BOUNDS ON INTERNAL AND FREE ENERGIES OF MANY-BODY SYSTEMS*

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ABSTRACT

Upper and lower bounds on the internal energy and Helmholtz free enery of a many-body system are derived for power-law and Lennard-Jones potentials.

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Recently Kleban[1] and Kleban and Lange[2] have shown the way in which the Bogoliubov inequality, used with certain other relations including the virial theorem, leads to inequalities for the internal energy per particle u and the Helmholtz free energy per particle f. The systems considered in refs. [1] and [2] have a pair potential of the Lennard-Jones form

$$v(r) = \lambda\left(r^{-n} + \text{const}\, r^{-m}\right) \tag{1}$$

and of a generalized Coulomb form (between particles of species i and j)

$$v_{ij}(r) = e_i e_j r_{ij}^{-n}. \tag{2}$$

In this note we extend the work of Kleban[1] and of Kleban and Lange[2] by showing the way in which a somewhat different use of essentially the same inequality and/or the virial theorem leads to additional bounds, some of which are stronger than those of refs. [1] and [2]. Elsewhere[3] we have shown the way in which still another application of the inequality leads to upper bounds on f in terms of hard-sphere quantities.

In the interest of brevety we shall simply take over the more-or-less standard notation of refs. [1] and [2] with one minor change. In that notation, the virial theorem can be written

$$\frac{p}{\rho} = \frac{2}{d} e_{kin} - \frac{1}{2d\rho} \int g_T(r)\,(\underline{r}\cdot\nabla)\,v(r)\,d^d r \tag{3}$$

for a mixture of species (as well as for the single-species system) in the absence of an external field, where p is the pressure, ρ the total number density, d the dimensionality, e_{kin} the average total kinetic energy per particle, and $g_T(r)$ a total pair correlation (distribution) function. We shall write $g_T(r)$ as $\rho^2 g(r)$ however, to conform to widely used notation in which g(r) represents a dimensionless function. In a single-component, single-phase fluid, g(r) is then just the well-known radial distribution function that goes to 1 as $r \to \infty$. For the generalized Coulomb potential given by (2), Eq. (3) immediately implies that

$$\frac{p}{\rho} = \frac{2-n}{d} e_{kin} + \frac{n}{d} u$$

so

$$\frac{p}{\rho} \geq \frac{n}{d} u \text{ for } n \leq 2 \; ; \; \frac{p}{\rho} \leq \frac{n}{d} u \text{ for } n \geq 2 \, , \tag{4}$$

which is one of our starting points. Since $\frac{p}{\rho} = \rho\left(\frac{\partial u}{\partial \rho}\right)_s = \rho\left(\frac{\partial f}{\partial \rho}\right)_T$ where s is the entropy per particle and T the temperature, we have for $n \leq 2$,

$$\rho\left(\frac{\partial u}{\partial \rho}\right)_s \geq \frac{n}{d} u \, , \tag{5}$$

and since $f = u - Ts$, Eq. (4) and the inequality $s \geq 0$ further imply for $n \leq 2$ that

$$\rho\left(\frac{\partial f}{\partial \rho}\right)_T \geq \frac{n}{d} f \, . \tag{6}$$

(We note that the postulate $s \geq 0$ is only applicable to a quantum mechanical system.) If we follow ref.[1] and [2] in further postulating that there exists a ρ_1 such that $u(\rho, s) \geq 0$ for $\rho \geq \rho_1$ and a ρ_0 such that $f(\rho, T) \geq 0$ for $\rho \geq \rho_0$, then from (5) and (6) we conclude that

$$u(\rho, s) \geq [u(\eta, s)/\eta^{n/d}]\rho^{n/d} \text{ for } \rho \geq \eta \geq \rho_1 \tag{7}$$

and

$$f(\rho, T) \geq [f(\eta, T)/\eta^{n/d}]\rho^{n/d} \text{ for } \rho \geq \eta \geq \rho_0 \, . \tag{8}$$

These results are stronger than Eqs. (25) and (33) of ref.[2].

Our second set of inequalities are bounds for classical systems based upon the Gibbs-Bogoliubov inequality[4] plus certain scaling properties[5,6] that hold when (1) or (2) are satisfied if the system under consideration is a classical one. For simplicity we shall consider only the single-species case, for which Eq. (2) can be written

$$v(r) = \lambda r^{-n} \tag{9}$$

so that $1/kT$ times the average potential energy per particle, e_{pot}/kT, becomes a function $E(\rho^*)$ of the single variable $\rho^* = \rho(\lambda/kT)^{d/n}$;

$$e_{pot}/kT = (\lambda\rho/2kT)\int g(r)\, r^{-n}\, d^d r = E(\rho^*). \tag{10}$$

We shall find it useful to introduce the function $J(\lambda, R)$ where $R = \rho(kT)^{-d/n} = \rho^*/\lambda^{d/n}$, by writing $J(\lambda, R) = (\rho/2kT)\int g(r)\, r^{-n}\, d^d r$ so that

$$E(\rho^*) = \lambda\, J(\lambda, R).$$

Let λ_0 and R_0 be such that $\lambda_0^{d/n} R_0 = \rho^* = \lambda^{d/n} R$. We have

$$J(\lambda_0, R_0) = (\lambda/\lambda_0)\, J(\lambda, R). \tag{11}$$

The form of the Gibbs-Bogoliubov inequality which we shall use in this note involves f and $g(r)$ for a potential $v(r) = v_0(r) + v_1(r)$ in a comparison with f and g(r) for the potential $v_0(r)$ at the same ρ and T. In obvious notation, it can be written

$$f_{v_0} + \tfrac{1}{2}\rho\int g_v(r)\, v_1(r)\, d^d r \le f_v \le f_{v_0} + \tfrac{1}{2}\rho\int g_{v_0}(r)\, v_1(r)\, d^d r. \tag{12}$$

Let $v_0 = \lambda_0 r^{-n}$ and $v_1 = (\lambda - \lambda_0) r^{-n}$. Eq. (12) directly implies that for $\lambda_0 \leq \lambda$,

$$J(\lambda, R_0) \leq J(\lambda_0, R_0). \tag{13}$$

Eqs. (10), (11), and (13) yield, for $R \leq R_0$,

$$(R/R_0)^{n/d} E(R_0 \lambda^{d/n}) \leq E(R\lambda^{d/n}). \tag{14}$$

For arbitrary fixed density η and fixed temperature $\mathcal{T}$, Eq. (14) provides a lower bound on $e_{pot}(\rho,T)$ when $\rho \leq \eta$ (and an upper bound when $\rho \geq \eta$) in terms of $e_{pot}(\eta, T)$ as well as a lower bound on $e_{pot}(\rho,T)$ when $T \geq \mathcal{T}$ (and an upper bound when $T \leq \mathcal{T}$) in terms of $e_{pot}(\rho, \mathcal{T})$.

The free energy is given by $f_{id} + f_{ex}$ where $f_{ex}/kT = I(\rho^*) = \int_0^\lambda J(\tilde{\lambda}, R)\, d\tilde{\lambda}$. Here f_{ex} is the configurational free energy and f_{id} the ideal-gas contribution. Hence (11) and (13) yield the inequality, for $R \leq R_0$,

$$(R/R_0)^{n/d}\, I(R_0 \lambda^{d/n}) \leq I(R\lambda^{d/n}). \tag{15}$$

Eq. (15) provides upper and lower bounds on $f_{ex}(\rho,T)$ in terms of $f_{ex}(\eta, T)$ and $f_{ex}(\rho,\mathcal{T})$ corresponding to the bounds on $e_{pot}(\rho,T)$ in terms of $e_{pot}(\eta,T)$ and $e_{pot}(\rho,\mathcal{T})$ that are provided by (14). For example, for $T \geq \mathcal{T}$,

$$f_{ex}(\rho, T) \geq f_{ex}(\rho, \mathcal{T}). \tag{16}$$

In the case of a Lennard-Jones potential given by (1), Eq. (10) is no longer true since e_{pot}/kT is a function of a second parameter, say λ/kT, in addition to ρ^*. The parameters T and λ are still found only in the combination λ/T however, and as a result our previous results still go through for fixed ρ. Thus Eq. (16) remains true for a classical system with $v(r)$ given by (1), as does $e_{pot}(\rho, T) \geq e_{pot}(\rho, \mathcal{T})$ for $T \geq \mathcal{T}$.

Our third set of inequalities are upper bounds based on the use of (4). If $n \geq 2$ in (9), we have, instead of (5),

$$\rho\left(\frac{\partial u}{\partial \rho}\right)_s \leq \left(\frac{n}{d}\right)u \; . \tag{17}$$

So if $u_1 \geq 0$ for $\rho \geq \rho_1$, then integration of (17) yields

$$u(\rho, s) \leq u(\eta, T)\rho^{n/d}/\eta^{n/d} \quad for \; \rho \geq \eta \geq \rho_1 \; . \tag{18}$$

If $n=2$, then (18) is a strict equality for all ρ and all η. Eq. (18) compliments Eq.(21) of ref.(1). When $n \geq 2$ we also have

$$\rho\left(\frac{\partial f}{\partial \rho}\right)_T \leq \frac{n}{d}u = \frac{n}{d}f + \frac{n}{d}Ts \, . \tag{19}$$

Let $s = s_{ex} + s_{id}$ where $Ts_{id} = kTd/2 - f_{id}$. Here s_{id} is the ideal-gas contribution to s for a given ρ and T; in the classical case $s = s_{id,c} = k[d/2 + 1 - \ln \Lambda^d \rho]$ where Λ is a thermal wavelength. We also introduce $f_{id,c}/kT = \ln \Lambda^d \rho - 1$. From Eq.(12), with V_0 set equal to zero, it follows that $u_{pot} \leq f_{ex}$. Since $f_{ex} = u_{pot} - Ts_{ex}$, this means $s_{ex} \leq 0$, which implies

$$\rho(\partial f/\partial \rho)_T \leq (n/d)f + (n/d)Ts_{id} \; . \tag{20}$$

Let $\tilde{f} = f - f_{id,c} + (d/2)kT$. Then (20) can be rewritten as $\rho(\partial \tilde{f}/\partial \rho) \leq (n/d)\tilde{f}$, and if ρ_2 exists such that $\tilde{f} \geq 0$ for $\rho \geq \rho_2$, it follows that

$$\tilde{f}(\rho, T) \leq \tilde{f}(\eta, T)\rho^{n/d}/\eta^{n/d} \quad for \; \rho \geq \eta \geq \rho_2 \; . \tag{21}$$

This is a stronger result than Eq. (27) of ref. [1] for $\rho \to \infty$. In the classical case, for which $f - f_{id} = f_{ex}$, it reduces to a result for f_{ex} that is slightly weaker than our Eq. (15) as $\rho \to \infty$, owing to the extra $\left(\frac{1}{2} - \frac{1}{n}\right) d k T (\rho/q)^{n/d}$ that is present when (21) is written in terms of f_{ex}.

Finally, we note that if v is the Lennard-Jones potential given by (1), with $\lambda > 0$, $const < 0$, $n > m > d$, and if v_0 is the repulsive power-law potential λr^{-n}, then (12) implies that any upper bound on f for the repulsive power-law potential is also an upper bound on f for the Lennard-Jones potential at a given ρ and T. As reported by us elsewhere[3] Eq.(12) also directly provides upper bounds in the Lennard-Jones case (as well as the power-law case) if one lets v_0 be a hard-sphere potential.

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