and $\boldsymbol{r}_a = \boldsymbol{x}_{\mathrm{c}} + \boldsymbol{s}_a = \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}a})$

energy

$$Z = \int_{\Gamma} dv(\boldsymbol{r})\, dv(\boldsymbol{p}) e^{-H(\boldsymbol{r},\boldsymbol{p})/k_{\mathrm{B}}\theta}, \qquad \Psi := -k_{\mathrm{B}}\theta \ln Z, \tag{1}$$

respectively, are determined, as well as ensemble averaging

$$\langle \varphi \rangle := \int_{\Gamma} dv(\boldsymbol{r})\, dv(\boldsymbol{p}) w\, \varphi, \quad w := \frac{1}{N!\, h^{3N}} \frac{e^{-H/k_{\mathrm{B}}\theta}}{Z}, \tag{2}$$

with respect to the canonical distribution function w. The short-hand notation $dv(\boldsymbol{r}) := dv(\boldsymbol{r}_1) \cdots dv(\boldsymbol{r}_N)$ and $dv(\boldsymbol{p}) := dv(\boldsymbol{p}_1) \cdots dv(\boldsymbol{p}_N)$ is employed here and in what follows, with $dv(\boldsymbol{x})$ the volume element induced by $d\boldsymbol{x}$.

Central to the current canonical formulation is the finite, non-affine generalization[1]

$$\boldsymbol{r}_{\mathrm{r}a} := \boldsymbol{\chi}^{-1}(\boldsymbol{r}_a) \tag{3}$$

of the "standard" infinitesimal, affine transformation $\boldsymbol{r}_{\mathrm{r}a} := \boldsymbol{F}^{-1}\boldsymbol{r}_a$ (in the current notation) of phase-space position "coordinates" (e.g., [30, §7], or [23, Eq. (8.45)]). Here, $\boldsymbol{\chi}$ is the continuum deformation field, $\boldsymbol{F} = \nabla\boldsymbol{\chi}$ the deformation gradient, and $\boldsymbol{x}_{\mathrm{r}}$ the reference location of an arbitrary continuum material element with current location $\boldsymbol{x}_{\mathrm{c}} = \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}})$ (Fig. 1). In the context of (3) and Fig. 1, the formulation to follow is with respect to a fixed, but otherwise arbitrary, continuum material element located at $\boldsymbol{x}_{\mathrm{r}}$ in the reference, and at $\boldsymbol{x}_{\mathrm{c}}$ in the current, configuration of the material in question. Analogous to its infinitesimal, affine counterpart

[1] In this work, the subscript r stands for reference, and c for current.

(e.g., [23, §8.1.3]), (3) couples atomic and continuum kinematics. In particular, (3) induces the transformation $\dot{\boldsymbol{r}}_a = \boldsymbol{F}(\boldsymbol{r}_{\mathrm{r}a})\,\dot{\boldsymbol{r}}_{\mathrm{r}a}$ of velocities, and so the "canonical" transformation

$$K = \frac{1}{2}\sum_a \boldsymbol{p}_a \cdot \dot{\boldsymbol{r}}_a = \frac{1}{2}\sum_a \boldsymbol{p}_{\mathrm{r}a} \cdot \dot{\boldsymbol{r}}_{\mathrm{r}a}, \qquad \boldsymbol{p}_{\mathrm{r}a} := \boldsymbol{F}^{\mathrm{T}}(\boldsymbol{r}_{\mathrm{r}a})\,\boldsymbol{p}_a, \tag{4}$$

of K, with $\sum_a := \sum_{a=1}^{N}$. This results in the "discrete" functional

$$K_{\mathrm{r}}[\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}}, \boldsymbol{p}_{\mathrm{r}}] := \sum_a \boldsymbol{F}^{-\mathrm{T}}(\boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}a})\,\boldsymbol{p}_{\mathrm{r}a} \cdot \boldsymbol{F}^{-\mathrm{T}}(\boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}a})\,\boldsymbol{p}_{\mathrm{r}a}/2m_a \tag{5}$$

of $\boldsymbol{F}$. In addition, integration of

$$d\boldsymbol{r}_a = \boldsymbol{F}(\boldsymbol{r}_{\mathrm{r}a})\,d\boldsymbol{r}_{\mathrm{r}a} = \boldsymbol{F}(\boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}a})\,d\boldsymbol{s}_{\mathrm{r}a} \tag{6}$$

of (3) yields the functional

$$\boldsymbol{r}_a[\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}a}] = \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}}) + \int_{\boldsymbol{0}}^{\boldsymbol{s}_{\mathrm{r}a}} \boldsymbol{F}(\boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}})\,d\boldsymbol{s}_{\mathrm{r}}, \tag{7}$$

of $\boldsymbol{F}$, and so the corresponding one

$$U_{\mathrm{r}}[\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}}] := U\big(\boldsymbol{r}_1[\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}1}] \ldots, \boldsymbol{r}_N[\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}N}]\big), \tag{8}$$

for the potential energy. Further, $(6)_1$ and $d\boldsymbol{p}_a = \boldsymbol{F}^{-\mathrm{T}}(\boldsymbol{r}_{\mathrm{r}a})\,d\boldsymbol{p}_{\mathrm{r}a}$ (at constant $\boldsymbol{r}_{\mathrm{r}a}$) from $(4)_2$ imply

$$dv(\boldsymbol{r}_a) = \det \boldsymbol{F}(\boldsymbol{r}_{\mathrm{r}a})\,dv(\boldsymbol{r}_{\mathrm{r}a}), \qquad dv(\boldsymbol{p}_a) = \det \boldsymbol{F}^{-\mathrm{T}}(\boldsymbol{r}_{\mathrm{r}a})\,dv(\boldsymbol{p}_{\mathrm{r}a}), \tag{9}$$

for the corresponding volume elements. Then $dv(\boldsymbol{r}_a)\,dv(\boldsymbol{p}_a) = dv(\boldsymbol{r}_{\mathrm{r}a})\,dv(\boldsymbol{p}_{\mathrm{r}a})$ is invariant, Z from $(1)_1$ is equal to[2]

$$Z_{\mathrm{r}}[\theta, \boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}] = \int_{\Gamma_{\mathrm{r}}} dv(\boldsymbol{s}_{\mathrm{r}})\,dv(\boldsymbol{p}_{\mathrm{r}}) e^{-H_{\mathrm{r}}[\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}}, \boldsymbol{p}_{\mathrm{r}}]/k_{\mathrm{B}}\theta}, \tag{10}$$

and

$$\Psi_{\mathrm{r}}[\theta, \boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}] := -k_{\mathrm{B}}\theta\, \ln Z_{\mathrm{r}}[\theta, \boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}] \tag{11}$$

holds for the system free energy $(1)_2$.

System properties derived from (11) include as usual the entropy and internal energy

$$S_{\mathrm{r}} = -\partial_\theta \Psi_{\mathrm{r}} = -\theta^{-1}\Psi_{\mathrm{r}} + \theta^{-1} E_{\mathrm{r}}, \qquad E_{\mathrm{r}} = \langle H_{\mathrm{r}} \rangle, \tag{12}$$

respectively. In addition, the (functional) derivatives

$$\mathcal{D}_{\boldsymbol{F}} K_{\mathrm{r}} = -\sum_a \boldsymbol{p}_a \otimes \boldsymbol{F}^{-1}(\boldsymbol{r}_{\mathrm{r}a})\,\boldsymbol{p}_a/m_a, \qquad \mathcal{D}_{\boldsymbol{F}} U_{\mathrm{r}} = \sum_a (\mathcal{D}_{\boldsymbol{F}} \boldsymbol{r}_a)^{\mathrm{T}} \partial_{\boldsymbol{r}_a} U, \tag{13}$$

from (5) and (8) determine

$$\mathcal{D}_{\boldsymbol{F}} \Psi_{\mathrm{r}} = \langle \mathcal{D}_{\boldsymbol{F}} H_{\mathrm{r}} \rangle = \langle \mathcal{D}_{\boldsymbol{F}} U_{\mathrm{r}} + \mathcal{D}_{\boldsymbol{F}} K_{\mathrm{r}} \rangle \tag{14}$$

[2] Since $\boldsymbol{x}_{\mathrm{r}}$ and so $\boldsymbol{x}_{\mathrm{c}} = \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}})$ are fixed, note that $d\boldsymbol{r}_a = d\boldsymbol{s}_a$ and $d\boldsymbol{r}_{\mathrm{r}a} = d\boldsymbol{s}_{\mathrm{r}a}$.

via ensemble averaging. Note that $(\mathcal{D}_{\boldsymbol{F}}\boldsymbol{r}_a)^{\mathrm{T}}\boldsymbol{a}\cdot\boldsymbol{Z}:=\boldsymbol{a}\cdot(\mathcal{D}_{\boldsymbol{F}}\boldsymbol{r}_a)\,\boldsymbol{Z}$. In addition, $(\mathcal{D}_{\boldsymbol{F}}\boldsymbol{r}_a)\,\boldsymbol{Z}=\int_{\boldsymbol{0}}^{\boldsymbol{s}_{\mathrm{r}a}}\boldsymbol{Z}(\boldsymbol{x}_{\mathrm{r}}+\boldsymbol{s}_{\mathrm{r}})\,d\boldsymbol{s}_{\mathrm{r}}$ from (7) for any $\boldsymbol{Z}(\boldsymbol{r}_{\mathrm{r}})$. In particular, the choice $\boldsymbol{Z}(\boldsymbol{r}_{\mathrm{r}})=\boldsymbol{A}\boldsymbol{F}(\boldsymbol{r}_{\mathrm{r}})$ yields $(\mathcal{D}_{\boldsymbol{F}}\boldsymbol{r}_a)\,\boldsymbol{A}\boldsymbol{F}=\boldsymbol{A}\boldsymbol{r}_a$, and so

$$(\mathcal{D}_{\boldsymbol{F}}K_{\mathrm{r}})\boldsymbol{F}^{\mathrm{T}}=-\sum_a\boldsymbol{p}_a\otimes\boldsymbol{p}_a/m_a,\qquad(\mathcal{D}_{\boldsymbol{F}}U_{\mathrm{r}})\boldsymbol{F}^{\mathrm{T}}=\sum_a\partial_{\boldsymbol{r}_a}U\otimes\boldsymbol{r}_a,\tag{15}$$

via "push-forward" of $\mathcal{D}_{\boldsymbol{F}}K_{\mathrm{r}}$ and $\mathcal{D}_{\boldsymbol{F}}U_{\mathrm{r}}$, respectively, from (13). In turn,

$$\big(\mathcal{D}_{\boldsymbol{F}}\Psi_{\mathrm{r}}\big)\boldsymbol{F}^{\mathrm{T}}=\sum_a\langle\partial_{\boldsymbol{r}_a}U\otimes\boldsymbol{r}_a-\boldsymbol{p}_a\otimes\boldsymbol{p}_a/m_a\rangle\tag{16}$$

then holds from (14).

In the context of material frame-indifference, the reduced form

$$U_{\mathrm{r}}[\boldsymbol{F};\boldsymbol{x}_{\mathrm{r}},\boldsymbol{s}_{\mathrm{r}}]=U_{\mathrm{d}}\big(r_{12}[\boldsymbol{F};\boldsymbol{x}_{\mathrm{r}},\boldsymbol{s}_{\mathrm{r}1},\boldsymbol{s}_{\mathrm{r}2}]\ldots,r_{N-1\,N}[\boldsymbol{F};\boldsymbol{x}_{\mathrm{r}},\boldsymbol{s}_{\mathrm{r}N-1},\boldsymbol{s}_{\mathrm{r}N}]\big),\tag{17}$$

of (8) follows from (A.3), with $\boldsymbol{r}_{ab}:=\boldsymbol{r}_a-\boldsymbol{r}_b$ and

$$r_{ab}[\boldsymbol{F};\boldsymbol{x}_{\mathrm{r}},\boldsymbol{s}_{\mathrm{r}a},\boldsymbol{s}_{\mathrm{r}b}]:=\big|\boldsymbol{r}_{ab}[\boldsymbol{F};\boldsymbol{x}_{\mathrm{r}},\boldsymbol{s}_{\mathrm{r}a},\boldsymbol{s}_{\mathrm{r}b}]\big|\tag{18}$$

from (7). In particular, (17) results in the reduction

$$\mathcal{D}_{\boldsymbol{F}}U_{\mathrm{r}}=\sum_{a<b}U_{ab}(\mathcal{D}_{\boldsymbol{F}}\boldsymbol{r}_{ab})^{\mathrm{T}}\boldsymbol{d}_{ab}\tag{19}$$

of $(13)_1$ in terms of the bond force $U_{ab}:=\partial_{r_{ab}}U_{\mathrm{d}}$ and bond direction $\boldsymbol{d}_{ab}:=\boldsymbol{r}_{ab}/r_{ab}$, with $\sum_{a<b}:=\sum_{a=1}^{N}\sum_{b=a+1}^{N}$. Likewise, $(15)_1$ reduces to

$$(\mathcal{D}_{\boldsymbol{F}}U_{\mathrm{r}})\boldsymbol{F}^{\mathrm{T}}=\sum_{a<b}U_{ab}\boldsymbol{r}_{ab}\otimes\boldsymbol{r}_{ab}/r_{ab},\tag{20}$$

and so (16) to the symmetric form

$$(\mathcal{D}_{\boldsymbol{F}}\Psi_{\mathrm{r}})\boldsymbol{F}^{\mathrm{T}}=\Big\langle\sum_{a<b}U_{ab}\boldsymbol{r}_{ab}\otimes\boldsymbol{r}_{ab}/r_{ab}-\sum_a\boldsymbol{p}_a\otimes\boldsymbol{p}_a/m_a\Big\rangle.\tag{21}$$

Clearly, the symmetry of $(\mathcal{D}_{\boldsymbol{F}}U_{\mathrm{r}})\boldsymbol{F}^{\mathrm{T}}$, and so that of $(\mathcal{D}_{\boldsymbol{F}}\Psi_{\mathrm{r}})\boldsymbol{F}^{\mathrm{T}}$, here is a direct consequence of the material frame-indifference of $U_{\mathrm{r}}[\boldsymbol{F};\boldsymbol{x}_{\mathrm{r}},\boldsymbol{s}_{\mathrm{r}}]$ in (17). This is also true in the WNL formulation of energetic thermoelasticity, to which we now turn.

3 Weakly Non-local Canonical Formulation

This is based on the Taylor series expansions[3]

$$\begin{aligned}\boldsymbol{\chi}(\boldsymbol{r}_{\mathrm{r}a})&=\boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}})+\sum_{i=0}^{n}(\Pi_{i+1}\boldsymbol{s}_{\mathrm{r}a})\,\nabla^{i+1}\boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}})+\cdots,\\ \boldsymbol{F}(\boldsymbol{r}_{\mathrm{r}a})&=\boldsymbol{F}(\boldsymbol{x}_{\mathrm{r}})+\sum_{i=1}^{n}(\Pi_i\boldsymbol{s}_{\mathrm{r}a})\,\nabla^{i}\boldsymbol{F}(\boldsymbol{x}_{\mathrm{r}})+\cdots,\end{aligned}\tag{22}$$

[3]More formally, $(22)_1$ for example defines the $(n+1)$-jet $(J^{n+1}_{\boldsymbol{x}_{\mathrm{r}}}\boldsymbol{\chi})(\boldsymbol{s}_{\mathrm{r}})$ of $\boldsymbol{\chi}$ with "base point" $\boldsymbol{x}_{\mathrm{r}}$. By varying this point, one obtains a vector-valued polynomial of at most order $n+1$ at every point of the base manifold.

where $(\Pi_i \boldsymbol{a})\mathcal{A} := \frac{1}{i!}(\cdots(\mathcal{A}\boldsymbol{a})\boldsymbol{a}\cdots)\boldsymbol{a}$ (i times) is a projection. From (22) follow

$$\begin{aligned}\boldsymbol{r}_a(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_{\mathrm{r}a}) &= \boldsymbol{\chi}(\boldsymbol{x}_\mathrm{r}) + \sum_{i=0}^{n}(\Pi_{i+1}\boldsymbol{s}_{\mathrm{r}a})\,\boldsymbol{F}_i(\boldsymbol{x}_\mathrm{r}),\\ \boldsymbol{F}_{\mathrm{r}a}(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_{\mathrm{r}a}) &= \boldsymbol{F}(\boldsymbol{x}_\mathrm{r}) + \sum_{i=1}^{n}(\Pi_i\boldsymbol{s}_{\mathrm{r}a})\,\boldsymbol{F}_i(\boldsymbol{x}_\mathrm{r}),\end{aligned} \tag{23}$$

analogous to $\boldsymbol{r}_a[\boldsymbol{F};\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_{\mathrm{r}a}]$ and $\boldsymbol{F}(\boldsymbol{r}_{\mathrm{r}a})$, respectively, with

$$\boldsymbol{F}_i := \nabla^i\boldsymbol{F} = \nabla^{i+1}\boldsymbol{\chi}, \qquad \boldsymbol{F}_0 := \boldsymbol{F} = \nabla^1\boldsymbol{\chi} = \nabla\boldsymbol{\chi}. \tag{24}$$

In turn, (23) result in

$$\begin{aligned}&K_\mathrm{r}(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_\mathrm{r},\boldsymbol{p}_\mathrm{r})\\ &\quad= \frac{1}{2}\sum_a \boldsymbol{F}_{\mathrm{r}a}^{-\mathrm{T}}(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_{\mathrm{r}a})\,\boldsymbol{p}_{\mathrm{r}a}\cdot\boldsymbol{F}_{\mathrm{r}a}^{-\mathrm{T}}(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_{\mathrm{r}a})\,\boldsymbol{p}_{\mathrm{r}a}/m_a,\\ &U_\mathrm{r}(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_\mathrm{r})\\ &\quad= U\big(\boldsymbol{r}_1(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_{\mathrm{r}1}),\ldots,\boldsymbol{r}_N(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_{\mathrm{r}N})\big),\end{aligned} \tag{25}$$

analogous to (5) and (8), respectively, as well as

$$\begin{aligned}Z_\mathrm{r}(\theta,\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r}) &= \int_{\Gamma_\mathrm{r}} dv(\boldsymbol{s}_\mathrm{r})\,dv(\boldsymbol{p}_\mathrm{r})\,e^{-H_\mathrm{r}(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r},\boldsymbol{s}_\mathrm{r},\boldsymbol{p}_\mathrm{r})/k_\mathrm{B}\theta},\\ \Psi_\mathrm{r}(\theta,\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r}) &= -k_\mathrm{B}\theta\,\ln Z_\mathrm{r}(\theta,\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_\mathrm{r}),\end{aligned} \tag{26}$$

analogous to (10), and (11), respectively.

As for the SNL case (12),

$$S_\mathrm{r} = -\partial_\theta\Psi_\mathrm{r} = -\theta^{-1}\Psi_\mathrm{r} + \theta^{-1}E_\mathrm{r}, \quad E_\mathrm{r} = \langle H_\mathrm{r}\rangle, \tag{27}$$

determine the entropy and internal energy, respectively, now with respect to (25) and (26). On the other hand, in the context of these,

$$\partial_{\boldsymbol{F}_i}\Psi_\mathrm{r} = \langle\partial_{\boldsymbol{F}_i}U_\mathrm{r} + \partial_{\boldsymbol{F}_i}K_\mathrm{r}\rangle, \quad i = 0,\ldots,n, \tag{28}$$

"replace" $\mathcal{D}_{\boldsymbol{F}}\Psi_\mathrm{r}$ in the WNL case. Here,

$$\partial_{\boldsymbol{F}_i}K_\mathrm{r} = -\sum_a(\partial_{\boldsymbol{F}_i}\boldsymbol{F}_{\mathrm{r}a})^\mathrm{T}\big[(\boldsymbol{p}_a\otimes\boldsymbol{p}_a/m_a)\,\boldsymbol{F}_{\mathrm{r}a}^{-\mathrm{T}}\big], \qquad \partial_{\boldsymbol{F}_i}U_\mathrm{r} = \sum_a(\partial_{\boldsymbol{F}_i}\boldsymbol{r}_a)^\mathrm{T}\partial_{\boldsymbol{r}_a}U, \tag{29}$$

from (25) with

$$\begin{aligned}(\partial_{\boldsymbol{F}_i}\boldsymbol{r}_a)^\mathrm{T}\boldsymbol{a}\cdot\boldsymbol{A}_i &:= \boldsymbol{a}\cdot(\partial_{\boldsymbol{F}_i}\boldsymbol{r}_a)\,\boldsymbol{A}_i \;\;= \boldsymbol{a}\cdot(\Pi_{i+1}\boldsymbol{s}_{\mathrm{r}a})\boldsymbol{A}_i,\\ (\partial_{\boldsymbol{F}_i}\boldsymbol{F}_{\mathrm{r}a})^\mathrm{T}\boldsymbol{A}\cdot\boldsymbol{A}_i &:= \boldsymbol{A}\cdot(\partial_{\boldsymbol{F}_i}\boldsymbol{F}_{\mathrm{r}a})\,\boldsymbol{A}_i = \boldsymbol{A}\cdot(\Pi_i\boldsymbol{s}_{\mathrm{r}a})\boldsymbol{A}_i,\end{aligned} \tag{30}$$

via (23). The "push-forward" forms

$$(\partial_{\boldsymbol{F}_i}K_\mathrm{r})\boldsymbol{F}_i^\mathrm{T} = -\sum_a(\boldsymbol{p}_a\otimes\boldsymbol{p}_a/m_a)\big(\boldsymbol{G}_{\mathrm{r}a}^i\boldsymbol{F}_{\mathrm{r}a}^{-1}\big)^\mathrm{T}, \qquad (\partial_{\boldsymbol{F}_i}U_\mathrm{r})\boldsymbol{F}_i^\mathrm{T} = \sum_a\partial_{\boldsymbol{r}_a}U\otimes\boldsymbol{g}_{\mathrm{r}a}^i, \tag{31}$$

of (29) determine that

$$(\partial_{\boldsymbol{F}_i}\Psi_{\mathrm{r}})\boldsymbol{F}_i^{\mathrm{T}} = \sum_a \left\langle \partial_{\boldsymbol{r}_a} U \otimes \boldsymbol{g}^i_{\mathrm{r}a} - (\boldsymbol{p}_a \otimes \boldsymbol{p}_a/m_a)\left(\boldsymbol{G}^i_{\mathrm{r}a}\boldsymbol{F}^{-1}_{\mathrm{r}a}\right)^{\mathrm{T}} \right\rangle \tag{32}$$

of (28) with

$$\boldsymbol{g}^i_{\mathrm{r}a} := (\Pi_{i+1}\boldsymbol{s}_{\mathrm{r}a})\boldsymbol{F}_i, \qquad \boldsymbol{G}^i_{\mathrm{r}a} := (\Pi_i \boldsymbol{s}_{\mathrm{r}a})\boldsymbol{F}_i, \tag{33}$$

via (30). Whereas $\boldsymbol{g}^i_{\mathrm{r}a}$ has units of length, note that $\boldsymbol{G}^i_{\mathrm{r}a}$ is dimensionless (e.g., like $\boldsymbol{F}$ and $\boldsymbol{F}_{\mathrm{r}a}$ in (23)). In contrast to $\partial_{\boldsymbol{F}_i}\Psi_{\mathrm{r}}$, which is of order $(2+i)$, note that $(\partial_{\boldsymbol{F}_i}\Psi_{\mathrm{r}})\boldsymbol{F}_i^{\mathrm{T}}$ is of order 2 for all i. Related to this is the fact that the former has (SI) units of $\mathrm{J m}^i$, while those J of the latter are independent i.

Like in the SNL case above, we have the reduced form

$$\begin{aligned} &U_{\mathrm{r}}(\boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}}) \\ &\quad = U_{\mathrm{d}}\big(r_{12}(\boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}1}, \boldsymbol{s}_{\mathrm{r}2}), \ldots, r_{N-1\,N}(\boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}N-1}, \boldsymbol{s}_{\mathrm{r}N})\big) \end{aligned} \tag{34}$$

of $(25)_2$ in the context of the MFI of U and (A.3), with

$$r_{ab}(\boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}a}, \boldsymbol{s}_{\mathrm{r}b}) := \left| \sum_{i=0}^{n} \left(\Pi_{i+1}\boldsymbol{s}_{\mathrm{r}}\right)_{ab} \boldsymbol{F}_i(\boldsymbol{x}_{\mathrm{r}}) \right| \tag{35}$$

from $(23)_1$ and $(\Pi_i \boldsymbol{s}_{\mathrm{r}})_{ab} := (\Pi_i \boldsymbol{s}_{\mathrm{r}a}) - (\Pi_i \boldsymbol{s}_{\mathrm{r}b})$. In turn, (34) results in the reductions

$$\partial_{\boldsymbol{F}_i} U_{\mathrm{r}} = \sum_{a<b} U_{ab}(\partial_{\boldsymbol{F}_i}\boldsymbol{r}_{ab})^{\mathrm{T}}\boldsymbol{d}_{ab}, \qquad (\partial_{\boldsymbol{F}_i}U_{\mathrm{r}})\boldsymbol{F}_i^{\mathrm{T}} = \sum_{a<b} U_{ab}\boldsymbol{d}_{ab} \otimes \boldsymbol{g}^i_{\mathrm{r}ab}, \tag{36}$$

of $(29)_1$ and $(31)_1$, respectively, with $\boldsymbol{g}^i_{\mathrm{r}ab} := \boldsymbol{g}^i_{\mathrm{r}a} - \boldsymbol{g}^i_{\mathrm{r}b}$. Likewise,

$$(\partial_{\boldsymbol{F}_i}\Psi_{\mathrm{r}})\boldsymbol{F}_i^{\mathrm{T}} = \left\langle \sum_{a<b} U_{ab}\boldsymbol{d}_{ab} \otimes \boldsymbol{g}^i_{\mathrm{r}ab} - \sum_a (\boldsymbol{p}_a \otimes \boldsymbol{p}_a/m_a)\left(\boldsymbol{G}^i_{\mathrm{r}a}\boldsymbol{F}^{-1}_{\mathrm{r}a}\right)^{\mathrm{T}} \right\rangle \tag{37}$$

holds for the reduced form of (32). As shown in the continuum thermodynamic formulation of WNL energetic thermoelasticity in Sect. 5 below, $(\partial_{\boldsymbol{F}_0}\Psi_{\mathrm{r}})\boldsymbol{F}_0^{\mathrm{T}}, \ldots, (\partial_{\boldsymbol{F}_n}\Psi_{\mathrm{r}})\boldsymbol{F}_n^{\mathrm{T}}$ determine for example the WNL form of the Kirchhoff stress. More on this later.

4 Quasi-harmonic Formulation

The quasi-harmonic (QH) approximation (e.g., [23, §11.4]) to the canonical formulation employed in the last two sections is based on the assumption that each mass point remains "close" to its mean position $\bar{\boldsymbol{r}}_a$ on the timescale of interest, i.e.,

$$\boldsymbol{r}_a = \bar{\boldsymbol{r}}_a + \boldsymbol{w}_a, \quad |\boldsymbol{w}_a| \ll 1. \tag{38}$$

In addition, mean atomic positions are assumed to "deform" with the continuum (Cauchy-Born). Consequently, the current QH formulation is based on the (finite, non-affine) generalization

$$\bar{\boldsymbol{r}}_{\mathrm{r}a} := \boldsymbol{\chi}^{-1}(\bar{\boldsymbol{r}}_a) \tag{39}$$

of the (infinitesimal, affine) Cauchy-Born relation $\bar{\boldsymbol{r}}_{ra} := \boldsymbol{F}^{-1}(\boldsymbol{x}_r)\,\bar{\boldsymbol{r}}_a$ (i.e., for primitive lattices; for the case of multilattices, see, e.g., [23, §11.2.2]). Analogous to the formulation of (7) and $(23)_1$ based on (3), then, we have

$$\begin{aligned}\bar{\boldsymbol{r}}_a[\boldsymbol{F};\boldsymbol{x}_r,\bar{\boldsymbol{s}}_{ra}] &= \boldsymbol{\chi}(\boldsymbol{x}_r) + \int_{\boldsymbol{0}}^{\bar{\boldsymbol{s}}_{ra}} \boldsymbol{F}(\boldsymbol{x}_r+\bar{\boldsymbol{s}}_r)\,d\bar{\boldsymbol{s}}_r,\\ \bar{\boldsymbol{r}}_a(\boldsymbol{F}_0,\ldots,\boldsymbol{F}_n;\boldsymbol{x}_r,\bar{\boldsymbol{s}}_{ra}) &= \boldsymbol{\chi}(\boldsymbol{x}_r) + \sum_{i=0}^{n}(\Pi_{i+1}\bar{\boldsymbol{s}}_{ra})\,\boldsymbol{F}_i(\boldsymbol{x}_r),\end{aligned} \tag{40}$$

in the SNL QH, and WNL QH, cases, respectively.

In the context of restricted ensemble averaging (e.g., [23, §11.1]), the assumption (38) facilitates analytic evaluation of the system partition function $(1)_1$, resulting in the corresponding analytic form

$$\Psi^{\mathrm{qh}}(\theta,\bar{\boldsymbol{r}}) = \Psi_{\mathrm{K}}^{\mathrm{qh}}(\theta) + U(\bar{\boldsymbol{r}}) + \frac{1}{2}\,k_{\mathrm{B}}\theta\,\ln\det\frac{\boldsymbol{\Phi}_*(\bar{\boldsymbol{r}})}{2\pi k_{\mathrm{B}}\theta} \tag{41}$$

(e.g., [23, §11.4]) of the QH approximation to Ψ in $(1)_2$. Here, $\Psi_{\mathrm{K}}^{\mathrm{qh}}$ represents the kinetic part of Ψ^{qh}, and

$$\boldsymbol{\Phi}_* := \sum_{r=1}^{m}\lambda_r\mathbf{e}_r\otimes\mathbf{e}_r \tag{42}$$

is the spectral form of the symmetric "force-constant" matrix

$$\boldsymbol{\Phi}(\bar{\boldsymbol{r}}) := \sum_a\sum_b \Phi_{kl}^{ab}(\bar{\boldsymbol{r}})\,\mathbf{i}_k^a\otimes\mathbf{i}_l^b,\quad \Phi_{kl}^{ab}(\bar{\boldsymbol{r}}) := \boldsymbol{i}_k\cdot\partial_{\boldsymbol{r}_b}\partial_{\boldsymbol{r}_a}U(\bar{\boldsymbol{r}})\,\boldsymbol{i}_l, \tag{43}$$

(summation convention over $k,l=1,2,3$) relative to the 3-dimensional $(\boldsymbol{i}_1,\boldsymbol{i}_2,\boldsymbol{i}_3)$ and $3N$-dimensional $(\mathbf{i}_1^1,\mathbf{i}_2^1,\mathbf{i}_3^1,\ldots,\mathbf{i}_1^N,\mathbf{i}_2^N,\mathbf{i}_3^N)$ Cartesian bases. In the current bulk (periodic) case, $m=3N-3$ non-zero eigenvalues $\lambda_1,\ldots,\lambda_m$ and corresponding eigenvectors $\mathbf{e}_1,\ldots,\mathbf{e}_m$ determine $\boldsymbol{\Phi}_*$ in (42). With U given by (A.3), note that

$$\begin{aligned}\partial_{\boldsymbol{r}_b}\partial_{\boldsymbol{r}_a}U(\bar{\boldsymbol{r}}) &= \sum_{c<d}\sum_{e<f}\delta_{acd}\,\bar{U}_{cdef}\,(\bar{\boldsymbol{d}}_{cd}\otimes\bar{\boldsymbol{d}}_{ef})\,\delta_{bef}\\ &\quad+\begin{cases}\sum_{c=a+1}^{N}\bar{U}_{ac}\,(\boldsymbol{I}-\bar{\boldsymbol{d}}_{ac}\otimes\bar{\boldsymbol{d}}_{ac})/\bar{r}_{ac} & a=b\\ -\bar{U}_{ab}\,(\boldsymbol{I}-\bar{\boldsymbol{d}}_{ab}\otimes\bar{\boldsymbol{d}}_{ab})/\bar{r}_{ab} & a\neq b\end{cases}\end{aligned} \tag{44}$$

holds, with $U_{abcd} := \partial_{r_{cd}}\partial_{r_{ab}}U_{\mathrm{d}}$ the bond stiffness, and $\delta_{abc} := \delta_{ab}-\delta_{ac}$. In what follows, the derivatives

$$\begin{aligned}\partial_\theta\Psi^{\mathrm{qh}} &= \partial_\theta\Psi_{\mathrm{K}}^{\mathrm{qh}} + \frac{1}{2}\,k_{\mathrm{B}}\sum_{r=1}^{m}\big[\ln(\lambda_r/2\pi k_{\mathrm{B}}\theta)-1\big],\\ \partial_{\bar{\boldsymbol{r}}_a}\Psi^{\mathrm{qh}} &= \sum_{a<b}\left[\bar{U}_{ab}+\frac{1}{2}\,k_{\mathrm{B}}\theta\sum_{r=1}^{m}\partial_{\bar{r}_{ab}}\ln\lambda_r\right]\bar{\boldsymbol{d}}_{ab},\end{aligned} \tag{45}$$

of (41) via (42) will be useful. Note that $(45)_2$ is based on the assumption that λ_r depends on $\bar{\boldsymbol{r}}_{ab}$ only through its magnitude $\bar{r}_{ab}$ (e.g., [23, Eqs. (11.110) and (11.111)]), such that $\partial_{\bar{\boldsymbol{r}}_{ab}}\ln\lambda_r = (\partial_{\bar{r}_{ab}}\ln\lambda_r)\,\bar{\boldsymbol{r}}_{ab}/\bar{r}_{ab}$ holds.

Combination of (40) and (41) then results in the QH approximations

$$\begin{aligned}&\Psi_{\mathrm{r}}^{\mathrm{qh}}[\theta, \boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \bar{\boldsymbol{s}}_{\mathrm{r}}]\\&\quad := \Psi_{\mathrm{qh}}\big(\theta, \bar{\boldsymbol{r}}_1[\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \bar{s}_{\mathrm{r}1}], \ldots, \bar{\boldsymbol{r}}_N[\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \bar{s}_{\mathrm{r}N}]\big),\\&\Psi_{\mathrm{r}}^{\mathrm{qh}}(\theta, \boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}, \bar{\boldsymbol{s}}_{\mathrm{r}})\\&\quad := \Psi_{\mathrm{qh}}\big(\theta, \bar{\boldsymbol{r}}_1(\boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}, \bar{s}_{\mathrm{r}1}), \ldots, \bar{\boldsymbol{r}}_N(\boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}, \bar{s}_{\mathrm{r}N})\big)\end{aligned} \tag{46}$$

to $\Psi_{\mathrm{r}}[\theta, \boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}, \bar{\boldsymbol{s}}_{\mathrm{r}}]$ from (11), and to $\Psi_{\mathrm{r}}(\theta, \boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}, \boldsymbol{s}_{\mathrm{r}})$ from $(26)_2$, respectively. From $(45)_2$ and the first of these, we have

$$\big(\mathcal{D}_{\boldsymbol{F}}\Psi_{\mathrm{r}}^{\mathrm{qh}}\big)\boldsymbol{F}^{\mathrm{T}} = \sum_{a<b}\left[\bar{U}_{ab} + \frac{1}{2}k_{\mathrm{B}}\theta\sum_{r=1}^{m}\partial_{\bar{r}_{ab}}\ln\lambda_r\right]\bar{\boldsymbol{r}}_{ab}\otimes\bar{\boldsymbol{r}}_{ab}/\bar{r}_{ab} \tag{47}$$

as the QH approximation to the SNL relation $(\mathcal{D}_{\boldsymbol{F}}\Psi_{\mathrm{r}})\boldsymbol{F}^{\mathrm{T}}$ from (21). Similarly, $(45)_2$ and $(46)_2$ result in the QH approximation

$$\big(\partial_{\boldsymbol{F}_i}\Psi_{\mathrm{r}}^{\mathrm{qh}}\big)\boldsymbol{F}_i^{\mathrm{T}} = \sum_{a<b}\left[\bar{U}_{ab} + \frac{1}{2}k_{\mathrm{B}}\theta\sum_{r=1}^{m}\partial_{\bar{r}_{ab}}\ln\lambda_r\right]\bar{\boldsymbol{d}}_{ab}\otimes\bar{\boldsymbol{g}}_{\mathrm{r}ab}^{i} \tag{48}$$

to the WNL relation $(\partial_{\boldsymbol{F}_i}\Psi_{\mathrm{r}})\boldsymbol{F}_i^{\mathrm{T}}$ from (37). Analogous to the WNL canonical case discussed above, $(\partial_{\boldsymbol{F}_0}\Psi_{\mathrm{r}}^{\mathrm{qh}})\boldsymbol{F}_0^{\mathrm{T}}, \ldots, (\partial_{\boldsymbol{F}_n}\Psi_{\mathrm{r}}^{\mathrm{qh}})\boldsymbol{F}_n^{\mathrm{T}}$ determine in particular the WNL QH form of the Kirchhoff stress in the continuum thermodynamic formulation of WNL energetic thermoelasticity.

5 Continuum Thermodynamic Formulation

Since the current treatment neglects heat conduction, the following is restricted to spatially uniform temperature θ. In this context, a direct generalization of the (referential or "Lagrangian") formulation of the first-order case in [20] to the current nth-order one is pursued here. For further simplicity, quasi-static conditions are assumed, and supplies are neglecting.

Given these conditions and assumptions, the total energy balance reduces to

$$\dot{\varepsilon}_{\mathrm{r}} = \operatorname{div}\boldsymbol{h}_{\mathrm{r}} \tag{49}$$

in terms of the internal energy density ε_{r} and the (mechanical) referential energy flux density $\boldsymbol{h}_{\mathrm{r}}$. In the zeroth-order case of simple materials (e.g., [29, §3.6]), $\boldsymbol{h}_{\mathrm{r}} = \boldsymbol{P}^{\mathrm{T}}\dot{\boldsymbol{\chi}}$ is determined by the material velocity[4] $\dot{\boldsymbol{\chi}}$ and the first Piola-Kirchhoff stress $\boldsymbol{P}$. Direct generalization of this to the current case yields[5]

$$\boldsymbol{h}_{\mathrm{r}} = \boldsymbol{P}^{\mathrm{T}}\dot{\boldsymbol{\chi}} + \sum_{i=1}^{n}\boldsymbol{P}_i^{\mathrm{T}}\nabla^i\dot{\boldsymbol{\chi}} = \sum_{i=0}^{n}\boldsymbol{P}_i^{\mathrm{T}}\nabla^i\dot{\boldsymbol{\chi}}, \tag{50}$$

in terms of the higher-order hyperstresses $\boldsymbol{P}_1, \ldots, \boldsymbol{P}_n$. As done here, we work with the notation $\boldsymbol{P}_0 := \boldsymbol{P}$ analogous to $\boldsymbol{F}_0 := \boldsymbol{F}$ in what follows for simplicity. By analogy with the zeroth- and first-order cases (e.g., [20]), the form of the energy balance resulting from (49)

[4] For simplicity, the notation $\boldsymbol{\chi}$ is used for both the deformation and motion fields in this work.

[5] $\boldsymbol{P}_k^{\mathrm{T}}$ in (50) is defined by $\boldsymbol{P}_k^{\mathrm{T}}\boldsymbol{A}_{k-1}\cdot\boldsymbol{a} := \boldsymbol{A}_{k-1}\cdot\boldsymbol{P}_k\boldsymbol{a}$ for $k \geqslant 1$.

and (50) is Euclidean frame-indifferent (e.g., [29, Chap. 6]) iff linear and angular momentum balance

$$\operatorname{div} \boldsymbol{P} = \boldsymbol{0}, \qquad \operatorname{skw} \boldsymbol{K} = \boldsymbol{0}, \tag{51}$$

respectively, hold, where[6]

$$\boldsymbol{K} = \sum_{i=1}^{n} \big(\boldsymbol{P}_{i-1} + \operatorname{div} \boldsymbol{P}_i\big)\boldsymbol{F}_{i-1}^{\mathrm{T}} + \boldsymbol{P}_n \boldsymbol{F}_n^{\mathrm{T}} \tag{52}$$

is the (generalized) Kirchhoff stress. As in the first-order case (e.g., [20]), the standard (i.e., zeroth-order) forms (51) of momentum balance apply in the nth-order case as well. Note that $\boldsymbol{K}$ from (52) reduces to its standard form $\boldsymbol{P}_0\boldsymbol{F}_0^{\mathrm{T}} = \boldsymbol{P}\boldsymbol{F}^{\mathrm{T}}$ for $n = 0$. Together with energy balance (49) and linear momentum balance $(51)_1$, the entropy balance $\dot{\eta}_{\mathrm{r}} = \pi_{\mathrm{r}}$ for the current case of uniform temperature implies

$$\theta\pi_{\mathrm{r}} = \sum_{i=1}^{n} (\boldsymbol{P}_{i-1} + \operatorname{div} \boldsymbol{P}_i) \cdot \dot{\boldsymbol{F}}_{i-1} + \boldsymbol{P}_n \cdot \dot{\boldsymbol{F}}_n - \eta_{\mathrm{r}}\dot{\theta} - \dot{\psi}_{\mathrm{r}} \tag{53}$$

for the dissipation rate density in terms of the free energy density $\psi_{\mathrm{r}} := \varepsilon_{\mathrm{r}} - \theta\eta_{\mathrm{r}}$.

Except perhaps for the energy flux form (50) relevant to higher-order deformation gradient continua without heat conduction, the above formulation is independent of any (further) constitutive assumptions. Restricting attention now to energetic thermoelasticity in this context, we have

$$\psi_{\mathrm{r}}(\theta, \boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \boldsymbol{x}_{\mathrm{r}}), \quad \eta_{\mathrm{r}} = -\partial_\theta \psi_{\mathrm{r}}. \tag{54}$$

Substituting these into (53), we have

$$\theta\pi_{\mathrm{r}} = \sum_{i=1}^{n} \big[(\boldsymbol{P}_{i-1} + \operatorname{div} \boldsymbol{P}_i) - \partial_{\boldsymbol{F}_{i-1}}\psi_{\mathrm{r}}\big] \cdot \dot{\boldsymbol{F}}_{i-1} + (\boldsymbol{P}_n - \partial_{\boldsymbol{F}_n}\psi_{\mathrm{r}}) \cdot \dot{\boldsymbol{F}}_n. \tag{55}$$

In the current energetic thermoelastic context, exploitation of the dissipation principle (e.g., [29, §9.5 for supply-free case]) then yields the thermoelastic relations

$$\begin{aligned}
\boldsymbol{P}_n &= \partial_{\boldsymbol{F}_n}\psi_{\mathrm{r}}, \\
\boldsymbol{P}_{n-1} &= \partial_{\boldsymbol{F}_{n-1}}\psi_{\mathrm{r}} - \operatorname{div} \boldsymbol{P}_n = \delta^1_{\boldsymbol{F}_{n-1}}\psi_{\mathrm{r}}, \\
&\vdots \\
\boldsymbol{P}_1 &= \partial_{\boldsymbol{F}_1}\psi_{\mathrm{r}} - \operatorname{div} \boldsymbol{P}_2 \quad = \delta^{n-1}_{\boldsymbol{F}_1}\psi_{\mathrm{r}}, \\
\boldsymbol{P}_0 &= \partial_{\boldsymbol{F}_0}\psi_{\mathrm{r}} - \operatorname{div} \boldsymbol{P}_1 \quad = \delta^{n}_{\boldsymbol{F}_0}\psi_{\mathrm{r}},
\end{aligned} \tag{56}$$

and so $\pi_{\mathrm{r}} = 0$. Here,

$$\delta^i_\phi := \partial_\phi - \sum_{j=1}^{i} (-1)^{j+1} \operatorname{div}^j \partial_{\nabla^j \phi}, \quad \operatorname{div}^j = \underbrace{\operatorname{div} \circ \cdots \circ \operatorname{div}}_{j\times} \tag{57}$$

[6] $\boldsymbol{F}_k^{\mathrm{T}}$ in (52) is defined by $\boldsymbol{A}_k\boldsymbol{F}_k^{\mathrm{T}} \cdot \boldsymbol{A} := \boldsymbol{A}_k \cdot \boldsymbol{A}\boldsymbol{F}_k$ for $k \geqslant 0$.

represents the ith-order variational derivative operator. On the basis of (54) and (56), we also have the reduced form

$$\boldsymbol{K} = \sum_{i=0}^{n} (\partial_{\boldsymbol{F}_i} \psi_{\mathrm{r}}) \boldsymbol{F}_i^{\mathrm{T}} \tag{58}$$

for the Kirchhoff stress from (52).

6 Results Based on Free Energy Models from EST

Specific forms of (54) are determined by either the WNL canonical relations $(26)_2$ and $(27)_1$, or by the corresponding WNL QH relations $(46)_2$ and $(45)_1$, respectively. In the WNL canonical formulation based on the reduced MFI form (34) of U, $(\partial_{\boldsymbol{F}_i} \Psi_{\mathrm{r}}) \boldsymbol{F}_i^{\mathrm{T}}$ is determined by (37). Substituting this into (58), we obtain

$$\boldsymbol{K} = V_{\mathrm{r}}^{-1} \sum_{i=0}^{n} \left\langle \sum_{a<b} U_{ab} \boldsymbol{d}_{ab} \otimes \boldsymbol{g}_{\mathrm{r}ab}^{i} - \sum_{a} (\boldsymbol{p}_a \otimes \boldsymbol{p}_a / m_a) \big(\boldsymbol{G}_{\mathrm{r}a}^{i} \boldsymbol{F}_{\mathrm{r}a}^{-1} \big)^{\mathrm{T}} \right\rangle \tag{59}$$

relative to the reference volume V_{r}. Since $\sum_{i=0}^{n} \boldsymbol{g}_{\mathrm{r}ab}^{i} = \boldsymbol{r}_{ab}$ and $\sum_{i=0}^{n} \boldsymbol{G}_{\mathrm{r}a}^{i} = \boldsymbol{F}_{\mathrm{r}a}$ in the context of (23), the right-hand side of (59) simplifies to

$$\begin{aligned} &\sum_{i=0}^{n} \left\langle \sum_{a<b} U_{ab} \boldsymbol{d}_{ab} \otimes \boldsymbol{g}_{\mathrm{r}ab}^{i} - \sum_{a} (\boldsymbol{p}_a \otimes \boldsymbol{p}_a / m_a) \big(\boldsymbol{G}_{\mathrm{r}a}^{i} \boldsymbol{F}_{\mathrm{r}a}^{-1} \big)^{\mathrm{T}} \right\rangle \\ &\quad = \left\langle \sum_{a<b} U_{ab} \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab} / r_{ab} - \sum_{a} \boldsymbol{p}_a \otimes \boldsymbol{p}_a / m_a \right\rangle. \end{aligned} \tag{60}$$

Substituting this back into (58) yields the WNL canonical form

$$\boldsymbol{K} = V_{\mathrm{r}}^{-1} \left\langle \sum_{a<b} U_{ab} \boldsymbol{r}_{ab} \otimes \boldsymbol{r}_{ab} / r_{ab} - \sum_{a} \boldsymbol{p}_a \otimes \boldsymbol{p}_a / m_a \right\rangle, \tag{61}$$

of the Kirchhoff stress. This is the same form as that of $(\mathcal{D}_{\boldsymbol{F}} \psi_{\mathrm{r}}) \boldsymbol{F}^{\mathrm{T}}$ resulting from (16) in SNL canonical case. Both of these can be compared with the WNL QH relation

$$\boldsymbol{K} = V_{\mathrm{r}}^{-1} \sum_{a<b} \left[\bar{U}_{ab} + \frac{1}{2} k_{\mathrm{B}} \theta \sum_{r=1}^{m} \partial_{\bar{r}_{ab}} \ln \lambda_r \right] \bar{\boldsymbol{r}}_{ab} \otimes \bar{\boldsymbol{r}}_{ab} / \bar{r}_{ab} \tag{62}$$

for $\boldsymbol{K}$ resulting from (48), and with the SNL-QH relation for $(\mathcal{D}_{\boldsymbol{F}} \psi_{\mathrm{r}}^{\mathrm{qh}}) \boldsymbol{F}^{\mathrm{T}}$ resulting from (47). Since all of these relations are constitutively symmetric via material frame-indifference and (A.3), they satisfy angular momentum balance $(51)_2$ identically.

Finally, consider the second derivatives of ψ_{r} based on the WNL canonical formulation, $(26)_2$ and (54), which determine equilibrium thermoelastic material properties (e.g., [29, Chap. 10]). These include the referential heat capacity

$$-\theta \partial_\theta \partial_\theta \psi_{\mathrm{r}} = V_{\mathrm{r}}^{-1} \operatorname{cov}(H_{\mathrm{r}}, H_{\mathrm{r}}) / k_{\mathrm{B}} \theta^2, \tag{63}$$

the higher-order referential thermal expansion

$$\partial_\theta \partial_{\boldsymbol{F}_i} \psi_{\mathrm{r}} = V_{\mathrm{r}}^{-1} \operatorname{cov}(H_{\mathrm{r}}, \partial_{\boldsymbol{F}_i} H_{\mathrm{r}}) / k_{\mathrm{B}} \theta^2, \tag{64}$$

as well as higher-order referential elastic stiffness

$$\partial_{\boldsymbol{F}_j}\partial_{\boldsymbol{F}_i}\psi_{\mathrm{r}} = V_{\mathrm{r}}^{-1}\langle\partial_{\boldsymbol{F}_j}\partial_{\boldsymbol{F}_i}H_{\mathrm{r}}\rangle - V_{\mathrm{r}}^{-1}\mathrm{cov}(\partial_{\boldsymbol{F}_i}H_{\mathrm{r}}, \partial_{\boldsymbol{F}_j}H_{\mathrm{r}})/k_{\mathrm{B}}\theta, \tag{65}$$

with $\mathrm{cov}(a,b) := \langle(a-\langle a\rangle)\otimes(b-\langle b\rangle)\rangle = \langle a\otimes b\rangle - \langle a\rangle\otimes\langle b\rangle$ the covariance. In particular, note that

$$\begin{aligned}\partial_{\boldsymbol{F}_j}\partial_{\boldsymbol{F}_i}H_{\mathrm{r}} = &\sum_{a<b}\sum_{c<d}U_{abcd}(\partial_{\boldsymbol{F}_i}\boldsymbol{r}_{ab})^{\mathrm{T}}(\boldsymbol{d}_{ab}\otimes\boldsymbol{d}_{cd})(\partial_{\boldsymbol{F}_j}\boldsymbol{r}_{cd})\\ &+\sum_{a<b}U_{ab}r_{ab}^{-1}(\partial_{\boldsymbol{F}_i}\boldsymbol{r}_{ab})^{\mathrm{T}}(\boldsymbol{I}-\boldsymbol{d}_{ab}\otimes\boldsymbol{d}_{ab})(\partial_{\boldsymbol{F}_j}\boldsymbol{r}_{ab})\\ &-\sum_{a}(\partial_{\boldsymbol{F}_i}\boldsymbol{F}_{\mathrm{r}a})^{\mathrm{T}}(\boldsymbol{p}_a\otimes\boldsymbol{p}_a/m_a)\big(\partial_{\boldsymbol{F}_j}\boldsymbol{F}_{\mathrm{r}a}^{-\mathrm{T}}\big)\end{aligned} \tag{66}$$

is obtained from $(29)_1$ and $(36)_1$. The relations (64) and (65) represent direct generalizations of standard (i.e., $n=0$) referential thermoelastic properties (e.g., [29, §§10.5–10.6]) to the current context. As done in the standard case, referential material properties such as $\partial_\theta\partial_{\boldsymbol{F}_i}\psi_{\mathrm{r}}$ and $\partial_{\boldsymbol{F}_j}\partial_{\boldsymbol{F}_i}\psi_{\mathrm{r}}$ can also be expressed in spatial form. For example, the latter is transformed into the spatial form $\boldsymbol{\mathcal{S}}_{\mathrm{c}2}^{ij}$ via the definition

$$\boldsymbol{A}\cdot\boldsymbol{\mathcal{S}}_{\mathrm{c}2}^{ij}\boldsymbol{B} := (\det\boldsymbol{F})^{-1}\boldsymbol{A}\boldsymbol{F}_i\cdot(\partial_{\boldsymbol{F}_j}\partial_{\boldsymbol{F}_i}\psi_{\mathrm{r}})[\boldsymbol{B}\boldsymbol{F}_j]. \tag{67}$$

We then have

$$\boldsymbol{\mathcal{S}}_{\mathrm{c}2}^{ij} = V_{\mathrm{c}}^{-1}\big\langle\boldsymbol{\mathcal{H}}_{\mathrm{r}2}^{ij}\big\rangle - V_{\mathrm{c}}^{-1}\mathrm{cov}\big((\partial_{\boldsymbol{F}_i}H_{\mathrm{r}})\boldsymbol{F}_i^{\mathrm{T}}, (\partial_{\boldsymbol{F}_j}H_{\mathrm{r}})\boldsymbol{F}_j^{\mathrm{T}}\big)/k_{\mathrm{B}}\theta, \tag{68}$$

with $V_{\mathrm{c}} = (\det\boldsymbol{F})V_{\mathrm{r}}$, $(\partial_{\boldsymbol{F}_i}H_{\mathrm{r}})\boldsymbol{F}_i^{\mathrm{T}}$ from (36), and $\boldsymbol{\mathcal{H}}_{\mathrm{r}2}^{ij}$ defined by

$$\boldsymbol{A}\cdot\boldsymbol{\mathcal{H}}_{\mathrm{r}2}^{ij}\boldsymbol{B} := \boldsymbol{A}\boldsymbol{F}_i\cdot(\partial_{\boldsymbol{F}_j}\partial_{\boldsymbol{F}_i}H_{\mathrm{r}})[\boldsymbol{B}\boldsymbol{F}_j] \tag{69}$$

analogous to $\boldsymbol{\mathcal{S}}_{\mathrm{c}2}^{ij}$. On this basis, one obtains

$$\begin{aligned}\boldsymbol{\mathcal{H}}_{\mathrm{r}2}^{ij} = &\sum_{a<b}\sum_{c<d}U_{abcd}\big(\boldsymbol{d}_{ab}\otimes\boldsymbol{g}_{\mathrm{r}ab}^{i}\big)\otimes\big(\boldsymbol{d}_{cd}\otimes\boldsymbol{g}_{\mathrm{r}cd}^{j}\big)\\ &+\sum_{a<b}U_{ab}r_{ab}^{-1}\big[\boldsymbol{I}\,\square\,\big(\boldsymbol{g}_{\mathrm{r}ab}^{j}\otimes\boldsymbol{g}_{\mathrm{r}ab}^{i}\big)-\big(\boldsymbol{d}_{ab}\otimes\boldsymbol{g}_{\mathrm{r}ab}^{i}\big)\otimes\big(\boldsymbol{d}_{ab}\otimes\boldsymbol{g}_{\mathrm{r}ab}^{j}\big)\big]\\ &+\sum_{a}(\boldsymbol{p}_a\otimes\boldsymbol{p}_a/m_a)\big(\boldsymbol{G}_{\mathrm{r}a}^{j}\boldsymbol{F}_{\mathrm{r}a}^{-1}\big)^{\mathrm{T}}\triangle\big(\boldsymbol{G}_{\mathrm{r}a}^{i}\boldsymbol{F}_{\mathrm{r}a}^{-1}\big)^{\mathrm{T}}\end{aligned} \tag{70}$$

via (30) and (66) in terms of $(\boldsymbol{A}\,\square\,\boldsymbol{B})\boldsymbol{C} := \boldsymbol{A}\boldsymbol{C}\boldsymbol{B}$ and $(\boldsymbol{A}\triangle\boldsymbol{B})\boldsymbol{C} := \boldsymbol{A}\boldsymbol{C}^{\mathrm{T}}\boldsymbol{B}$. In contrast to that $(4+i+j)$ of $\partial_{\boldsymbol{F}_j}\partial_{\boldsymbol{F}_i}\psi_{\mathrm{r}}$, note that the order of $\boldsymbol{\mathcal{S}}_{\mathrm{c}2}^{ij}$ is 4, independent of i and j. Analogously, the (SI) units $\mathrm{J/m}^{3-i-j}$ of $\partial_{\boldsymbol{F}_j}\partial_{\boldsymbol{F}_i}\psi_{\mathrm{r}}$ depend on i and j, while those $\mathrm{J/m}^3$ of $\boldsymbol{\mathcal{S}}_{\mathrm{c}2}^{ij}$ do not. Consequently, $\boldsymbol{\mathcal{S}}_{\mathrm{c}2}^{ij}$ has the same units as the fourth-order elastic stiffness tensor in standard equilibrium thermoelasticity for all i and j.

7 Example: Second-Order Gradient Elasticity

As an illustration and example of selected theoretical results in this work, consider lastly approximation of the EST-based WNL free energy $(26)_2$ by specific forms of the phenomeno-

logical free energy density (54). For simplicity, attention is restricted to zero temperature and $n \leqslant 2$ in this section.

7.1 Free Energy

In the context of material frame-indifference (see Appendix B), the phenomenological free energy density (54) takes the reduced form[7]

$$\psi_{\mathrm{r}}(0, \boldsymbol{F}_0, \boldsymbol{F}_1, \boldsymbol{F}_2) = \psi_{\mathrm{i}}(0, \boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2) \tag{71}$$

via (B.2) for $n = 2$ at zero temperature with respect to the right Cauchy-Green deformation $\boldsymbol{C}_0 = \boldsymbol{F}^{\mathrm{T}}\boldsymbol{F}_0 = \boldsymbol{F}^{\mathrm{T}}\boldsymbol{F} = \boldsymbol{C}$ as well as the first-order $\boldsymbol{C}_1 = \boldsymbol{F}^{\mathrm{T}}\boldsymbol{F}_1$ and second-order $\boldsymbol{C}_2 = \boldsymbol{F}^{\mathrm{T}}\boldsymbol{F}_2$ strain-gradient-like deformation measures from (B.3). Likewise, the EST-based WNL free energy $(26)_2$ simplifies to

$$\Psi_{\mathrm{r}}(0, \boldsymbol{F}_0, \boldsymbol{F}_1, \boldsymbol{F}_2) = U_{\mathrm{i}}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2) - U_{\mathrm{i}}(\boldsymbol{I}, \boldsymbol{0}, \boldsymbol{0}) \tag{72}$$

at zero-temperature for $n = 2$. Here,

$$U_{\mathrm{i}}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2) := U_{\mathrm{d}}\big(r_{12}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2), \ldots, r_{N-1\,N}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)\big) \tag{73}$$

is determined by the interatomic potential (A.3), and

$$r_{ab}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2) := \sqrt{\boldsymbol{c}_{ab}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2) \cdot \boldsymbol{C}_0^{-1}\boldsymbol{c}_{ab}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)} \tag{74}$$

follows from (35) with

$$\begin{aligned}\boldsymbol{c}_{ab}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2) := {} & \boldsymbol{C}_0\boldsymbol{s}_{ra} - \boldsymbol{C}_0\boldsymbol{s}_{rb} + (\boldsymbol{C}_1\boldsymbol{s}_{ra})\boldsymbol{s}_{ra} - (\boldsymbol{C}_1\boldsymbol{s}_{rb})\boldsymbol{s}_{rb} \\ & + \big((\boldsymbol{C}_2\boldsymbol{s}_{ra})\boldsymbol{s}_{ra}\big)\boldsymbol{s}_{ra} - \big(\big(\boldsymbol{C}_2\boldsymbol{s}_{rb}\big)\boldsymbol{s}_{rb}\big)\boldsymbol{s}_{rb}.\end{aligned} \tag{75}$$

Assuming centrosymmetry (e.g., [1]), let (71) be given by the specific form

$$\begin{aligned}V_{\mathrm{r}}\psi_{\mathrm{i}}(0, \boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2) = {} & \frac{1}{2}\boldsymbol{C}_0 \cdot (\partial_{\boldsymbol{C}_0}\partial_{\boldsymbol{C}_0}U_{\mathrm{i}})|_0\boldsymbol{C}_0 + \frac{1}{2}\boldsymbol{C}_1 \cdot (\partial_{\boldsymbol{C}_1}\partial_{\boldsymbol{C}_1}U_{\mathrm{i}})|_0\boldsymbol{C}_1 \\ & + (\partial_{\boldsymbol{C}_2}U_{\mathrm{i}})|_0 \cdot \boldsymbol{C}_2 + \frac{1}{2}\boldsymbol{C}_2 \cdot (\partial_{\boldsymbol{C}_2}\partial_{\boldsymbol{C}_2}U_{\mathrm{i}})|_0\boldsymbol{C}_2\end{aligned} \tag{76}$$

based on second-order Taylor-series expansion of (73) about $(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2) = (\boldsymbol{I}, \boldsymbol{0}, \boldsymbol{0})$ with respect to a reference volume V_{r}. Here, $(\partial_{\boldsymbol{C}_2}U_{\mathrm{i}})|_0 := (\partial_{\boldsymbol{C}_2}U_{\mathrm{i}})(0, \boldsymbol{I}, \boldsymbol{0}, \boldsymbol{0})$ and so on. In the standard $n = 0$ case, this is formally analogous for example to the approach of [24] based on material-symmetry-adapted strain tensor components. In particular, note that $\partial_{\boldsymbol{C}_0}U_{\mathrm{i}}|_0 \equiv \boldsymbol{0}$ for zero stress (e.g., Kirchhoff stress (85) below), while $\partial_{\boldsymbol{C}_1}U_{\mathrm{i}}|_0$ and $\partial_{\boldsymbol{C}_1}\partial_{\boldsymbol{C}_2}U_{\mathrm{i}}|_0$ vanish identically via centrosymmetry since $\boldsymbol{C}_1$ is determined by an odd gradient of $\boldsymbol{F}$. On the other hand, since $\boldsymbol{C}_2$ is even in this sense,

$$(\partial_{\boldsymbol{C}_2}U_{\mathrm{i}})|_0 = \sum_{a<b} U_{ab}|_0\,(\partial_{\boldsymbol{C}_2}r_{ab})|_0 \tag{77}$$

[7] Except where needed, $\boldsymbol{x}_{\mathrm{r}}$ and $\boldsymbol{s}_{\mathrm{r}}$ are suppressed in the notation from now on for brevity.

is generally non-zero. Besides this last relation, (73) also yields

$$(\partial_{\boldsymbol{C}_i}\partial_{\boldsymbol{C}_j}U_{\mathrm{i}})|_0 = \sum_{a<b}\sum_{c<d} U_{abcd}|_0(\partial_{\boldsymbol{C}_i}r_{ab})|_0 \otimes (\partial_{\boldsymbol{C}_j}r_{cd})|_0 + \sum_{a<b} U_{ab}|_0(\partial_{\boldsymbol{C}_i}\partial_{\boldsymbol{C}_j}r_{ab})|_0 \tag{78}$$

with $U_{ab} := \partial_{r_{ab}}U_{\mathrm{d}}$ the atomic bond force, and $U_{abcd} := \partial_{r_{ab}}\partial_{r_{cd}}U_{\mathrm{d}}$ the atomic bond stiffness. Here,

$$\begin{aligned}
r_{ab}(\boldsymbol{I},\boldsymbol{0},\boldsymbol{0}) &= \boldsymbol{s}_{\mathrm{r}a} - \boldsymbol{s}_{\mathrm{r}b},\\
(\partial_{\boldsymbol{C}_0}r_{ab})(\boldsymbol{I},\boldsymbol{0},\boldsymbol{0}) &= \boldsymbol{d}_{\mathrm{r}ab} \otimes (\boldsymbol{s}_{\mathrm{r}a} - \boldsymbol{s}_{\mathrm{r}b}),\\
(\partial_{\boldsymbol{C}_1}r_{ab})(\boldsymbol{I},\boldsymbol{0},\boldsymbol{0}) &= \boldsymbol{d}_{\mathrm{r}ab} \otimes (\boldsymbol{s}_{\mathrm{r}a} \otimes \boldsymbol{s}_{\mathrm{r}a} - \boldsymbol{s}_{\mathrm{r}b} \otimes \boldsymbol{s}_{\mathrm{r}b}),\\
(\partial_{\boldsymbol{C}_2}r_{ab})(\boldsymbol{I},\boldsymbol{0},\boldsymbol{0}) &= \boldsymbol{d}_{\mathrm{r}ab} \otimes (\boldsymbol{s}_{\mathrm{r}a} \otimes \boldsymbol{s}_{\mathrm{r}a} \otimes \boldsymbol{s}_{\mathrm{r}a} - \boldsymbol{s}_{\mathrm{r}b} \otimes \boldsymbol{s}_{\mathrm{r}b} \otimes \boldsymbol{s}_{\mathrm{r}b}),\\
(\partial_{\boldsymbol{C}_i}\partial_{\boldsymbol{C}_j}r_{ab})(\boldsymbol{I},\boldsymbol{0},\boldsymbol{0}) &= (\Pi_{i+1}\boldsymbol{s}_{\mathrm{r}})^{\mathrm{T}}_{ab}\boldsymbol{D}_{\mathrm{r}ab}(\Pi_{j+1}\boldsymbol{s}_{\mathrm{r}})_{ab},
\end{aligned} \tag{79}$$

from (74) with

$$\boldsymbol{d}_{\mathrm{r}ab} := (\boldsymbol{s}_{\mathrm{r}a} - \boldsymbol{s}_{\mathrm{r}b})/|\boldsymbol{s}_{\mathrm{r}a} - \boldsymbol{s}_{\mathrm{r}b}|, \qquad \boldsymbol{D}_{\mathrm{r}ab} := (\boldsymbol{I} - \boldsymbol{d}_{\mathrm{r}ab} \otimes \boldsymbol{d}_{\mathrm{r}ab})/|\boldsymbol{s}_{\mathrm{r}a} - \boldsymbol{s}_{\mathrm{r}b}|. \tag{80}$$

In particular, then, the isothermal elastic stiffness $V_{\mathrm{r}}^{-1}(\partial_{\boldsymbol{C}_0}\partial_{\boldsymbol{C}_0}U_{\mathrm{i}})|_0$ as well as the corresponding first-order $V_{\mathrm{r}}^{-1}(\partial_{\boldsymbol{C}_1}\partial_{\boldsymbol{C}_1}U_{\mathrm{i}})|_0$ and second-order $V_{\mathrm{r}}^{-1}(\partial_{\boldsymbol{C}_2}\partial_{\boldsymbol{C}_2}U_{\mathrm{i}})|_0$ "gradient" stiffnesses, are determined by (78).

7.2 Computational Comparisons

The following comparisons are based on the "plane-wave" deformation

$$\boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}}) = \boldsymbol{x}_{\mathrm{r}} + \boldsymbol{a}\cos(k\boldsymbol{\kappa}\cdot\boldsymbol{x}_{\mathrm{r}} + \pi/6) \tag{81}$$

of a fcc primitive unit cell with volume $V_{\mathrm{r}} = a^3/4$ and central atom located at $\boldsymbol{x}_{\mathrm{r}}$. Here, a is the lattice parameter, $\boldsymbol{a}$ is the displacement amplitude, $\boldsymbol{\kappa} \equiv 2\pi[001]/a$ is a wave vector in the first Brillouin zone, and $k \in [0, 1]$. In turn, (81) implies

$$\begin{aligned}
\boldsymbol{C}_0(\boldsymbol{x}_{\mathrm{r}}) &= \boldsymbol{I} + k^2|\boldsymbol{a}|^2\sin^2(k\boldsymbol{\kappa}\cdot\boldsymbol{x}_{\mathrm{r}} + \pi/6)\boldsymbol{\kappa}\otimes\boldsymbol{\kappa},\\
\boldsymbol{C}_1(\boldsymbol{x}_{\mathrm{r}}) &= \tfrac{1}{2}k^3|\boldsymbol{a}|^2\sin(2k\boldsymbol{\kappa}\cdot\boldsymbol{x}_{\mathrm{r}} + \pi/3)\boldsymbol{\kappa}\otimes\boldsymbol{\kappa}\otimes\boldsymbol{\kappa},\\
\boldsymbol{C}_2(\boldsymbol{x}_{\mathrm{r}}) &= -k^4|\boldsymbol{a}|^2\sin^2(k\boldsymbol{\kappa}\cdot\boldsymbol{x}_{\mathrm{r}} + \pi/6)\boldsymbol{\kappa}\otimes\boldsymbol{\kappa}\otimes\boldsymbol{\kappa}\otimes\boldsymbol{\kappa}.
\end{aligned} \tag{82}$$

As k increases, then, gradients of higher-order become increasingly important.

In the undeformed reference configuration (lattice), $\boldsymbol{s}_{\mathrm{r}} = (\boldsymbol{s}_{\mathrm{r}1}, \ldots, \boldsymbol{s}_{\mathrm{r}N})$ are known and prescribed. In this case, (82) determine $r_{ab}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)$ from (74). Given in addition U_{d}, $U_{\mathrm{i}}(\boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)$, $(\partial_{\boldsymbol{C}_2}U_{\mathrm{i}})|_0$, $(\partial_{\boldsymbol{C}_0}\partial_{\boldsymbol{C}_0}U_{\mathrm{i}})|_0$, $(\partial_{\boldsymbol{C}_1}\partial_{\boldsymbol{C}_1}U_{\mathrm{i}})|_0$, and $(\partial_{\boldsymbol{C}_2}\partial_{\boldsymbol{C}_2}U_{\mathrm{i}})|_0$, are then all determined, and so $\psi_{\mathrm{i}}(0, \boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)$ from (76).

As an example comparison of $V_{\mathrm{r}}^{-1}\Psi_{\mathrm{r}}(0, \boldsymbol{F}_0, \boldsymbol{F}_1, \boldsymbol{F}_2)$ from (72) and $\psi_{\mathrm{i}}(0, \boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)$ from (76), consider the results in Fig. 2 based on the EAM potential for Al of [32, 33] for U_{d}. The displacement amplitude $\boldsymbol{a}$ is assumed parallel to $\boldsymbol{\kappa}$ with magnitude $\|\boldsymbol{a}\| = 0.05\,V_{\mathrm{r}}^{1/3}$ (much smaller than the cutoff radius of the potential). As evident, the zero- and first-order strain-gradient energies (brown and green curves) begin to deviate both qualitatively and quantitatively from the second-order strain-gradient and EST-based cases (blue and red curves) for k above about 0.09. For k above about 0.34, even $\psi_{\mathrm{i}}(0, \boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)$ begins to deviate quantitatively from $V_{\mathrm{r}}^{-1}\Psi_{\mathrm{r}}(0, \boldsymbol{F}_0, \boldsymbol{F}_1, \boldsymbol{F}_2)$.

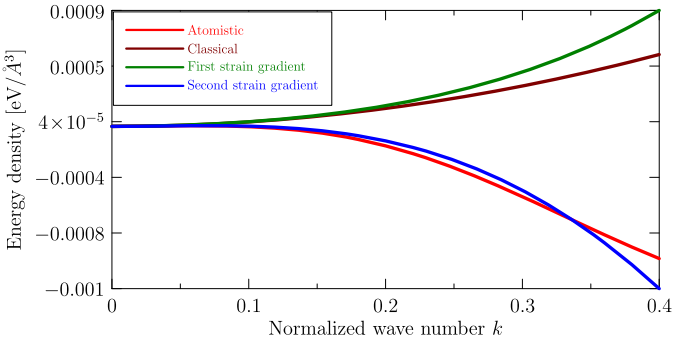

Fig. 2 Comparison of $V_\mathrm{r}^{-1}\Psi_\mathrm{r}(0, \boldsymbol{F}_0, \boldsymbol{F}_1, \boldsymbol{F}_2)$ from (72) (red curve) and $\psi_\mathrm{i}(0, \boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)$ from (76) as a function of k for $\boldsymbol{a}$ parallel to $\boldsymbol{\kappa}$ (i.e., [001]). Brown curve (classical): $\psi_\mathrm{i}(0, \boldsymbol{C}_0, \boldsymbol{0}, \boldsymbol{0})$. Green curve (first strain gradient): $\psi_\mathrm{i}(0, \boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{0})$. Blue curve (second strain gradient): $\psi_\mathrm{i}(0, \boldsymbol{C}_0, \boldsymbol{C}_1, \boldsymbol{C}_2)$. See text for discussion (Color figure online)

8 Summary and Discussion

In this work, model relations for the energetic thermoelasticity of non-simple materials have been obtained with the help of equilibrium statistical thermodynamics (EST) as well as phenomenologically via continuum thermodynamics.

In the EST context, both the (unrestricted) canonical formulation, as well as the (restricted) quasi-harmonic (QH) approximation, have been considered. With respect to these, both strongly non-local (SNL) and weakly non-local (WNL) formulations of energetic thermoelasticity have been pursued. Principle results of the formulation include the SNL continuum form (11) for the EST canonical free energy Ψ_r and its WNL approximation (26). In addition, the approximations (46) to these have been formulated in the context of the QH approximation to the unrestricted canonical formulation. As discussed in the text, the WNL form of either of these can be used to determine the phenomenological free energy density (54) for higher-order deformation gradient thermoelasticity.

A basic aspect of the continuum thermodynamic formulation of higher-order deformation gradient thermoelasticity in Sect. 5 is the generalization (50) of the (mechanical) energy flux $\boldsymbol{h}_\mathrm{r}$ in terms of the higher-order (hyper)stress measures $\boldsymbol{P}_1, \ldots, \boldsymbol{P}_n$ conjugate to $\boldsymbol{F}_1, \ldots, \boldsymbol{F}_n$. Exploiting the Euclidean frame-indifference of the energy balance (e.g., [29, Chap. 6]), a direct consequence of (50) is the generalized Kirchhoff stress (52). In the context of the dissipation principle, (50) and (54) result in the generalized hyperelastic relations (56) for $\boldsymbol{P}_1, \ldots, \boldsymbol{P}_n$ and so the corresponding form (58) for the Kirchoff stress. As shown by the variational formulation of the corresponding boundary-value problem in Appendix C, the direct formulation of Sect. 5 is completely consistent with a variational one in the spirit of [14, 15].

Central to the current treatment of atomistic-continuum coupling is the finite, non-affine relation $\boldsymbol{r}_a = \boldsymbol{\chi}(\boldsymbol{r}_{ra})$ from (3) for the effect of continuum deformation on atomic position. For uniform (affine) local deformation $\boldsymbol{\chi}(\boldsymbol{x}_\mathrm{r}) = \boldsymbol{F}\,\boldsymbol{x}_\mathrm{r}$, note that (3) reduces to the "standard" infinitesimal, affine relation $\boldsymbol{r}_a = \boldsymbol{\chi}(\boldsymbol{x}_\mathrm{r}) + \boldsymbol{F}(\boldsymbol{x}_\mathrm{r})\,\boldsymbol{s}_{ra} = \boldsymbol{F}\,\boldsymbol{r}_{ra}$ (e.g., [23, §8.1.3]). From the point of view of Hamilton's equations, (3) represents a so-called "canonical" transformation of $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$ (e.g., [8, 11, 18, 23, §8.1]). Indeed, the corresponding generator takes the form $G(\boldsymbol{p}, \boldsymbol{r}_\mathrm{r}) = -\sum_a \boldsymbol{p}_a \cdot \boldsymbol{\chi}(\boldsymbol{r}_{ra})$ [cf. 23, Eq. (8.46)]. Then $\boldsymbol{r}_a = -\partial_{\boldsymbol{p}_a} G = \boldsymbol{\chi}(\boldsymbol{r}_{ra})$ corresponds to (3), and $\boldsymbol{p}_{ra} = -\partial_{\boldsymbol{r}_{ra}} G = \boldsymbol{F}^\mathrm{T}(\boldsymbol{r}_{ra})\,\boldsymbol{p}_a$ to $(4)_2$. This is in contrast to the quasi-harmonic

(QH) case, in which the mean atomic positions are assumed to deform with the continuum according to the generalized Cauchy-Born relation (39). As from (3) via in particular (7) and (23) in the canonical case, both SNL- and WNL-based QH formulations of energetic thermoelasticity ensue from (39) via (40).

The WNL formulation of atomistic-continuum kinematics in Sect. 3 and in particular $(22)_1$ can be compared for example with the recent treatment of [1]. They work with the polynomial-map-based approximation

$$\tilde{\boldsymbol{x}} = \tilde{\boldsymbol{\chi}}(\boldsymbol{x}_\mathrm{r}) = \boldsymbol{\chi}_0 + \boldsymbol{F}_0\boldsymbol{x}_\mathrm{r} + \cdots + \frac{1}{(m+1)!}\left(\cdots\left(\boldsymbol{F}_0^{(m)}\boldsymbol{x}_\mathrm{r}\right)\boldsymbol{x}_\mathrm{r}\cdots\right)\boldsymbol{x}_\mathrm{r} \tag{83}$$

to $\boldsymbol{\chi}(\boldsymbol{x}_\mathrm{r})$. Here, $\boldsymbol{\chi}_0$ is a constant vector, $\boldsymbol{F}_0$ a constant second-order tensor, and $\boldsymbol{F}_0^{(i)}$ $(i = 1, \ldots, m)$ constant symmetric tensors of order $i + 2$. The distance $\tilde{r}^{\alpha\beta} := |\tilde{\boldsymbol{r}}^{\alpha\beta}|$ between atoms (or primitive unit cells) α and β with $\tilde{\boldsymbol{r}}^{\alpha\beta} := \tilde{\boldsymbol{x}}^\alpha - \tilde{\boldsymbol{x}}^\beta$ is then determined by $\tilde{r}^{\alpha\beta}(\boldsymbol{x}_\mathrm{r}^\alpha, \boldsymbol{x}_\mathrm{r}^\beta; \boldsymbol{C}_0, \boldsymbol{C}_0^{(1)}, \ldots, \boldsymbol{C}_0^{(m)})$ in terms of the higher-order continuum deformation measures $\boldsymbol{C}_0^{(i)} := \boldsymbol{F}_0^\mathrm{T}\boldsymbol{F}_0^{(i)}$ formally analogous to $\boldsymbol{C}_i$ in (B.3). As discussed in [1], this can also be expressed with respect to $\boldsymbol{E}_0$ and $\boldsymbol{E}_0^{(1)}$, with $\boldsymbol{C}_0 = \boldsymbol{I} + 2\boldsymbol{E}_0$, and $\boldsymbol{C}_0^{(1)} = \mathrm{cyc}\,\boldsymbol{E}_0^{(1)}$ analogous to (B.9).

Although not treated explicitly in the text, the energetic constitutive relations formulated in the context of EST satisfy material frame-indifference (MFI). For example, in the (unrestricted) SNL case, $K_\mathrm{r}[\boldsymbol{F}] = K_\mathrm{r}[\boldsymbol{Q}\boldsymbol{F}]$ holds for (5), $U_\mathrm{r}[\boldsymbol{F}] = U_\mathrm{r}[\boldsymbol{Q}\boldsymbol{F}]$ for (17), and so $\Psi_\mathrm{r}[\theta, \boldsymbol{F}] = \Psi_\mathrm{r}[\theta, \boldsymbol{Q}\boldsymbol{F}]$ for (11), for all orthogonal $\boldsymbol{Q}$. Likewise, $\Psi_\mathrm{r}(\theta, \boldsymbol{F}_0, \ldots, \boldsymbol{F}_n) = \Psi_\mathrm{r}(\theta, \boldsymbol{Q}\boldsymbol{F}_0, \ldots, \boldsymbol{Q}\boldsymbol{F}_n)$ for $(26)_2$ holds in the (unrestricted) WNL case when $U_\mathrm{r}(\boldsymbol{F}_0, \ldots, \boldsymbol{F}_n)$ is given by (34). On the other hand, neither (11) nor $(26)_2$ are in MFI-based reduced form (e.g., [5, 21]). As discussed in detail in Appendix B, $\psi_\mathrm{i}(\theta, \boldsymbol{C}, \boldsymbol{C}_1, \ldots, \boldsymbol{C}_n)$ from (B.2), and $\psi_\mathrm{s}(\theta, \boldsymbol{E}, \nabla^1\boldsymbol{E}, \ldots, \nabla^n\boldsymbol{E})$ from (B.10), are but two among many possible such reduced forms for $\psi_\mathrm{r}(\theta, \boldsymbol{F}, \nabla^1\boldsymbol{F}, \ldots, \nabla^n\boldsymbol{F})$ from (54). Indeed, for example, ψ_i itself determines a third reduced form

$$\psi_\mathrm{e}(\theta, \boldsymbol{C}, \boldsymbol{E}_1, \ldots, \boldsymbol{E}_n) := \psi_\mathrm{i}(\theta, \boldsymbol{C}, \boldsymbol{C}\boldsymbol{E}_1, \ldots, \boldsymbol{C}\boldsymbol{E}_n) \tag{84}$$

of the free energy density in terms of the Eringen measures $\boldsymbol{E}_1, \ldots, \boldsymbol{E}_n$ with $\boldsymbol{E}_i := \boldsymbol{F}^{-1}\nabla^i\boldsymbol{F}$. Any of these reduced forms, and in particular (B.2), result in turn in corresponding reduced forms of energetic constitutive quantities. For example, the continuum thermodynamic relation (58) for the Kirchhoff stress reduces to

$$\boldsymbol{K} = 2\,\mathrm{sym}\sum_{i=0}^{n}\boldsymbol{F}(\partial_{\boldsymbol{C}_i}\psi_\mathrm{i})\boldsymbol{F}_i^\mathrm{T} \tag{85}$$

in the context of (B.2). Since $\boldsymbol{K}$ as given by (85) is symmetric, it satisfies angular momentum balance $(51)_2$ identically. Long ago, Noll (see, e.g., [17] or [27, §84]) established the fact that the MFI of ψ_r implies the symmetry of the Cauchy, and so Kirchhoff, stress for simple materials. As shown by (85), this holds in the more general WNL case as well.

As investigated in previous work (e.g., [6, 7, 16, 19, 22]), other issues from material theory for gradient continua besides MFI include higher-order material symmetry restrictions. As discussed in detail for example in [22], since $\nabla^1\boldsymbol{F}, \ldots, \nabla^n\boldsymbol{F}$ do not transform tensorially under change of compatible reference configuration, such material symmetry restrictions invariably involve the consideration of higher-order jets. On the atomistic side, the material symmetry of U_d from (A.3) is inherited by $\psi_\mathrm{i}(\boldsymbol{C}_0, \ldots, \boldsymbol{C}_n)$. Yet another issue concerns a dependence of free energy on higher-order (e.g., anharmonic) strain terms such as $\boldsymbol{E}\cdot(\boldsymbol{M}_4\boldsymbol{E})\boldsymbol{E}$

in comparison to strain gradient terms like $\boldsymbol{C}_1 \cdot \boldsymbol{G}_4 \boldsymbol{C}_1$. Although the corresponding moduli $\boldsymbol{M}_4$ and $\boldsymbol{G}_4$ are of the same order, they are different in character. Indeed, in contrast to $\boldsymbol{G}_4$, $\boldsymbol{M}_4$ is lengthscale-independent. In any case, these and other issues represent work in progress to be reported on in the future.

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Appendix A: Reduced Forms of the Interatomic Potential

Consider the action

$$a_{(\boldsymbol{t},\boldsymbol{Q})} U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = U(\boldsymbol{t} + \boldsymbol{Q}\boldsymbol{r}_1, \ldots, \boldsymbol{t} + \boldsymbol{Q}\boldsymbol{r}_N) \tag{A.1}$$

of the Euclidean group on U, including in particular pure translation ($\boldsymbol{Q} = \boldsymbol{I}$) and pure orthogonal transformation ($\boldsymbol{t} = \boldsymbol{0}$). As usual, the material frame-indifference (MFI) of U takes the form

$$a_{(\boldsymbol{t},\boldsymbol{Q})} U = U \quad \forall (\boldsymbol{t}, \boldsymbol{Q}), \qquad \sum_a \boldsymbol{r}_a \times \partial_{\boldsymbol{r}_a} U = \boldsymbol{0}. \tag{A.2}$$

For example, $U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = U_{\mathrm{t}}(\boldsymbol{r}_{12}, \ldots, \boldsymbol{r}_{N-1N})$ satisfies translational MFI (recall $\boldsymbol{r}_{ab} := \boldsymbol{r}_a - \boldsymbol{r}_b$). Using the Cauchy's representation theorem for simultaneous vector invariants (e.g., [27]), U_{t} can be shown (e.g., [2, 3]) to satisfy orthogonal MFI iff it can be expressed as a function of $\boldsymbol{d}_{12} \cdot \boldsymbol{d}_{23}, \ldots, \boldsymbol{d}_{N-2\,N-1} \cdot \boldsymbol{d}_{N-1\,N}$ (recall $\boldsymbol{d}_{ab} := \boldsymbol{r}_{ab}/r_{ab}$). As usual, the simpler distance-based form

$$U(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = U_{\mathrm{d}}(r_{12}, \ldots, r_{N-1\,N}) \tag{A.3}$$

is (at least) sufficient to satisfy orthogonal MFI, and satisfies differential orthogonal MFI $\sum_a \boldsymbol{r}_a \times \partial_{\boldsymbol{r}_a} U = \sum_{a<b} r_{ab}^{-1} (\partial_{r_{ab}} U_{\mathrm{d}})\, \boldsymbol{r}_{ab} \times \boldsymbol{r}_{ab} = \boldsymbol{0}$ identically. On the other hand, as discussed by [2, 4, 25], U_{d} is not unique for potentials beyond 4-body interactions. For such cases, the "cluster" form

$$U_{\mathrm{d}}(r_{12}, \ldots, r_{N-1\,N}) = \sum_{n=2}^{N} \sum_{l^n=1}^{M_n} U_{l^n}(r_{l_1^n l_2^n}, \ldots, r_{l_{n-1}^n l_n^n}) \tag{A.4}$$

of U_{d} is appropriate. In this form, each U_{l^n} is a n-body potential, and $M_n \leqslant (N/n)$ is the number of n-body interactions among N mass points. By requiring that each U_{l^n} vanish in the limit as the distance of any one of the interacting mass points to the others approaches infinity, this expansion can be formulated in a unique fashion.

Appendix B: Reduced Forms for the Continuum Free Energy Density

In the context of the continuum thermodynamic formulation from Sect. 5, the requirement of material frame-indifference

$$\psi_{\mathrm{r}}\big(\theta, \boldsymbol{F}, \nabla^1\boldsymbol{F}, \ldots, \nabla^n\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}\big) = \psi_{\mathrm{r}}\big(\theta, \boldsymbol{Q}\boldsymbol{F}, \boldsymbol{Q}\nabla^1\boldsymbol{F}, \ldots, \boldsymbol{Q}\nabla^n\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}\big) \quad \forall \boldsymbol{Q} \tag{B.1}$$

on $(54)_1$ and the choice $\boldsymbol{Q} \equiv \boldsymbol{R}^{\mathrm{T}} = \boldsymbol{U}^{-1}\boldsymbol{F}^{\mathrm{T}}$ result for example in the reduced form

$$\psi_{\mathrm{r}}\big(\theta, \boldsymbol{F}, \nabla^1\boldsymbol{F}, \ldots, \nabla^n\boldsymbol{F}; \boldsymbol{x}_{\mathrm{r}}\big) = \psi_{\mathrm{i}}(\theta, \boldsymbol{C}, \boldsymbol{C}_1, \ldots, \boldsymbol{C}_n; \boldsymbol{x}_{\mathrm{r}}) \tag{B.2}$$

of ψ_{r}, with $\psi_{\mathrm{i}}(\theta, \boldsymbol{C}, \boldsymbol{C}_1, \ldots, \boldsymbol{C}_n; \boldsymbol{x}_{\mathrm{r}}) := \psi_{\mathrm{r}}(\theta, \boldsymbol{C}^{\frac{1}{2}}, \boldsymbol{C}^{-\frac{1}{2}}\boldsymbol{C}_1, \ldots, \boldsymbol{C}^{-\frac{1}{2}}\boldsymbol{C}_n; \boldsymbol{x}_{\mathrm{r}})$ (subscript i stands for indifferent), $\boldsymbol{U} = \boldsymbol{C}^{\frac{1}{2}}$, $\boldsymbol{C} = \boldsymbol{F}^{\mathrm{T}}\boldsymbol{F}$, and

$$\boldsymbol{C}_i := \boldsymbol{F}^{\mathrm{T}}\boldsymbol{F}_i = \boldsymbol{F}^{\mathrm{T}}\nabla^i\boldsymbol{F}. \tag{B.3}$$

Clearly, (B.2) is a direct generalization of the zeroth-order reduction $\psi_{\mathrm{r}}(\theta, \boldsymbol{F}) = \psi_{\mathrm{i}}(\theta, \boldsymbol{C})$ to the current nth-order case. Since $r_{ab}(\boldsymbol{F}_0, \ldots, \boldsymbol{F}_n; \ldots)$ from (35) reduces to $r_{ab}(\boldsymbol{C}_0, \ldots, \boldsymbol{C}_n; \ldots)$ directly, the reduced form ψ_{i} of ψ_{r} in (B.2) also follows directly from the statistical thermodynamic treatment in the text.

Note that the deformation measures $\boldsymbol{C}_1, \ldots, \boldsymbol{C}_n$ defined in (B.3) are strain-gradient-like. This can be seen by considering the change in squared relative distance

$$|\boldsymbol{s}_{\mathrm{c}}|^2 - |\boldsymbol{s}_{\mathrm{r}}|^2 = \boldsymbol{s}_{\mathrm{r}} \cdot 2\boldsymbol{E}\,\boldsymbol{s}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}} \cdot (\boldsymbol{\Pi}_2\boldsymbol{s}_{\mathrm{r}})\boldsymbol{C}_1 + (\boldsymbol{\Pi}_2\boldsymbol{s}_{\mathrm{r}})\boldsymbol{C}_1 \cdot \boldsymbol{C}^{-1}(\boldsymbol{\Pi}_2\boldsymbol{s}_{\mathrm{r}})\boldsymbol{C}_1 + \cdots \tag{B.4}$$

via $(22)_1$ in a neighborhood of $\boldsymbol{x}_{\mathrm{c}} = \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}})$ (see Fig. 1). Here, $\boldsymbol{s}_{\mathrm{c}} := \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}} + \boldsymbol{s}_{\mathrm{r}}) - \boldsymbol{\chi}(\boldsymbol{x}_{\mathrm{r}})$, and $\boldsymbol{E} := \frac{1}{2}(\boldsymbol{C} - \boldsymbol{I})$ is the Green strain. Note that the zeroth-order special case $|\boldsymbol{s}_{\mathrm{c}}|^2 - |\boldsymbol{s}_{\mathrm{r}}|^2 = \boldsymbol{s}_{\mathrm{r}} \cdot 2\boldsymbol{E}\boldsymbol{s}_{\mathrm{r}}$ of (B.4) is consistent with $|d\boldsymbol{x}_{\mathrm{c}}|^2 - |d\boldsymbol{x}_{\mathrm{r}}|^2 = d\boldsymbol{x}_{\mathrm{r}} \cdot 2\boldsymbol{E}\,d\boldsymbol{x}_{\mathrm{r}}$. Since $\boldsymbol{C}^{-1}$ and $\boldsymbol{s}_{\mathrm{r}}$ are non-zero, (B.4) implies that $|\boldsymbol{s}_{\mathrm{c}}| = |\boldsymbol{s}_{\mathrm{r}}|$ iff $\boldsymbol{E}, \boldsymbol{C}_1, \ldots, \boldsymbol{C}_n, \ldots$ vanish; hence, $\boldsymbol{C}_1, \ldots, \boldsymbol{C}_n, \ldots$ are strain-gradient-like. Moreover, $\boldsymbol{C}_1, \ldots, \boldsymbol{C}_n$ can be expressed as functions of $\nabla^1\boldsymbol{E}$, …, $\nabla^n\boldsymbol{E}$. To show this, consider the identities

$$\begin{aligned}
&(\boldsymbol{C}_2\boldsymbol{a}_1)\boldsymbol{a}_2 \\
&\quad = (\nabla_{\boldsymbol{a}_1}\boldsymbol{C}_1)\boldsymbol{a}_2 - (\nabla_{\boldsymbol{a}_1}\boldsymbol{F})^{\mathrm{T}}\nabla_{\boldsymbol{a}_2}\boldsymbol{F}, \\
&\big((\boldsymbol{C}_3\boldsymbol{a}_1)\boldsymbol{a}_2\big)\boldsymbol{a}_3 \\
&\quad = (\nabla_{\boldsymbol{a}_1}\nabla_{\boldsymbol{a}_2}\boldsymbol{C}_1)\boldsymbol{a}_3 - (\nabla_{\boldsymbol{a}_1}\boldsymbol{F})^{\mathrm{T}}\nabla_{\boldsymbol{a}_2}\nabla_{\boldsymbol{a}_3}\boldsymbol{F} - (\nabla_{\boldsymbol{a}_1}\nabla_{\boldsymbol{a}_2}\boldsymbol{F})^{\mathrm{T}}\nabla_{\boldsymbol{a}_3}\boldsymbol{F}, \\
&\quad \vdots \\
&\big(\big(\cdots\big((\boldsymbol{C}_n\boldsymbol{a}_1)\boldsymbol{a}_2\big)\cdots\big)\boldsymbol{a}_{n-1}\big)\boldsymbol{a}_n \\
&\quad = (\nabla_{\boldsymbol{a}_1}\cdots\nabla_{\boldsymbol{a}_{n-1}}\boldsymbol{C}_1)\boldsymbol{a}_n - (\nabla_{\boldsymbol{a}_1}\boldsymbol{F})^{\mathrm{T}}\nabla_{\boldsymbol{a}_2}\cdots\nabla_{\boldsymbol{a}_n}\boldsymbol{F} - \cdots,
\end{aligned} \tag{B.5}$$

and

$$\begin{aligned}
(\nabla_{\boldsymbol{a}_1}\boldsymbol{F})^{\mathrm{T}}\nabla_{\boldsymbol{a}_2}\boldsymbol{F} &= (\boldsymbol{\Gamma}_1\boldsymbol{a}_1)^{\mathrm{T}}\boldsymbol{C}_1\boldsymbol{a}_2, \\
(\nabla_{\boldsymbol{a}_1}\nabla_{\boldsymbol{a}_2}\boldsymbol{F})^{\mathrm{T}}\nabla_{\boldsymbol{a}_3}\boldsymbol{F} &= \big[(\nabla_{\boldsymbol{a}_1}\boldsymbol{C}_1)\boldsymbol{a}_2 - (\boldsymbol{\Gamma}_1\boldsymbol{a}_1)^{\mathrm{T}}\boldsymbol{C}_1\boldsymbol{a}_2\big]^{\mathrm{T}}\boldsymbol{\Gamma}_1\boldsymbol{a}_3, \\
(\nabla_{\boldsymbol{a}_1}\boldsymbol{F})^{\mathrm{T}}\nabla_{\boldsymbol{a}_2}\nabla_{\boldsymbol{a}_3}\boldsymbol{F} &= (\boldsymbol{\Gamma}_1\boldsymbol{a}_1)^{\mathrm{T}}\big[(\nabla_{\boldsymbol{a}_2}\boldsymbol{C}_1)\boldsymbol{a}_3 - (\boldsymbol{\Gamma}_1\boldsymbol{a}_2)^{\mathrm{T}}\boldsymbol{C}_1\boldsymbol{a}_3\big], \\
&\vdots
\end{aligned} \tag{B.6}$$

for constant $\boldsymbol{a}_1, \ldots, \boldsymbol{a}_n$ with

$$\boldsymbol{\Gamma}_i := \boldsymbol{F}^{-1}\nabla^i \boldsymbol{F} = \boldsymbol{C}^{-1}\boldsymbol{C}_i. \tag{B.7}$$

In particular, note that $\boldsymbol{\Gamma}_1$ represents the affine (linear, Kozsul) connection "symbols" induced by $\boldsymbol{F}$. Analogously, in the context of the interpretation of $\boldsymbol{C}$ as a Riemann metric (e.g., [12, 13, 28]), $\boldsymbol{C}_1$ for example represents the corresponding metric connection symbols. Note that the results (B.5)–(B.7) determine $\boldsymbol{C}_2, \ldots, \boldsymbol{C}_n$ as functions of $\boldsymbol{C}$, $\boldsymbol{C}_1$, $\nabla^1\boldsymbol{C}_1$, …, $\nabla^{n-1}\boldsymbol{C}_1$. To proceed further, consider next the identity

$$2\,\boldsymbol{a}\cdot\big((\nabla\boldsymbol{E})\boldsymbol{c}\big)\boldsymbol{b} = \boldsymbol{a}\cdot\big(\boldsymbol{C}_1\boldsymbol{c}\big)\boldsymbol{b} + \boldsymbol{b}\cdot\big(\boldsymbol{C}_1\boldsymbol{c}\big)\boldsymbol{a} \tag{B.8}$$

between $\nabla\boldsymbol{E}$ and $\boldsymbol{C}_1$. Exploiting the symmetry $\boldsymbol{C}_1^{\mathrm{S}} = \boldsymbol{C}_1$ of $\boldsymbol{C}_1$ induced by that $(\nabla\boldsymbol{F})^{\mathrm{S}} = \nabla\boldsymbol{F}$ of $\nabla\boldsymbol{F} = \nabla\nabla\boldsymbol{\chi}$, (B.8) can be inverted via cyclic permutation of $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ to yield

$$\boldsymbol{C}_1(\nabla\boldsymbol{E}) = \mathrm{cyc}\,\nabla\boldsymbol{E} \tag{B.9}$$

with $\boldsymbol{a}\cdot((\mathrm{cyc}\,\boldsymbol{A}_1)\boldsymbol{c})\boldsymbol{b} := \boldsymbol{a}\cdot(\boldsymbol{A}_1\boldsymbol{c})\boldsymbol{b} + \boldsymbol{c}\cdot(\boldsymbol{A}_1\boldsymbol{b})\boldsymbol{a} - \boldsymbol{b}\cdot(\boldsymbol{A}_1\boldsymbol{a})\boldsymbol{c}$. Note that (B.9) implies that $\boldsymbol{C}_1$ is a linear function of $\nabla\boldsymbol{E}$. Consequently, (B.9) also implies that $\nabla^{i-1}\boldsymbol{C}_1$ is a linear function of $\nabla^i\boldsymbol{E}$ for $i = 2, \ldots, n$. In summary, then, $\boldsymbol{C}_1$, …, $\boldsymbol{C}_n$ are determined by $\boldsymbol{C}(\boldsymbol{E})$, $\nabla^1\boldsymbol{E}$, …, $\nabla^n\boldsymbol{E}$. Consequently, $\psi_{\mathrm{i}}(\theta, \boldsymbol{C}, \boldsymbol{C}_1, \ldots, \boldsymbol{C}_n; \boldsymbol{x}_{\mathrm{r}})$ always induces

$$\psi_{\mathrm{s}}\big(\theta, \boldsymbol{E}, \nabla^1\boldsymbol{E}, \ldots, \nabla^n\boldsymbol{E}; \boldsymbol{x}_{\mathrm{r}}\big) = \psi_{\mathrm{i}}(\theta, \boldsymbol{C}, \boldsymbol{C}_1, \ldots, \boldsymbol{C}_n; \boldsymbol{x}_{\mathrm{r}}) \tag{B.10}$$

in the context of higher-order strain-gradient thermoelasticity.

Appendix C: Variational Formulation of the Boundary-Value Problem

In order to connect with previous work for non-simple materials based on variational methods, and for completeness, the boundary-value problem implied by the direct formulation of higher-order deformation gradient energetic thermoelasticity in Sect. 5 is formulated here in variational form. Since the formulation is purely referential, we dispense with the subscript r on referential quantities in the rest of this section.

To this end, note that $(51)_1$ and the result for $\boldsymbol{P} = \boldsymbol{P}_0$ from (56) together imply the variational form

$$\delta^{n+1}_{\boldsymbol{\chi}}\psi = -\,\mathrm{div}\,\delta^n_{\boldsymbol{F}}\psi = \boldsymbol{0} \tag{C.1}$$

for linear momentum balance in the current context. For boundary conditions, attention is restricted to generalized displacement-traction-type (conservative) loading (e.g., [29, §13.3]) here. Let B represent a reference configuration, and ∂B its (smooth) boundary with (outward) unit normal $\boldsymbol{n}$. Generalizing the considerations of [15] to the current nth-order case, only the "normal" part $\nabla^i_{\boldsymbol{n}}\boldsymbol{\chi}$ of $\nabla^i\boldsymbol{\chi}$ is kinematically independent on ∂B. In this case,

$$W[\boldsymbol{\chi}] := -\int_{\partial_{\mathrm{f}}B}\big(\boldsymbol{t}_0\cdot\boldsymbol{\chi} + \boldsymbol{t}_1\cdot\nabla^1_{\boldsymbol{n}}\boldsymbol{\chi} + \cdots + \boldsymbol{t}_n\cdot\nabla^n_{\boldsymbol{n}}\boldsymbol{\chi}\big)\,da \tag{C.2}$$

represents the potential energy of loading in terms of the corresponding tractions $\boldsymbol{t}_0, \boldsymbol{t}_1, \ldots, \boldsymbol{t}_n$ on the flux part $\partial_{\mathrm{f}}B$ of ∂B. Then

$$P[\boldsymbol{\chi}] = F[\boldsymbol{\chi}] + W[\boldsymbol{\chi}], \qquad F[\boldsymbol{\chi}] := \int_B \psi\big(\nabla^1\boldsymbol{\chi}, \nabla^2\boldsymbol{\chi}, \ldots, \nabla^{n+1}\boldsymbol{\chi}\big)\,dv \tag{C.3}$$

represents the total (canonical) free energy (e.g., [29, §13.4]). Given (C.3), one obtains in turn

$$\begin{aligned}\delta P = &\int_B \big(\partial_{\nabla^1\boldsymbol{\chi}}\psi\cdot\delta\nabla^1\boldsymbol{\chi}+\cdots+\partial_{\nabla^{n+1}\boldsymbol{\chi}}\psi\cdot\delta\nabla^{n+1}\boldsymbol{\chi}\big)\,dv\\ &-\int_{\partial B}\big(\boldsymbol{t}_0\cdot\delta\boldsymbol{\chi}+\boldsymbol{t}_1\cdot\delta\nabla^1_{\boldsymbol{n}}\boldsymbol{\chi}+\cdots+\boldsymbol{t}_n\cdot\delta\nabla^n_{\boldsymbol{n}}\boldsymbol{\chi}\big)\,da\end{aligned}\tag{C.4}$$

for the first variation δP of P. Repeated integration by parts and application of the divergence theorem then yields

$$\delta P=\int_B \delta^{n+1}_{\boldsymbol{\chi}}\psi\cdot\delta\boldsymbol{\chi}\,dv+\int_{\partial B}\left\{(\boldsymbol{p}_0-\boldsymbol{t}_0)\cdot\delta\boldsymbol{\chi}+\sum_{i=1}^{n}(\boldsymbol{p}_i-\boldsymbol{t}_i)\cdot\nabla^i_{\boldsymbol{n}}\delta\boldsymbol{\chi}\right\}da\tag{C.5}$$

for δP with

$$\begin{aligned}\boldsymbol{p}_0&:=\boldsymbol{P}\boldsymbol{n}+\boldsymbol{p}_{01}+\cdots+\boldsymbol{p}_{0n},\\ \boldsymbol{p}_1&:=(\boldsymbol{P}_1\boldsymbol{n})\boldsymbol{n}+\boldsymbol{p}_{12}+\cdots+\boldsymbol{p}_{1n},\\ &\vdots\\ \boldsymbol{p}_{n-1}&:=\big(\cdots(\boldsymbol{P}_{n-1}\boldsymbol{n})\boldsymbol{n}\cdots\big)\boldsymbol{n}+\boldsymbol{p}_{n-1\,n},\\ \boldsymbol{p}_n&:=\big(\cdots(\boldsymbol{P}_n\boldsymbol{n})\boldsymbol{n}\cdots\big)\boldsymbol{n},\end{aligned}\tag{C.6}$$

via (56). Here, $\boldsymbol{p}_{ij}$ represents the sum of all terms depending on $\boldsymbol{P}_j\boldsymbol{n}$ which contribute to the ith-order boundary condition. As usual, $\delta\boldsymbol{\chi},\nabla^1_{\boldsymbol{n}}\delta\boldsymbol{\chi},\ldots,\nabla^n_{\boldsymbol{n}}\delta\boldsymbol{\chi}$ vanish on the kinematic part $\partial B\setminus\partial_{\mathrm{f}}B$ of ∂B by definition. Given (C.5), then,

$$\boldsymbol{0}=\delta^{n+1}_{\boldsymbol{\chi}}\psi=-\operatorname{div}\delta^{n}_{\nabla^1\boldsymbol{\chi}}\psi\tag{C.7}$$

in B, and

$$\boldsymbol{p}_0|_{\partial_{\mathrm{f}}B}=\boldsymbol{t}_0,\qquad \boldsymbol{p}_1|_{\partial_{\mathrm{f}}B}=\boldsymbol{t}_1,\qquad\ldots,\qquad \boldsymbol{p}_n|_{\partial_{\mathrm{f}}B}=\boldsymbol{t}_n,\tag{C.8}$$

on $\partial_{\mathrm{f}}B$, are necessary for $\delta P=0$. In particular, (C.7) is clearly consistent with $(51)_1$ in the form (C.1).

Determination of $\boldsymbol{p}_{01},\ldots,\boldsymbol{p}_{n-1\,n}$ in (C.6) follows via direct generalization of the approach of [15] to the current context. In particular, this is based on the split

$$\nabla=(\boldsymbol{n}\otimes\boldsymbol{n})\nabla+\nabla^{\mathrm{s}}\tag{C.9}$$

of the gradient operator into normal and tangential parts. In addition, the operator identity

$$\boldsymbol{S}_{i+1}\cdot\nabla^{\mathrm{s}}\boldsymbol{T}_i=\mathcal{D}_{\mathrm{s}}\boldsymbol{S}_{i+1}\cdot\boldsymbol{T}_i,\quad \mathcal{D}_{\mathrm{s}}\boldsymbol{S}_{i+1}:=(\operatorname{div}_{\mathrm{s}}\boldsymbol{n})\boldsymbol{S}_{i+1}\boldsymbol{n}-\operatorname{div}_{\mathrm{s}}\boldsymbol{S}_{i+1},\tag{C.10}$$

induced by the (smooth) surface divergence theorem, and the constraint

$$\boldsymbol{n}\cdot\boldsymbol{n}=1\quad\Longrightarrow\quad(\nabla\boldsymbol{n})^{\mathrm{T}}\boldsymbol{n}=\boldsymbol{0}\tag{C.11}$$

are employed in what follows. On this basis, consider the hierarchical system

$$\begin{aligned}
\boldsymbol{S}\cdot\nabla^1\boldsymbol{w} &= \boldsymbol{S}\boldsymbol{n}\cdot\nabla^1_{\boldsymbol{n}}\boldsymbol{w}+\mathcal{D}^1_{\mathrm{s}}\boldsymbol{S}\cdot\boldsymbol{w},\\
\boldsymbol{S}_1\cdot\nabla^2\boldsymbol{w} &= \boldsymbol{S}_1\boldsymbol{n}\cdot\nabla^1_{\boldsymbol{n}}\nabla^1\boldsymbol{w}+\mathcal{D}^1_{\mathrm{s}}\boldsymbol{S}_1\cdot\nabla^1\boldsymbol{w},\\
\boldsymbol{S}_2\cdot\nabla^3\boldsymbol{w} &= \boldsymbol{S}_2\boldsymbol{n}\cdot\nabla^1_{\boldsymbol{n}}\nabla^2\boldsymbol{w}+\mathcal{D}^1_{\mathrm{s}}\boldsymbol{S}_2\cdot\nabla^2\boldsymbol{w},\\
&\vdots\\
\boldsymbol{S}_{n-1}\cdot\nabla^n\boldsymbol{w} &= \boldsymbol{S}_{n-1}\boldsymbol{n}\cdot\nabla^1_{\boldsymbol{n}}\nabla^{n-1}\boldsymbol{w}+\mathcal{D}^1_{\mathrm{s}}\boldsymbol{S}_{n-1}\cdot\nabla^{n-1}\boldsymbol{w},
\end{aligned}\tag{C.12}$$

of relations via (C.9) and (C.10). In particular, $\boldsymbol{w}=\delta\boldsymbol{\chi}$, $\boldsymbol{S}=\boldsymbol{P}_1\boldsymbol{n}$, $\boldsymbol{S}_1=\boldsymbol{P}_2\boldsymbol{n}$, …, $\boldsymbol{S}_{n-1}=\boldsymbol{P}_n\boldsymbol{n}$. As it turns out, this hierarchy is partially recursive with respect to dependence on $\boldsymbol{w}$, $\nabla^1_{\boldsymbol{n}}\boldsymbol{w}$, …, $\nabla^n_{\boldsymbol{n}}\boldsymbol{w}$, in the following sense. Given $(\text{C.12})_1$, one obtains for example

$$\mathcal{D}^1_{\mathrm{s}}\boldsymbol{S}_1\cdot\nabla^1\boldsymbol{w}=\big(\mathcal{D}^1_{\mathrm{s}}\boldsymbol{S}_1\big)\boldsymbol{n}\cdot\nabla^1_{\boldsymbol{n}}\boldsymbol{w}+\mathcal{D}^2_{\mathrm{s}}\boldsymbol{S}_1\cdot\boldsymbol{w}\tag{C.13}$$

for the second term in $(\text{C.12})_2$. Together with

$$\begin{aligned}
\boldsymbol{S}_1\boldsymbol{n}\cdot\nabla^1_{\boldsymbol{n}}\nabla^1\boldsymbol{w} &= \boldsymbol{S}_1\boldsymbol{n}\cdot\nabla^1\nabla^1_{\boldsymbol{n}}\boldsymbol{w}-\boldsymbol{S}_1\boldsymbol{n}\cdot\big(\nabla^1\boldsymbol{w}\big)\big(\nabla^1\boldsymbol{n}\big)\\
&= (\boldsymbol{S}_1\boldsymbol{n})\boldsymbol{n}\cdot\nabla^2_{\boldsymbol{n}}\boldsymbol{w}+\mathcal{D}^1_{\mathrm{s}}(\boldsymbol{S}_1\boldsymbol{n})\cdot\nabla^1_{\boldsymbol{n}}\boldsymbol{w}+\mathrm{div}_{\mathrm{s}}\big((\boldsymbol{S}_1\boldsymbol{n})\big(\nabla^1\boldsymbol{n}\big)^{\mathrm{T}}\big)\cdot\boldsymbol{w}
\end{aligned}\tag{C.14}$$

via (C.9)–(C.11), (C.13) determines $(\text{C.12})_2$ in terms of $\boldsymbol{w}$, $\nabla^1_{\boldsymbol{n}}\boldsymbol{w}$, and $\nabla^2_{\boldsymbol{n}}\boldsymbol{w}$, i.e.,

$$\begin{aligned}
\boldsymbol{S}_1\cdot\nabla^2\boldsymbol{w} = (\boldsymbol{S}_1\boldsymbol{n})\boldsymbol{n}\cdot\nabla^2_{\boldsymbol{n}}\boldsymbol{w}&+\big\{\mathcal{D}^1_{\mathrm{s}}(\boldsymbol{S}_1\boldsymbol{n})+\big(\mathcal{D}^1_{\mathrm{s}}\boldsymbol{S}_1\big)\boldsymbol{n}\big\}\cdot\nabla^1_{\boldsymbol{n}}\boldsymbol{w}\\
&+\big\{\mathrm{div}_{\mathrm{s}}\big((\boldsymbol{S}_1\boldsymbol{n})\big(\nabla^1\boldsymbol{n}\big)^{\mathrm{T}}\big)+\mathcal{D}^2_{\mathrm{s}}\boldsymbol{S}_1\big\}\cdot\boldsymbol{w}.
\end{aligned}\tag{C.15}$$

In recursive fashion, (C.15) also determines the second term on the right-hand side of $(\text{C.12})_3$ in terms of $\boldsymbol{w}$, $\nabla^1_{\boldsymbol{n}}\boldsymbol{w}$, and $\nabla^2_{\boldsymbol{n}}\boldsymbol{w}$. Likewise, $(\text{C.12})_1$ and (C.15) determine the last two terms on the right-hand side of

$$\begin{aligned}
\boldsymbol{S}_2\boldsymbol{n}\cdot\nabla^1_{\boldsymbol{n}}\nabla^2\boldsymbol{w} &= \boldsymbol{S}_2\boldsymbol{n}\cdot\nabla^2\nabla^1_{\boldsymbol{n}}\boldsymbol{w}\\
&\quad+\big\{2\,\mathrm{div}_{\mathrm{s}}\big((\boldsymbol{S}_2\boldsymbol{n})\big(\nabla^1\boldsymbol{n}\big)^{\mathrm{T}}\big)-(\boldsymbol{S}_2\boldsymbol{n})\big(\nabla^2\boldsymbol{n}\big)^{\mathrm{T}}\big\}\cdot\nabla^1\boldsymbol{w}
\end{aligned}\tag{C.16}$$

in terms of these. Together with

$$\begin{aligned}
\boldsymbol{S}_2\boldsymbol{n}\cdot\nabla^2\nabla^1_{\boldsymbol{n}}\boldsymbol{w} = (\boldsymbol{S}_2\boldsymbol{n})\boldsymbol{n}\cdot\nabla^3_{\boldsymbol{n}}\boldsymbol{w}&+\big\{\mathcal{D}^1_{\mathrm{s}}\big((\boldsymbol{S}_2\boldsymbol{n})\boldsymbol{n}\big)+\big(\mathcal{D}^1_{\mathrm{s}}(\boldsymbol{S}_2\boldsymbol{n})\big)\boldsymbol{n}\big\}\cdot\nabla^2_{\boldsymbol{n}}\boldsymbol{w}\\
&+\big\{\mathrm{div}_{\mathrm{s}}\big(\big((\boldsymbol{S}_2\boldsymbol{n})\boldsymbol{n}\big)\big(\nabla^1\boldsymbol{n}\big)^{\mathrm{T}}\big)+\mathcal{D}^2_{\mathrm{s}}(\boldsymbol{S}_2\boldsymbol{n})\big\}\cdot\nabla^1_{\boldsymbol{n}}\boldsymbol{w},
\end{aligned}\tag{C.17}$$

these determine $(\text{C.12})_3$ in terms of $\boldsymbol{w}$, $\nabla^1_{\boldsymbol{n}}\boldsymbol{w}$, $\nabla^2_{\boldsymbol{n}}\boldsymbol{w}$, and $\nabla^3_{\boldsymbol{n}}\boldsymbol{w}$. In this fashion, one can successively determine all identities in (C.12) in terms of $\boldsymbol{w}$, $\nabla^1_{\boldsymbol{n}}\boldsymbol{w}$, …, $\nabla^n_{\boldsymbol{n}}\boldsymbol{w}$. In turn, these can be used to determine $\boldsymbol{p}_{ij}$ in (C.6).

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