evaluated the intensity of a higher order of scattering by ignoring any further energy changes after the second scattering. An alternative method is the use of MUSE code. The detailed calculations of Slaggie[4] have shown that the third- and higher-order scattering corrections are less than 20% of the second-order scattering correction. It therefore appears that for most of the inelastic-scattering experiments the effect of third- and higher-order scattering corrections can be ignored, considering the current state of knowledge of the scattering model.

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[1] G. H. Vineyard, Phys. Rev. 96, 93 (1954).

[2] I. A. Blech and B. L. Averbach, Phys. Rev. 137, A1113 (1965).

[3] S. J. Cocking and C. R. T. Heard, Atomic Energy Research Establishment, Harwell, Berkshire, Report No. AERE-R5016, 1965 (unpublished).

[4] E. L. Slaggie, Nucl. Sci. Eng. 30, 199 (1967).

[5] S. J. Cocking, Atomic Energy Research Establishment, Harwell, Berkshire, Report No. AERE-R5867, 1968 (unpublished); K. R. Rao, B. A. Dasannacharya, and S. Yip (private communication).

[6] A. K. Agrawal, S. G. Das, and F. M. Mueller, Argonne National Laboratory Report No. ANL-7780, 1971 (unpublished).

[7] K. E. Larsson (private communication).

[8] B. A. Dasannacharya and G. Venkataraman, Phys. Rev. 156, 196 (1967).

[9] We use $\hbar = k_B = 1$.

[10] A. K. Agrawal and S. Yip, Nucl. Sci. Eng. 37, 369 (1969).

[11] A. K. Agrawal and S. G. Das, Trans. Am. Nucl. Soc. 14, 351 (1971).

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Bounds on the Thermodynamic Behavior of Systems with Generalized Coulomb Interactions

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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, complementing an upper bound of the same form in the isentropic case, recently derived by Kleban and Puff, and (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.

For $n < 2$, our lower bounds are complementary to the recently derived upper bounds of Kleban and Puff,[1] and when combined with their bounds, show that the pressure p behaves under isentropic compression like $\rho^{1+2/\nu}$ for $n < 2$ and like $\rho^{1+n/\nu}$ for $n > 2$, $n > \nu$, where ρ is the density and ν the dimensionality. The case $n = 1$, $\nu = 3$ describes "real" 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 ensure the existence of thermodynamic functions,[2] a charge-neutrality condition, $\sum_i e_i \rho_i = 0$, 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; $\sum \rho_i = \rho$. For $n > \nu$, on the other hand, one expects the existence of thermodynamic functions if $e_i \geq 0$ for all i.

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

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

where u is the mean total 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

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

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 nonnegative. It follows that

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

or equivalently

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

where f is the Helmholtz free energy per particle, and k is a concave function. In the quantum-mechanical case k is also nonincreasing 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 that

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

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 nondecreasing function of s at fixed ρ. For Fermi statistics (10) reduces, (3), to

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

To obtain the corresponding result for f, we consider it as a function of ρ and $\tau = T\rho^{-n/\nu}$ and note that

$$\left(\frac{\partial f}{\partial \rho}\right)_\tau = \left(\frac{\partial f}{\partial \rho}\right)_T + \left(\frac{\partial f}{\partial T}\right)_\rho \left(\frac{\partial T}{\partial \rho}\right)_\tau = p/\rho^2 - \left(\frac{nsT}{\nu\rho}\right) .$$

Thus (9) can be written

$$\left(\frac{\partial f\rho^{-n/\nu}}{\partial \rho}\right)_\tau \geq (2-n)\rho^{-1-n/\nu} g(\rho)/\nu ,$$

and it follows that

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

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

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

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

Case III, $n > 2$: Here Eqs. (1) and (2) imply that

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

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,

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

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

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

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 $u_{\text{pot}} = u - u_{\text{kin}}$. 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) $\omega_i \geq K_\nu R_i^\nu$ where the right-hand side is the volume of a ν-dimensional sphere of diameter R_i. The potential energy Nu_{pot} therefore satisfies

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

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

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

where $B_\nu = e^2 K_\nu^{n/\nu}$. Integrating by the same methods as used on (9), we obtain

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

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

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

and, for quantum systems,

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

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 the same density and temperature. The relevant form of (1) is $p_{\text{ex}}/\rho = (n/\nu) u_{\text{ex}}$ and by an analysis similar to that of case I we find, for example, that

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

and, consequently, that

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

where

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

Since the excess specific heat is non-negative, L is a nondecreasing function; it follows by (25) that $d^2 K_{\text{ex}}(x)/dx^2 \leq 0$, and consequently, since $f_{\text{ex}}/T \to 0$ as $T \to \infty$, that K_{ex} is also a nondecreasing function. Both L and K_{ex} are positive. Equations (23) and (24) 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 $K_{\text{ex}}(x)$ and $L(x)$ can be obtained from a straightforward use[9] of the Gibbs-Bogoliubov inequality, instead of the arguments given above. The result

$$f_{\text{ex}} \leq \text{const}\rho^{n/\nu} \quad \text{as } \rho \text{ increases isothermally}$$

was also obtained previously[10] by one of us using different methods.

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[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] We 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, London, 1958), p. 92.

[5] R. M. Mazo, J. Math. Phys. 8, 1546 (1967).

[6] Reference 4, p. 91.

[7] G. A. Baker, Jr., Am. J. Phys. 27, 29 (1959). This is a lucid and thorough investigation of the thermodynamics of a classical system with a homogeneous potential energy.

[8] J. L. Lebowitz, Phys. Letters 28A, 596 (1969).

[9] G. Stell, SUNY College of Engineering Report No. 157 (1969) (unpublished).

[10] G. Stell, Chem. Phys. Letters 4, 651 (1970).