NONLINEAR RECIPROCITY: STATISTICAL FOUNDATIONS AND APPLICATIONS TO NONLINEAR EFFECTS IN HEAT TRANSPORT AND CHEMICAL REACTIONS

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Abstract

Robertson has derived from the Liouville equation an exact equation for the maxent distribution which depends on a set of moments. The exact equations for these moments verify predictions of Grad for the Maxwell and Cattaneo relaxation equations in a dilute gas. Nonlinear reciprocity is applied to estimate contributions quadratic in heat flux $\vec{Q}$, to thermal conductivity and to second-order effects in $\vec{Q}$, diffusion flux $\vec{J}_D$, and traceless pressure $\overset{\circ}{P}_{\alpha\beta}$ in the reaction rate in a dilute gas mixture. All non-linear effects are too small to see readily.

Keywords: nonlinear reciprocity, nonlinear effects.

1. Introduction

The maximum entropy formalism of JAYNES [1] (maxent) maximizes an entropy functional to obtain a distribution $\sigma(x, t)$ in the space of phase coordinates x which yields the best estimate $\langle \hat{A} \rangle = \mathrm{Tr}(\hat{A}\sigma)$ at time t of a dynamical function $\hat{A}(x)$, subject to specification of a set of values $\langle \{\hat{A}_i\} \rangle$ $(1 \leq i \leq \nu)$ representing the available measured information at t. From σ we calculate

$$S = -\kappa \, \mathrm{Tr} \, (\sigma \ln \sigma) \tag{1}$$

which yields the information-theoretic model of entropy. Since σ depends on only a finite number of moments, it is not a solution of the Liouville equation. Jaynes constructed a solution $\rho(t)$ of the latter at $t' > t$ by setting

$$\rho(t') = \exp[-i\hat{L}(t' - t)]\sigma(t) , \tag{2}$$

where $\hat{L}$ is the Liouville operator.

To obtain a statistical derivation of the evolution equations of extended thermodynamics (EIT), we need to express $\dot{\rho}(t)$ as a functional of values of

the $\langle \hat{A}_i \rangle$ at t or over a range of times. We shall proceed in the next section to consider two much-used ways of using σ to construct approximate solutions of the Liouville equation.

To prove that non-linear reciprocity does or does not exist and investigate whether terms introduced from symmetry [2, 3] into the rate equations really belong there, we need an exact equation for $\dot{\sigma}$ of the type introduced by ROBERTSON [4]. We study the latter in the third section. Specific examples for a dilute gas are discussed in the fourth section.

In the fifth section, we use the phenomenology to estimate the quadratic term in

$$\lambda = \lambda_0 + \lambda_2 Q^2 + O(Q^4) \tag{3}$$

for dilute-gas thermal conductivity, with $\vec{Q}$ = heat flux. The $O(Q^2)$ will be found to be very small.

The sixth section uses maxent to calculate chemical potentials $\{\tilde{\mu}_i\}$ in a reacting gas mixture in which there is a heat flux, a diffusion flow, or a traceless pressure, $\overset{\circ}{\mathbf{P}} \neq 0$. The reaction rate is proportional to $\sum_i \tilde{\mu}_i \tilde{\nu}_i$, where the $\{\tilde{\nu}_i\}$ are stoichiometric coefficients.

2. Derivation of EIT from Approximate Solutions to the Liouville Equation

If we have an approximate solution $\rho(t)$ of the Liouville equation which depends on a finite set of moments, we can substitute this expression into the right-hand member of

$$\dot{\rho} = -i\hat{L}\rho \tag{4}$$

and take moments. This yields self-consistent moment equations which, together with the ansatz for $\rho(t)$, solve *Eq.* (4) when the number of moments becomes infinite.

The simplest such approach is the GRAD ansatz [5] used in the dilute-gas Boltzmann equation. The GRAD expression linearizes [6] a function which maximizes the entropy functional. A similar approach may be made to the Liouville equation. Let $\{\hat{A}_i(x)\}$ $(1 \leq i \leq \nu)$ be a set of phase functions which are even under momentum reversal. Then $\{\dot{A}_i(x)\} \equiv \{i\hat{L}\hat{A}_i\}$ are odd. Defining

$$\psi_a \equiv \prod_i \delta(\hat{A}_i - a_i)\delta(\dot{\hat{A}}_i - v_i) \equiv \delta(A - a)\delta(\dot{A} - v) \,. \tag{5}$$

$$g(a, v) \equiv \int \rho\psi_a \, dx \equiv \int \rho_0(x) \exp(i\hat{L}t)\psi_a \, dx \,, \tag{6}$$

$$P_\beta \equiv \int \rho_\beta \psi_a \, dx \,, \tag{7}$$

with ρ_β the equilibrium canonical distribution, we set up the probability amplitude g for the numerical values of $\{\hat{A}_i\}$, $\{\dot{A}_i\}$. We assume equilibrium with a heat bath at temperature T.

H. GRABERT [7] introduces a projection operator $\hat{P}$ into an identity for $\exp(i\hat{L}t)$. This leads to an evolution equation for $g(a, v)$:

$$\frac{\partial g}{\partial t} = -\sum_i \left[(\frac{\partial}{\partial a_i})(\tilde{v}_i g) + (\frac{\partial}{\partial v_i})(q_i g) \right] + \tag{8}$$

$$+ \int_0^t ds \sum_{ij} \frac{\partial}{\partial v_j} \int D_{ij}(a, a', t - s)(\frac{\partial}{\partial v_j'}) \left[g(a', s)/p_\beta(a') \right] da' \, dv' \,,$$

$$\tilde{v}_i \equiv \int p_\beta^{-1} \rho_\beta \psi_a \dot{A}_i \, dx \,, \tag{9}$$

$$q_i \equiv \int p_\beta^{-1} \psi_a (i\hat{L})^2 \hat{A}_i \rho_\beta \, dx \,, \tag{10}$$

$$D_{ij} \equiv \int dx \rho_\beta \psi_{a'} (i\hat{L})^2 \hat{A}_j (1 - \hat{P}) \exp\left[i\hat{L}(1 - \hat{P})(t - s) \right] \psi_a (i\hat{L})^2 \hat{A}_i \,. \tag{11}$$

The maxent expression for $g(a, v)$ is [8]:

$$\bar{g}(a, v, t) \equiv \int \sigma(x) \psi_a(x) \, dx = Z_c p_\beta(a, v) \exp \left[\beta F(\alpha, \eta) + \right.$$

$$\left. + \sum_i \{ \Phi_i(\alpha, \eta)(\alpha_i - a_i) + \tilde{\Phi}_i(\alpha, \eta)(\eta_i - v_i) \} \right] \,. \tag{12}$$

where $\sigma(x)$ maximizes the functional in (1) subject to the conditions:

$$\langle \hat{A}_i(x) \rangle = \alpha_i \,, \qquad \langle \dot{A}_i(x) \rangle = \eta_i \qquad (1 \leq i \leq \nu) \,. \tag{13}$$

Z_c is the canonical partition function and $F(\alpha, \eta)$ the Helmholtz function. $\sigma(x)$ is consistent with the Gibbs equation provided $\beta = (\kappa T)^{-1}$ and Φ_i, $\hat{\Phi}_i$ are thermodynamic forces.

If we substitute (12) into (8) and calculate first moments, these represent a self-consistent approximation in the sense of Grad. If we know the moments at time t, $\bar{g}$ in (12) is the distribution at t. Substituting this into the right hand member of (8), we can calculate $\bar{g}(t) + (\partial \bar{g}/\partial t)\Delta t$ which is a sufficient approximation if Δt is short, a fraction of the relaxation time of fast variables.

The moment equations resulting from use of $\bar{g}$ in (8) have the form [8]:

$$\dot{\alpha}_i = \eta_i = \sum_j L_{ij}^{(2)} \tilde{\Phi}_j \,, \tag{14}$$

$$\dot{\eta}_i = \sum_j L_{ij}^{(3)} \Phi_j + \sum_j L_{ij}^{(4)} \tilde{\Phi}_j \,. \tag{15}$$

Φ_i and $\tilde{\Phi}_j$ are nonlinear in deviations of the variables from equilibrium, and the $L_{ij}^{(k)}$ are nonlinear Φ- and $\tilde{\Phi}$-expansions to all orders. The $L_{ij}^{(k)}$ are not unique and satisfy reciprocity to arbitrary order in the expansions:

$$L_{ij}^{(3)} \;=\; -L_{ji}^{(2)} \,, \tag{16}$$

$$L_{ij}^{(4)} \;=\; L_{ji}^{(4)} \,. \tag{17}$$

Eqs. (16), (17) purport to justify nonlinear reciprocity under very general assumptions. A better approximate solution of the Liouville equation has been given by ZUBAREV [9]. One assumes a set $\{\phi_i\}$ of state variables which are classical or quantum mechanical operator averages $\langle \hat{F}_i \rangle$. The corresponding maxent distribution is [10, 11]

$$\sigma(t,0) = \exp\left[-\ln Z(t) - \beta(t)\hat{H} + \sum_a \tilde{\mu}_a(t)\hat{N}_a - \sum_i \beta\Phi_i(t)\hat{F}_i \right]. \tag{18}$$

The zero argument in σ indicates that the $\hat{N}_a$ and $\hat{F}_i$ operators are time-independent. Number operators $\hat{N}_a$ provide for particle non-conservation.

The Zubarev approximate solution has the form:

$$\rho_\epsilon(t) = \exp\left[\epsilon \int_{-\infty}^{t} e^{(t-t')} \ln \sigma(t', t' - t)\, dt' \right], \tag{19}$$

where the operators in (18) are here taken to be Heisenberg operators evaluated at $t' - t$. With ρ_ϵ, one calculates phenomenological equations in the form

$$\dot{\phi}_i = \mathrm{Tr}\left[\rho_\epsilon(t) i\hat{L}\,\hat{F}_i \right]. \tag{20}$$

3. The Exact Robertson Approach to Derivation of EIT

We generalize the foregoing results to a non-uniform system where the thermodynamic variables depend on position $\vec{r}$,

$$\phi_i(\vec{r},t) = \langle \hat{F}_i(\vec{r},x) \rangle = \mathrm{Tr}\left[\sigma \hat{F}_i(\vec{r},x) \right] \qquad (1 \le i \le \nu). \tag{21}$$

The maxent distribution is

$$\sigma(t) = Z^{-1} \exp\left[-\int d\vec{r} \sum_{n=1}^{\nu} \lambda_n(\vec{r},t)\hat{F}_n(\vec{r},x) - \beta\hat{H} \right], \tag{22}$$

where the $\{\lambda_n\}$ are Lagrange multipliers determined to satisfy *Eq.* (21) identically. The $\{\hat{F}_n\}$ may be quantum mechanical. We assume equilibrium with a heat bath at $T = 1/\kappa\beta$, although we can relax this assumption later.

Jaynesian statistical inference [1] predicts that $\sigma(t)$ is the phase-space distribution provided we can derive exact equations for the $\{\phi_i(\vec{r},t)\}$. The moment equations will be exact if σ plus these moment equations provide an exact solution for Robertson's equation. The latter is derived from the Liouville equation by introducing a non-Hermitian operator $\hat{P}_R$ with the property that $\dot{\sigma} = \hat{P}_R\dot{\rho}$, where $\dot{\sigma}$ solves *Eq.* (4). We define

$$\hat{P}_R(t)\chi(x) \equiv \sum_{n=1}^{\nu} \int d\vec{r}\, [\delta\sigma(t)/\delta\phi_n(\vec{r},t)] \; \mathrm{Tr}\, \left[\hat{F}_n(\vec{r},x)\chi\right]. \qquad (23)$$

Here $\delta\phi/\delta\phi_n$ is a functional derivative.

Operating with $\hat{P}_R$ on the Liouville equation, ROBERTSON derives [4]:

$$\begin{aligned}
\dot{\sigma} &= -i\hat{P}_R(t)\hat{L}(t)\sigma(t) \\
&\quad - \int_0^t dt'\, \hat{P}_R(t)\hat{L}(t)\hat{T}(t,t')\left[1 - \hat{P}_R(t')\right]\hat{L}(t')\sigma(t'), \qquad (24)
\end{aligned}$$

where $\hat{T}(t,t')$ is a solution of

$$\frac{\partial\hat{T}(t,t')}{\partial t'} = i\hat{T}(t,t')\left[1 - \hat{P}_R(t')\right]\hat{L}(t'). \qquad (25)$$

Multiplying (24) by $\hat{F}_i(\vec{r},x)$ and taking the trace, we obtain equations for the $\dot{\phi}_i$. Contributions from the first term on the right in (24) yield anti-reciprocal relations to all orders in the $\{\lambda_n\}$. Non-Hermiticity of $\hat{P}_R$ has frustrated the search for non-linear reciprocity from the second term in (24). ROBERTSON [4] derives it only for the linear case. However, we can learn much from the first term.

Let $\hat{F}_i(\vec{r},x)$ be a classical phase function, even under momentum reversal. We have, on multiplying (24) by $\hat{F}_i$ and integrating over phase space:

$$\dot{\Phi}_i(\vec{r},t) = \langle i\hat{L}\,\hat{F}_i(\vec{r},x)\rangle = \int d\vec{r}'\, \sum_{n\in 0} L_{in}^{(2)}(\vec{r},\vec{r}')\lambda_n(\vec{r}',t), \qquad (26)$$

where the sum is over forces λ_n/β odd under time reversal. If $\hat{F}_j$ is odd under momentum reversal,

$$\dot{\Phi}_j = \int d\vec{r}'\, \sum_{n\in\epsilon} L_{jn}^{(3)}(\vec{r},\vec{r}')\lambda_n(\vec{r}',t) + \cdots, \qquad (27)$$

where the sum is over even forces, and the ellipsis refers to Onsager symmetric terms, mainly from the $\hat{T}$ term in (24). The detailed derivation shows that

$$L_{ij}^{(2)}(\vec{r}, \vec{r}') = -L_{ni}^{(3)}(\vec{r}', \vec{r}) \tag{28}$$

to all orders in the $\{\lambda_n\}$.

4. Examples: Cattaneo–Vernotte and Maxwell Stress Relaxation Equations

We now derive from (24) the linear evolution equations for heat flux $\vec{Q}(\vec{r}, t)$ and traceless pressure $\overset{\circ}{P}_{\alpha\beta}(\vec{r}, t)$ in a dilute gas. The operators are:

$$\hat{\vec{Q}}(\vec{r}, x) = \sum_{i=1}^{N} \left[(\bar{p}_i^2/2m) - (5/2)\kappa T(\vec{r}_i) \right] (\bar{\vec{p}}_i/m)\delta(\vec{r}_i - \vec{r}) , \tag{29}$$

$$P_{\alpha\beta}(\vec{r}, x) = m^{-1} \sum_{i=1}^{N} \bar{p}_i{}^{\alpha} \bar{p}_i{}^{\beta} \delta(\vec{r}_i - \vec{r}) , \tag{30}$$

$$\bar{\vec{p}}_i \equiv \vec{p}_i - \vec{u}(\vec{r}_i) , \tag{31}$$

$$\hat{H}(\vec{r}, x) \equiv \sum_{i=1}^{N} (\bar{p}_i{}^2/2m)\delta(\vec{r}_i - \vec{r}) . \tag{32}$$

The maxent distribution (22) for this choice of variables is

$$\sigma(t) = Z^{-1} \exp \left[- \int d\vec{r}\,\beta(\vec{r})\{\hat{H}(\vec{r}, x) + \right.$$

$$\left. + \Phi_Q(\vec{r}, t) \cdot \hat{\vec{Q}}(\vec{r}, x) + \sum_{\alpha\beta} \Phi_{\alpha\beta,p}(\vec{r}, t)\hat{P}_{\alpha\beta}(\vec{r}, x)\} \right] . \tag{33}$$

In linear approximation, which suffices here, the conditions

$$\vec{Q} = \mathrm{Tr} \left[\sigma(t)\hat{\vec{Q}}(\vec{r}, x) \right] , \qquad P_{\alpha\beta} = \mathrm{Tr} \left[\sigma\hat{P}_{\alpha\beta} \right] \tag{34}$$

yield

$$\bar{\Phi}_Q = \nu_0 \vec{Q} + \cdots , \tag{35}$$

$$\Phi_{\alpha\beta,p} = \mu_0 \overset{\circ}{P}_{\alpha\beta} + \cdots , \tag{36}$$

where

$$\nu_0 = \frac{-2m\beta^2 V}{5N} , \tag{37}$$

$$\mu_0 = \frac{-V}{2N\kappa T(\vec{r})} . \tag{38}$$

If we substitute $\sigma(t)$ from (33) into (24), multiply by $\tilde{Q}(\vec{r},x)$ and $\hat{P}_{\alpha\beta}(\vec{r},x)$, and then integrate over phase space, we obtain the time-evolution equations:

$$\dot{\vec{Q}} = -(1/\tau_Q)\vec{Q} - (\kappa T/m)\nabla\overset{\circ}{\mathbf{P}} - K_Q(\nabla T/T) ,\text{(Cattaneo)} \tag{39}$$

$$\overset{\circ}{\dot{P}}_{\alpha\beta} = -(1/\tau_p)\overset{\circ}{P}_{\alpha\beta} - (4/5)(\nabla\vec{Q})^s - K_p(\nabla\vec{u})^s , \text{ (Maxwell)} \tag{40}$$

$$(\nabla\vec{Q})^s = \frac{1}{2}[(\nabla\vec{Q}) + (\nabla\vec{Q})^T] - \nabla\cdot\vec{Q}\vec{\delta} , \tag{41}$$

$$K_Q = \frac{5N(\kappa T)^2}{2Vm} = -(\nu_0)^{-1} , \tag{42}$$

$$K_p = \frac{2N\kappa T}{V} = -(\mu_0)^{-1} . \tag{43}$$

The terms involving τ_Q, τ_p stem from the second term on the right in (24) and the remaining terms from the other term in (24). The coefficients of $\nabla\overset{\circ}{\mathbf{P}}$ and $(\nabla\vec{Q})^s$ agree exactly with Grad theory. This answers questions previously raised [12, 13] about the need for these terms.

The structure of (39), (40) shows that the fluxes of $\vec{Q}$, $\overset{\circ}{\mathbf{P}}$ can be expressed in terms of these variables. To take these fluxes as members of a hierarchy of internal variables, thus modifying the exact moment equations, is equivalent to postulating an entropy model inconsistent with the information-theoretic one.

If we write the identities $\vec{Q} = \vec{Q}$ and $\overset{\circ}{\mathbf{P}} = \overset{\circ}{\mathbf{P}}$ in the form:

$$\vec{Q} = (1/\nu_0)\bar{\Phi}_Q + \cdots = -K_Q\bar{\Phi}_Q + \cdots \tag{44}$$

$$\overset{\circ}{P}_{\alpha\beta} = (1/\mu_0)\Phi_{\alpha\beta,p} + \cdots = -K_p\Phi_{\alpha\beta,p}, \tag{45}$$

then, to linear terms, we establish an anti-symmetric Onsager coupling between the $-T^{-1}\nabla T$ term in (39) and the $\bar{\Phi}_Q$ term in (44) and between the $-(\nabla\vec{u})^s$ term in (40) and the $\Phi_{\alpha\beta,p}$ term in (45). Such a coupling should be valid to all orders since it is a necessary condition for positive definiteness of irreversible entropy production.

5. Non-Linear Heat Conduction

The anti-reciprocal coupling in (39) and (44) can be applied to estimate λ_2 in Eq. (3) for a dilute gas. We extend (53) to the non-linear regime by

writing:

$$\dot{\vec{Q}} = L\vec{\Phi}_Q - K_Q T^{-1}\nabla T , \tag{46}$$

$$L = L_0 + L_2 Q^2 + O(Q^4) , \tag{47}$$

$$K_Q = K_0 + K_2 Q^2 + O(Q^4) , \tag{48}$$

$$\vec{\Phi}_q = \nu_0 \vec{Q} + \nu_2 Q^2 \vec{Q} + O(Q^4 \vec{Q}). \tag{49}$$

If $\overset{\circ}{\mathbf{P}}$ is proportional to $(\nabla \vec{u})^s$, when $\nabla \vec{u} \neq 0$, we can reasonably take $\overset{\circ}{\mathbf{P}} = 0$ in steady heat conduction if $\vec{u} = 0$. In $\sigma(t)$ we take $\overset{\circ}{\mathbf{P}} = 0$ and $\vec{Q}$ as variables and keep $\vec{\Phi}_Q$ and $\Phi_{\alpha\beta,p}$. We find that the presence of $\Phi_{\alpha\beta,p}$ modifies ν_2 but not ν_0. Then

$$\nu_2 = -\frac{19}{2}\frac{\nu_0^3 \kappa T}{V^2 m} . \tag{50}$$

ν_0 and ν_2 differ from (37) by a factor V, since here we take a small, homogeneous system and do not integrate over $\vec{r}$. From (44) and (49), we get [14]:

$$-K_0 \nu_0 = V , \tag{51}$$

$$-K_0 \nu_2 - K_2 \nu_0 = 0 . \tag{52}$$

Setting $\dot{\vec{Q}} = 0$ in (46) and comparing the result with Fourier's law, we get:

$$\lambda_0 = -T^{-1}\frac{K_0}{L_0 \nu_0} \tag{53}$$

$$\lambda_2 = -T^{-1}\frac{K_2}{L_0 \nu_0} + T^{-1}\frac{K_0}{(L_0 \nu_0)^2}(L_2 \nu_0 + L_0 \nu_2). \tag{54}$$

We estimate L_2 by supposing that $\tau_Q = (L\nu_0)^{-1} = l/v$ where ℓ = mean free path and v is rms speed, calculated from maxent. Finally, we obtain:

$$\lambda_2 = \lambda_0(33/25)\frac{m}{(N/V)^2(\kappa T)^3} . \tag{55}$$

For the case of Ar at 10^{-2}atm, 0 °C, $Q=1.209 \cdot 10^6$J/m^{2}s corresponding to $|\nabla T| \sim 7.3 \cdot 10^7$K/m, we find $|\lambda_2 Q^2/\lambda_0| \sim 6.6 \cdot 10^{-4}$. Large $|\nabla T|$ yields a second-order effect probably below the threshold of observability.

6. Second-Order Perturbations in Chemical Gas Kinetics

The quasi-steady reaction rate J in a dilute gas mixture is proportional to a chemical force

$$A = -\sum_i \tilde{\mu}_i \nu_i . \tag{56}$$

We have for the Helmholtz function differential, dF, when $\{N_i\}$ are numbers of molecules and $\vec{\Phi}_D$ the thermodynamic force associated with a binary diffusion flux, $\vec{J}_D$:

$$dF = -\vec{\Phi}_Q \cdot d\vec{Q} - \vec{\Phi}_D \cdot d\vec{J}_D - \sum_{\alpha\beta} \Phi_{\alpha\beta,p} d\overset{\circ}{P}_{\alpha\beta} + \sum_i \tilde{\mu}_i dN_i - \Phi dJ \ . \qquad (57)$$

The choice of variables is inspired by GARCIA-COLIN et al. [15].

The two vector forces in (57) are, in linear approximation:

$$\vec{\Phi}_Q = -\nu_{qq}\vec{Q} - \nu_{qD}\vec{J}_D \ , \qquad (58)$$

$$\vec{\Phi}_D = -\nu_{Dq}\vec{Q} - \nu_{DD}\vec{J}_D \ . \qquad (59)$$

These can be calculated from maxent, using (29), (30). For a four-component mixture with N_3, N_4 negligible, we get $\nu_{qD} = 0 = \nu_{Dq}$ and

$$\nu_{qq} = \frac{2V^2}{5(\kappa T)^2 \sum_i (N_i/m_i)} \ , \qquad (60)$$

$$\nu_{DD} = \frac{V^2}{m_1 N_1} \ . \qquad (61)$$

Contributions quadratic in $\vec{Q}$, $\vec{J}_D$ and $\overset{\circ}{\mathbf{P}}$ to the $\tilde{\mu}_i$ can be calculated from the integrability condition and substituted into A given by (56). For dissociation of NO_2 at 1125 K and $P_0 = 10^{-2}$ atm, we find the fractional change $\Delta J/J = -(1/3)(P_{xy}/P_0)^2$ produced by shear stress P_{xy}. We estimate that a shear rate $\partial u_x/\partial y \sim 10^6 \mathrm{s}^{-1}$ is required to make $\Delta J/J \sim 10^{-2}$. For an equimolar mixture of D_2 and HCl at 600 K at the start of the reaction

$$D_2 + HCl \rightarrow DH + DCl \qquad (62)$$
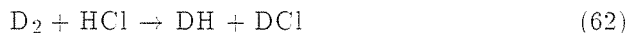
we estimate that, to have $\Delta J/J \sim 10^{-2}$ we need $|\nabla T| = 2.5 \cdot 10^5$ K/m when the concentration gradient vanishes and $|\nabla \rho_1| = 9.0$ kg/m^4 when $\nabla T = 0$. Very large gradients are needed for observability.

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