BOUNDS ON THE THERMODYNAMIC BEHAVIOR OF SYSTEMS WITH GENERALIZED COULOMB INTERACTIONS

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ABSTRACT

Various lower and upper bounds are derived for the energy, free energy, and pressure of particles interacting via an r^{-n} pair potential in ν dimensions. The results include (i) lower bounds for mixtures with $n < 2$ of the form const $\rho^{1+2/\nu}$ as ρ increases either isentropically or isothermally, complimenting a recently derived upper bound of Kleban and Puff of the same form in the isentropic case, (ii) upper and lower bounds for the case $n > \nu$, $n > 2$, which for the pressure are both of the form const $\rho^{1+n/\nu}$ as ρ increases isentropically.

We derive various upper and lower bounds for the energy, free energy, and pressure of a system of σ species of particles (including the $\sigma = 1$ case) such that the interaction potential for a pair of particles of species i and j is $e_i e_j/r^n$, where r is their separation and n is a positive constant.

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For $n < 2$, our lower bounds are complimentary to the recently derived upper bounds of Kleban and Puff,[1] and when combined with their bounds, show that if $n < 2$, the pressure p behaves under isentropic compression like $\rho^{1+2/\nu}$ for $n < 2$ and like $\rho^{1+n/\nu}$ for $n > 2$, where ρ is the density and ν the dimensionality. The case $n = 1$, $\nu = 3$ describes "real" charged matter (which we shall treat nonrelativistically) and is thus of special interest. In particular, our large-ρ results in this case are relevant to stellar matter. To insure the existence of thermodynamic functions,[2] a charge-neutrality condition, $\Sigma_i e_i \rho_i = 0$, must be assumed[3] in the $n = 1$, $\nu = 3$, case (and perhaps for all $n < \nu$, although existence proofs are currently lacking except for $n = 1$, $\nu = 3$), where ρ_i is the density of the ith species; $\Sigma \rho_i = \rho$. For $n > \nu$, on the other hand, one expects the existence of thermodynamic functions only if $e_i \geq 0$ for all i.

Our starting point is a form of the virial theorem[4]

$$\frac{p}{\rho} = \frac{2}{\nu} u_{kin} + \frac{n}{\nu} (u - u_{kin}) \tag{1}$$

where u is the total expected energy per particle, and u_{kin} the mean kinetic energy per particle. In classical mechanics, u_{kin} is $\frac{1}{2} \nu kT$. In quantum mechanics we do not know u_{kin} but we do have the lower bound

$$u_{kin} \geq g(\rho) \tag{2}$$

where $g(\rho)$ is the energy per particle for the corresponding ideal gas in its ground state, which for Fermi statistics has the form[5]

$$g(\rho) = A_\nu \, \rho^{2/\nu} \tag{3}$$

with $A_\nu = A_\nu (\hbar, m_i)$ independent of ρ.

We distinguish various cases, according to the value of n.

Case I, $n = 2$.

Here (1) reduces to

$$\frac{p}{\rho} = \rho\left(\frac{\partial u}{\partial \rho}\right)_s = \frac{2u}{\nu} \tag{4}$$

where s is the entropy per particle. The general solution of this differential equation has the form

$$u = \rho^{2/\nu}\, h(s) \tag{5}$$

where h is nondecreasing since $(\partial u/\partial s)_\rho = T$ is non-negative, giving

$$s = \text{function of } u\,\rho^{-2/\nu} \tag{6}$$

or equivalently

$$f = \rho^{2/\nu}\, k(T\rho^{-2/\nu}) \tag{7}$$

where f is the Helmholtz free energy per particle and k must be a non-increasing function in the quantum-mechanical case since $(\partial f/\partial T)_\rho = - s$ is negative. Thus the equation of state has the form

$$p = \rho^{1+2/\nu} \times \text{function of } T\rho^{-2/\nu}. \tag{8}$$

In particular, these functional relations apply to the ideal Fermi, Bose, and classical gases, where $e_i \equiv 0$ for all i.

Case II, $n < 2$. Here Eqs. (1) and (2) imply

$$\frac{p}{\rho} \geq \frac{2-n}{\nu}\, g(\rho) + \frac{n}{\nu}\, u, \tag{9}$$

i.e.

$$\frac{\partial(u\rho^{-n/\nu})}{\partial \rho} \geq \frac{2-n}{\nu}\, \rho^{-1-n/\nu} g(\rho),$$

so that

$$u = \rho^{n/\nu}\left[\frac{2-n}{\nu} \int_0^\rho \tilde{\rho}^{-1-n/\nu}\, g(\tilde{\rho})\, d\tilde{\rho} + h(\rho,s)\right] \tag{10}$$

where h is a nondecreasing function of ρ at fixed s. It is also a non-decreasing function of s at fixed ρ. For Fermi statistics (10) reduces, by (3), to

$$u = A_\nu \rho^{2/\nu} + \rho^{n/\nu} h(\rho,s) \quad . \tag{11}$$

To obtain the corresponding result for f we consider it as a function of ρ and $\tau = T\rho^{-n/\nu}$ and note $(\partial f/\partial\rho)_\tau = (\partial f/\partial\rho)_T + (\partial f/\partial T)_\rho (\partial T/\partial\rho)_T = p/\rho^2 - nsT/\nu\rho$. Thus (9) can be written $(\partial f\rho^{-n/\nu}/\partial\rho)_\tau \geq (2-n)\rho^{-1-n/\nu} g(\rho)/\nu$, and it follows that

$$f = \rho^{n/\nu}\left[\frac{2-n}{\nu} \int_0^\rho \tilde{\rho}^{-1-n/\nu} g(\tilde{\rho})d\tilde{\rho} + k(\rho, T\rho^{-n/\nu})\right] \tag{12}$$

where k is a nondecreasing function of ρ at fixed $T\rho^{-n/\nu}$. In the quantum-mechanical case k is also a nonincreasing function of $T\rho^{-n/\nu}$ at fixed ρ; k is then also a nondecreasing function of ρ at fixed T. For Fermi statistics, (12) reduces to

$$f = A_\nu \rho^{2/\nu} + \rho^{n/\nu}\, k(\rho, T\rho^{-n/\nu}). \tag{13}$$

A lower bound for the pressure can be obtained by substituting (10) into (9). By (3), this gives for Fermi systems

$$\frac{p}{\rho} \geq \frac{2}{\nu} A_\nu \rho^{2/\nu} + \frac{n}{\nu} \rho^{n/\nu} h(\rho,s). \tag{14}$$

For quantum systems a lower bound on p in terms of T rather than s can be obtained by using $u - f = Ts \geq 0$ with (12) in (9). In the Fermi case, from (3), this gives

$$\frac{p}{\rho} > \frac{2}{\nu} A_\nu {}^{2/\nu} + \frac{n}{\nu} \rho^{n/\nu}\, k(\rho, T\rho^{-n/\nu}). \tag{15}$$

Eq. (14) has the consequence that if at least one of the species present obeys Fermi statistics and the system is compressed isentropically, then $p - \frac{2}{\nu} A_\nu \rho^{1+2/\nu}$ cannot decrease. Thus p increases at least as fast as const $\rho^{1+2/\nu}$. On the other hand Kleban and Puff[1] show that p has an isentropic upper bound of the form $\rho^{1+2\nu}$ (const + const $\rho^{-(2-n)/\nu}$). Thus p must behave like $\rho^{1+2/\nu}$, in the sense that $p\,\rho^{-1-2/\nu}$ has positive upper and lower bounds as the system is compressed isentropically.

Case III, $n > 2$.

Here Eqs. (1) and (2) imply

$$\frac{p}{\rho} \le \frac{n}{\nu}\ u - \frac{n-2}{\nu}\, g(\rho)$$

and the method previously used above now gives upper rather than lower bounds. For example, in place of (14) we now have, for all statistics

$$\frac{p}{\rho} \le \frac{n}{\nu}\, \rho^{n/\nu}\ H(\rho,s) \tag{16}$$

where $H(\rho,s)$ is a nonincreasing function of ρ at fixed s. (We have left out the term that comes from $g(\rho)$ since it no longer dominates for large ρ, the case of greatest interest.) Similarly, for the free energy we have

$$f < \rho^{n/\nu} K\,(\rho, T\,\rho^{-n/\nu})$$

where K is a nonincreasing function of ρ at fixed $T\rho^{-n/\nu}$.

Case IV, $n > \nu$

It is also possible to obtain lower bounds if $n > \nu$, where for simplicity we consider only the single-species case, dropping the subscript 1 on e_1. The method depends on a lower bound for the potential energy per particle $u_{pot} = u - u_{kin}$. To obtain this lower bound, let ω_i denote the volume of the polyhedron comprising all points that are closer to the ith particle than to any other. Then if R_i denotes the distance from the ith particle to its nearest neighbor we have (ignoring surface effects) $\omega_i \ge K_\nu\, R_i^{\,\nu}$ where the right-hand side is the volume of a ν-dimensional sphere of diameter R_i. The potential energy $N\,u_{pot}$ therefore satisfies

$$N\,u_{pot} \geq \sum_i \frac{e^2}{R_i{}^n} \geq e^2\,\Sigma_i \left(\frac{K_\nu}{\omega_i}\right)^{n/\nu} . \tag{17}$$

From Holder's inequality $\Sigma\,|x_i y_i| \leq (\Sigma|x_i|^p)^{1/p}\,(\Sigma|y_i|^q)^{1/q}$, $(1/p + 1/q = 1)$, with $x_i = \omega_i{}^{n/(n+\nu)}$, $y_i = 1/x_i$, $p = (\nu+n)/n$, we obtain $u_{pot} \geq e^2(K_\nu\rho)^{n/\nu}$, and so (1) gives

$$\frac{p}{\rho} = \frac{2}{\nu}\,u + \frac{n-2}{\nu}\,u_{pot} > \frac{2}{\nu}\,u + \frac{n-2}{\nu}\,B_\nu\rho^{n/\nu} \tag{18}$$

where $B_\nu = e^2\,K_\nu{}^{n/\nu}$. Integrating by the same methods used on (10), we obtain

$$u = B_\nu\rho^{n/\nu} + \rho^{2/\nu}\,\tilde{h}(\rho,s) \tag{19}$$

$$f = B_\nu\rho^{n/\nu} + \rho^{2/\nu}\,\tilde{k}(\rho,T\rho^{-2/\nu}) \tag{20}$$

$$\frac{p}{\rho} \geq \frac{n}{\nu}\,B_\nu\rho^{n/\nu} + \frac{2}{\nu}\quad{}^{2/\nu}\,\tilde{h}(\rho,s) \tag{21}$$

$$\frac{p}{\rho} \geq \frac{n}{\nu}\,B_\nu\rho^{n/\nu} + \frac{2}{\nu}\,\rho^{2/\nu}\,\tilde{k}(\rho,T\rho^{-2/\nu}) \tag{22}$$

where $\tilde{h}$ and $\tilde{k}$ have the same monotonic properties as the h and k in (10) and (12). From these and upper bounds such as (16) we can estimate the behavior of thermodynamic quantities as ρ is increased when n exceeds both 2 and ν. For example (16) and (21) together imply that under isentropic compression p behaves like $\rho^{1+n/\nu}$ in the sense that $p\rho^{-1-n/\nu}$ has positive upper and lower bounds.

Finally, in the case of classical mechanics with $n > \nu$ we can obtain similar results for p_{ex}, u_{ex} and f_{ex}, the amounts by which p, u, and f exceed their ideal-gas values at a given density and temperature. The relevant form of (1) is $p_{ex}/\rho = (n/\nu)\,u_{ex}$ and by an analysis similar to that of Case I we find, for example,

$$f_{ex} = \rho^{n/\nu}\,K_{ex}\,(T\rho^{-n/\nu}) \tag{23}$$

and consequently

$$u_{ex} = \rho^{n/\nu}\,L\,(T\rho^{-n/\nu}) \tag{24}$$

where

$$L(x) = K_{ex}(x) - x\, dK_{ex}(x)/dx. \tag{25}$$

Since the excess specific heat is non-negative, L is a nondecreasing function; it follows by (25) that $d^2 L_{ex}(x)/dx^2 \leq 0$, and consequently, since $f_{ex}/T \to 0$ as $T \to \infty$, that K_{ex} is also a nondecreasing function. Both L and K_{ex} are positive. Equs. (24) and (25) show, for example, that f_{ex} and u_{ex} increase at most as fast as const $\rho^{n/\nu}$ as ρ increases at fixed T. The functional forms of the results (23) and (24) follow from general scaling considerations, and have been discussed before,[6-8] while the nondecreasing character of $K_{ex}(x)$ and $L(x)$ can be obtained from a straightforward use[9] of the Gibbs-Bogoliubov inequality, instead of the arguments given above. From (23) we have $f \leq$ const $\rho^{n/\nu}$ as ρ increases isothermally, a result that was also obtained previously[10] by one of us using different methods.

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FOOTNOTES

1. P. Kleban and R.D. Puff, Phys. Letters 31A, 340 (1970). We note that E_{in} has been printed with the wrong sign in Eq. (8) of this reference.
2. J.L. Lebowitz and E.H. Lieb, Phys. Rev. Letters 22,631 (1969).
3. Note that this neutrality condition implies that one must strictly neglect the gravitational contribution to the interaction potential.
4. L.D. Landau and E.M. Lifshitz, Statistical Physics (Pergamon Press, Ltd., London, 1958) p. 92.
5. R.M. Mazo, J. Math. Phys. 8, 1546 (1967).
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