LETTER TO THE EDITOR

Non-linear alternative extended thermodynamics

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Abstract. A Legendre transformation relates the Helmholtz F to a potential depending on the extended thermodynamic forces as state variables. This generates an alternative extended non-linear thermodynamics with reciprocity. It can be useful in chemical reactions or where the maximum entropy formalism does not give the extended entropy.

The maximum entropy formalism (Levine and Tribus 1979, Jaynes 1957a, b) generates a phase-space distribution $\rho(x)$ which maximises the entropy

$$S = -\kappa \int \rho \ln \rho \, \mathrm{d}x \tag{1}$$

subject to specified values of

$$E = \int \rho H \, \mathrm{d}x \tag{2a}$$

$$\alpha_i = \int \rho A_i(x) \, \mathrm{d}x \tag{2b}$$

$$\eta_i = \int \rho \dot{A}_i(x) \, \mathrm{d}x \tag{2c}$$

where the A_i are functions taken here to be even under momentum reversal, $\dot{A}_i \equiv iLA_i$ with L the Liouville operator, and H is the Hamiltonian. $\{\alpha_i\}$ and $\{\eta_i\}$ can be used as independent variables characterising the non-equilibrium state. The calculation is done in a frame in which the centre of mass is fixed, posing a restriction on the domain of the x integration. We obtain the variational solution

$$\rho = Z^{-1} \exp\left[-\beta \left(H + \sum_i (\Phi_i A_i + \tilde{\Phi}_i \dot{A}_i) \right) \right]. \tag{3}$$

Φ_i and $\tilde{\Phi}_i$ are introduced initially as Lagrange multipliers. They can be calculated self-consistently by substituting (3) into (2b) and (2c) (Nettleton 1988a). Introduction of (3) into (1) leads to their identification as thermodynamic forces, obeying

$$\Phi_i = -\partial F/\partial \alpha_i \qquad \tilde{\Phi}_i = -\partial F/\partial \eta_i \tag{4}$$

with F the Helmholtz function.

Z is a dynamic partition function (Jou *et al* 1984) which nomalises ρ to unity. We have from (1) and (3):

$$-\kappa T \ln Z = F + \sum_i (\Phi_i \alpha_i + \tilde{\Phi}_i \eta_i) \tag{5}$$

which is a Legendre transformation to a potential depending on N, V, T, $\{\Phi_i\}$ and $\{\tilde{\Phi}_i\}$ as state variables.

Equation (5) implies that we can interchange the roles of α and Φ as well as of η and $\tilde{\Phi}$. It is inconvenient to do this with α, since it does not vanish in general in equilibrium. A similar and more useful potential is

$$F = -\kappa T \ln \hat{Z} = F + \sum_i \tilde{\Phi}_i \eta_i \tag{6a}$$

$$\hat{Z} = \int \mathrm{d}x \exp\left[-\beta\left(H + \sum_i \Phi_i(A_i - \alpha_i) + \sum_i \tilde{\Phi}_i \dot{A}_i\right)\right]. \tag{6b}$$

In the particular case where the $\{A_i\}$ depend only on configuration coordinates, we can use (3) to calculate $\bar{K}$, the average kinetic energy. We find that

$$F - \tilde{F} = 2(\bar{K} - \tfrac{3}{2}N\kappa T). \tag{7}$$

If we write

$$\tilde{F} \equiv E - T\tilde{S} \tag{8}$$

then

$$T\,\mathrm{d}\tilde{S}/\mathrm{d}t = (S - \tilde{S})\dot{T} - \sum_i \eta_i \dot{\tilde{\Phi}} + \sum_i \Phi_i \dot{\alpha}_i \tag{9}$$

so that conjugate fluxes and forces, $\dot{\tilde{\Phi}}$ and $-\eta$, $\dot{\alpha}$ and Φ, may be extracted from the rate of change of the pseudo-entropy, $\tilde{S}$. These obey symmetric reciprocity relations in the non-linear regime. To show this, we remark that (Nettleton 1985)

$$\dot{\alpha}_i = \eta_i = \sum_j L_{ij}^{(2)} \Phi_j \tag{10a}$$

$$\dot{\eta}_i = \sum_j L_{ij}^{(4)} \tilde{\Phi}_j + \sum_j L_{ij}^{(3)} \Phi_j \tag{10b}$$

$$L_{ij}^{(4)} = L_{ji}^{(4)} \qquad L_{ij}^{(3)} = -L_{ji}^{(2)} \tag{10c}$$

where $L^{(3)}$, $L^{(4)}$, Φ and $\tilde{\Phi}$ are all non-linear functions of the deviations of their arguments from equilibrium. If we set

$$\Phi = \phi\eta \tag{11}$$

where $\tilde{\Phi}$ and η are vectors and ϕ a matrix, equation (10a) and (10b) become

$$\dot{\alpha} = -L^{(3)T}\phi\eta \tag{12a}$$

$$\dot{\eta} = L^{(4)}\phi\eta + L^{(3)}\Phi. \tag{12b}$$

Multiplying (12b) by ϕ, we find

$$\dot{\tilde{\Phi}} - \phi\dot{\eta} = \phi L^{(4)}\phi\eta + \phi L^{(3)}\Phi. \tag{13}$$

Since $\dot{\phi}$ is symmetric, we can set

$$\tilde{L}^{(4)} \equiv \dot{\phi} + \phi L^{(4)}\phi = \tilde{L}^{(4)T}. \tag{14}$$

Equations (12a) and (13) exhibit symmetric Onsager coupling between the dependence of $\tilde{\Phi}$ on Φ and $\dot{\alpha}$ on $-\eta$, as well as symmetric coupling of forces having the same time-reversal symmetry. This holds in the general non-linear case. However, if we have the heat flux, J, as an η-variable and introduce into J a term in ∇T which couples the system to the surroundings (Nettleton 1987), then non-linear reciprocity can be

demonstrated only for steady states, where $\dot{J} = 0$. The absence of antisymmetric Casimir coupling reflects the fact that its presence is a necessary condition for the irreversible entropy production to be positive. Since $\tilde{S}$ is not entropy, this condition is absent. In a steady state, the entropy production stems from $\Phi \dot{\alpha}$ in (9), while the preceding term is the rate of change of $T(\tilde{S} - S)$.

The alternative formulation, using $\overset{\star}{\Phi}$ instead of $\dot{\eta}$ as a flux, offers little advantage when $\tilde{\Phi}$ can be calculatd from (3) and (2c). An example where this is not possible is a chemical reaction with $\Phi = A$ being minus the chemical affinity and η the reaction-rate (García-Colín *et al* 1985, Nettleton 1988b). In this case, from (12a), take

$$L^{(3)} \simeq -\phi^{-1} \tag{15}$$

and write (13) in the form

$$\overset{\star}{\Phi} - \dot{\phi}\eta = (-1/\tau)\tilde{\Phi} - \Phi. \tag{16}$$

This is equivalent to the phenomenological assumption that we determine $L^{(4)}$ to make $\tilde{\Phi} \to 0$ at frequency $\omega > 1/\tau$, where τ is of the order of a collision time in a gas and the hypersound period in a liquid. No reactions can occur in so short a period and $\eta \to 0$. The inertial condition is satisfied if Φ, and therefore the chemical potentials, depends weakly on η at accessible frequencies. Under these circumstances, (16) becomes

$$\dot{\eta} = -(1/\tau)\eta - \phi^{-1}\Phi. \tag{17}$$

ϕ is determined to make $-\phi^{-1}\Phi\tau$ the reaction rate calculated from a non-linear model. One calculates first the η-independent terms in ϕ from the model; then the η-dependence of Φ follows from

$$\partial\Phi/\partial\eta = \partial\tilde{\Phi}/\partial\alpha. \tag{18}$$

One can then find the $O(\eta^2)$ dependence of ϕ from the model, and so on. The alternative formulation thus leads in a natural way to conditions providing an estimate of the higher η dependence of ϕ, which was not done in earlier work (Nettleton 1988b). If extant reaction-rate models are used, we should determine ϕ to make $\phi^{-1}\Phi$ independent of η.

References

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