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First-Order Thermodynamic Perturbation Theory is Exact in the Two-Dimensional Close-Packing Limit

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Upper and lower bounds are obtained for the potential energy of two-dimensional classical systems consisting of particles interacting via a short-range potential that has a hard-disk core. The bounds coincide in the close-packing limit, implying that first-order thermodynamic perturbation theory becomes exact in this limit.

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Thermodynamic perturbation theories have proved to be extremely successful in describing the behavior of simple liquids and solids near their triple point.[1] In this thermodynamic domain the relevant perturbation parameter is far from small; it is of order unity in typical dimensionless units of ϵ/kT, where ϵ is a measure of interaction strength outside the highly repulsive interparticle cores, k is Boltzmann's constant, and T is the absolute temperature. It has long been argued that the success of first-order theory for such thermodynamic states is due to the stringent configurational constraint imposed on a system of particles by their repulsive cores,[2] but except in one dimension[3] rigorous results in support of this plausible assertion have heretofore been lacking. Here we give such a result.

We consider a classical two-dimensional system of N particles confined to the interior of a hexagonal container of area A. The number density is $\rho = N/A$. The potential energy is the sum of a potential U_0 that describes a reference system of N hard disks of diameter a plus a perturbing term U that describes pairwise interaction of the disks via a short-range pair potential.[4] To facilitate applying our results to the thermodynamic limit, $N\to\infty$, $A\to\infty$, ρ finite, we introduce $u = U/N$. In terms of the Helmholtz free energy per particle f, first-order thermodynamic perturbation theory for the system we consider is the approximation

$$f \cong f_0 + \langle u\rangle_0 . \tag{1}$$

Here $\langle\cdots\rangle_0$ denotes the canonical ensemble average taken with respect to the reference system at the N, A, and T at which the other terms in (1) are evaluated. We use the subscript zero throughout to denote hard-disk reference-system quantities. The approximation (1) is an upper bound on f according to the well-known Gibbs-Bogoliubov inequalities, which, for the system under consideration, have the simple form

$$\langle u\rangle \leq f - f_0 \leq \langle u\rangle_0 , \tag{2}$$

where $\langle\cdots\rangle$ denotes an ensemble average in the perturbed system. Our theorem below gives upper and lower bounds (31) and (32) on u, and hence on $\langle u\rangle$ and $\langle u\rangle_0$. Thus from (2) our theorem also yields the same bounds on $f-f_0$, and since $f=\langle u\rangle+kT-Ts$, where s is the entropy per particle, our result yields similar bounds on $s-s_0$. Since these upper and lower bounds coalesce as ρ approaches the close-packing density $\rho_{\rm cp}$, T arbitrary, our bounds are all sharp in the vicinity of $\rho=\rho_{\rm cp}$. Moreover in the limit $\rho\to\rho_{\rm cp}$, $f-f_0\to\langle u\rangle_0$ and hence (because $f_0=kT-Ts_0$), $s-s_0\to 0$. Thus first-order thermodynamic perturbation theory is exact for the system in this limit.

Our theorem rests upon two lemmas.

Lemma 1.—If a convex hexagon H contains N nonoverlapping disks of diameter a, and if fewer than $3N(1-\alpha)-L(a+b)/4\pi a^2$ pairs of these disks have center-to-center separations less than b, where $0<\alpha<1$ and $a<b<2a/\sqrt{3}=(1.1547\ldots)a$, and L is the length of the perimeter of H, then the area A of H satisfies

$$A/A_{\rm cp}\geqslant 1+\alpha\beta(1-\tfrac{3}{2}\beta), \tag{3}$$

where $A_{\rm cp}=\frac{1}{2}\sqrt{3}Na^2$ is the area at close packing and $\beta=b^2/a^2-1$.

Proof of lemma 1.—We denote the centers of the N disks by $C_1, C_2, \ldots, C_N$. To each C_i we associate a polygonal region P_i consisting of all those points within H which are closer to C_i than to any other disk center. Denoting the area of the ith polygon by A_i, we have (with $k=1,\ldots,\nu_i$; $i=1,\ldots,N$)

$$A=\textstyle\sum_i A_i=\sum_i\sum_k \frac{1}{2}h_{ik}^2(\tan\theta_{ik}+\tan\theta_{ik}'), \tag{4}$$

where ν_i is the number of edges of P_i, h_{ik} is the length of the perpendicular from C_i to the kth edge of P_i, and θ_{ik} and θ_{ik}' are the angles between this perpendicular and the two lines joining C_i to the ends of this edge. The angles θ_{ik} satisfy the condition (with $k=1,\ldots,\nu_i$; $i=1,\ldots,N$)

$$\textstyle\sum_k(\theta_{ik}+\theta_{ik}')=2\pi \tag{5}$$

and the perpendiculars h_{ik} satisfy the condition $h_{ik}\geqslant\frac{1}{2}a$. The total number ν of perpendiculars satisfies[5] (with $i=1,\ldots,N$)

$$\nu=\textstyle\sum_i\nu_i\leqslant 6N. \tag{6}$$

Every edge in the network of polygons P_i is either part of the perpendicular bisector of the line between two disk centers or else part of the boundary of H. Therefore, if we denote by ν_α the number of perpendiculars h_{ik} whose lengths are less than $\frac{1}{2}b$, we have

$$\nu_\alpha\leqslant 2P(a,b)+N_B, \tag{7}$$

where $P(a,b)$ denotes the number of pairs of disk centers whose separations lie between a and b, and N_B denotes the number of disks whose centers are within a distance $\frac{1}{2}b$ of the boundary of H. These N_B disks are entirely contained in a strip of width $\frac{1}{2}b+\frac{1}{2}a$ just inside the boundary of H; the area of this strip is less than $(\frac{1}{2}b+\frac{1}{2}a)L$ where L is the perimeter of H, and since each disk occupies area πa^2 we have

$$N_B<\tfrac{1}{2}b+\tfrac{1}{2}a)L/\pi a^2. \tag{8}$$

Combining this with (7) and using the upper bound on $P(a,b)$ required by the statement of the lemma, we obtain

$$\nu_\alpha\leqslant 6N(1-\alpha). \tag{9}$$

For each perpendicular h_{ik} there are two angles θ_{ik}, θ_{ik}'; let the mean of the $2\nu_\alpha$ angles for which $\frac{1}{2}a\leqslant h_{ik}<\frac{1}{2}b$ be $\overline{\theta}_\alpha$, and let the mean of the $2\nu-2\nu_\alpha$ angles θ_{ik} and θ_{ik}' for which $h_{ik}\geqslant\frac{1}{2}b$ be $\overline{\theta}_\beta$. Then it follows from (5), after summing both sides over i and separating the terms for which $h_{ik}<\frac{1}{2}b$ from those for which $h_{ik}\geqslant\frac{1}{2}b$, that

$$2\nu_\alpha\overline{\theta}_\alpha+2(\nu-\nu_\alpha)\overline{\theta}_\beta=2\pi N. \tag{10}$$

Applying a similar decomposition to the double sum in (4) and then using Jensen's inequality for convex functions (in this case the tangent function) we obtain

$$\begin{aligned} A &\geqslant \tfrac{1}{4}a^2\nu_\alpha\tan\overline{\theta}_\alpha+\tfrac{1}{4}b^2(\nu-\nu_\alpha)\tan\overline{\theta}_\beta \\ &= \tfrac{1}{4}a^2[\nu_\alpha\tan\overline{\theta}_\alpha+\nu_\beta(1+\beta)\tan\overline{\theta}_\beta], \end{aligned} \tag{11}$$

where $\beta=b^2/a^2-1$ and $\nu_\beta=\nu-\nu_\alpha$.

To combine the inequalities (6), (9), and (11) into a useful formula, we define two angles φ_α, φ_β by the equations

$$(1-\alpha)\varphi_\alpha+\alpha\varphi_\beta=\pi/6, \tag{12}$$

$$\sec^2\varphi_\alpha=(1+\beta)\sec^2\varphi_\beta \tag{13}$$

and the condition $0\leqslant\varphi\leqslant\pi/2$ ($\varphi=\varphi_\alpha,\varphi_\beta$). By considering the behavior of the function $\sec^2x-(1+\beta)^{-1}\sec^2[(\pi/6-\alpha x)/(1-\alpha)]$ as x decreases from $\pi/6$, and using the condition $b\leqslant 2a/\sqrt{3}$ which implies $\beta>\frac{1}{3}$, Eqs. (12) and (13) can be shown to have a unique solution, satisfying the further condition

$$0\leqslant\varphi_\beta\leqslant\tfrac{1}{6}\pi\leqslant\varphi_\alpha\leqslant\tfrac{1}{2}\pi. \tag{14}$$

Now we use the convexity of the tangent function again, in the form

$$\tan\overline{\theta}\geqslant\tan\varphi+(\overline{\theta}-\varphi)\sec^2\varphi. \tag{15}$$

Using this and then (13) in (11), we obtain

$$4A/a^2 \geq (\nu_\alpha\bar{\theta}_\alpha + \nu_\beta\bar{\theta}_\beta)\sec^2\varphi_\alpha - \nu_\alpha[f(\varphi_\alpha) - (1+\beta)f(\varphi_\beta)] - \nu(1+\beta)f(\varphi_\beta), \quad (16)$$

where f is defined by

$$f(x) = x\sec^2 x - \tan x \quad (0 \leq x \leq \pi/2). \quad (17)$$

This function has the properties

$$f(x) = \tfrac{1}{2}[2x - \sin 2x]\sec^2 x \geq 0 \quad (18)$$

and [by (13) and (14)]

$$f(\varphi_\alpha) - (1+\beta)f(\varphi_\beta) = \tfrac{1}{2}\{[2\varphi_\alpha - \sin 2\varphi_\alpha] - [2\varphi_\beta - \sin 2\varphi_\beta]\}\sec^2\varphi_\alpha \geq 0 \quad (19)$$

since $2x - \sin 2x$ is an increasing function for $0 \leq x \leq \pi/2$. Now we insert Eqs. (10) and the inequalities (6) and (9) into (16); making use of (18) and (19) as well, we obtain

$$4A/a^2 \geq \pi N\sec^2\varphi_\alpha - 6N(1-\alpha)[f(\varphi_\alpha) - (1+\beta)f(\varphi_\beta)] - 6N(1+\beta)f(\varphi_\beta). \quad (20)$$

The right-hand side can be rearranged, using first (17) to eliminate f, then (13) to eliminate $\sec^2\varphi_\beta$, and finally (12), to give

$$4A/a^2 \geq 6N[(1-\alpha)\tan\varphi_\alpha + \alpha(1+\beta)\tan\varphi_\beta]. \quad (21)$$

To derive a simpler lower bound on A, we denote the right-hand side of (21) by $6Ng(\beta)$, treating α as a constant. This definition, together with (13) and (12), implies that

$$dg(\beta)/d\beta = \alpha\tan\varphi_\beta. \quad (22)$$

By (13) and (14), we have the lower bound

$$\begin{aligned}\tan^2\varphi_\beta &= \sec^2\varphi_\beta - 1\\ &\geq (1+\beta)^{-1}\sec^2\pi/6 - 1 = (1-3\beta)/3(1+\beta)\\ &\geq \tfrac{1}{3}(1-3\beta)^2 \quad (0 \leq \beta < \tfrac{1}{3}).\end{aligned} \quad (23)$$

Using this in (22), and then integrating from 0 to β, we obtain

$$\begin{aligned}g(\beta) &\geq g(0) + \alpha\int_0^\beta (1-3\beta)d\beta/\sqrt{3}\\ &= [1 + \alpha(\beta - \tfrac{3}{2}\beta^2)]/\sqrt{3}.\end{aligned} \quad (24)$$

Using the definition of g and combining with (21), we obtain a lower bound on A which is equivalent to the one given in the statement of lemma 1.

Lemma 2.—Under the conditions of lemma 1, the number $P(r_1, r_2)$ of pairs of disks whose centers are separated by distances in the interval $[r_1, r_2)$, where $a \leq r_1 < r_2 < \frac{1}{2}a\,\mathrm{cosec}\frac{1}{7}\pi = (1.1524\ldots)a$, satisfies

$$3N\left[1 - \frac{A/A_{\rm cp} - 1}{(1-\frac{3}{2}\beta_2)\beta_2}\right] - \frac{L(a+r_2)}{4\pi a^2} \leq P(a, r_2) \leq 3N, \quad (25)$$

where

$$\beta_2 = r_2^2/a^2 - 1. \quad (26)$$

Proof of lemma 2.—The upper bound $P(a, r_2) \leq 3N$ follows from the fact that it is not possible to place more than six disks so that their centers are within a distance r_2 of the center of another disk, without overlapping, unless $r_2 \geq \frac{1}{2}a\,\mathrm{cosec}\frac{1}{7}\pi$. The other bound comes from lemma 1; for with the choice

$$\alpha = 1 - P(a, b)/3N - L(a+b)/12\pi a^2 N \quad (27)$$

its result can be rearranged to give

$$P(a, b) \geq 3N\left[1 - \frac{A/A_{\rm cp} - 1}{(1-\frac{3}{2}\beta_2)\beta_2}\right] - \frac{L(a+b)}{4\pi a^2}. \quad (28)$$

The lower bound on $P(a, r_2)$ in lemma 2 now follows (since $\frac{1}{2}\mathrm{cosec}\frac{1}{7}\pi < 2/\sqrt{3}$) on replacing b by r_2.

Theorem.—In a two-dimensional system of particles with hard-disk cores of diameter a and a pair potential $\varphi(r)$ outside the core, let $\varphi(r)$ be continuous as $r \downarrow a$, bounded for all $r \geq a$, and zero for $r > c$, where $c = \frac{1}{2}a\,\mathrm{cosec}\frac{1}{7}\pi = (1.1524\ldots)a$. We split $\varphi(r)$ into an increasing and a decreasing part with

$$\varphi_i(c) = \varphi_d(c) = 0 \quad (29)$$

and

$$d\varphi_i \geq 0, \quad d\varphi_d \leq 0, \quad d\varphi = d\varphi_i + d\varphi_d. \quad (30)$$

Then for all configurations in which no interparticle separation is less than a, the potential energy per particle, u, has the bounds

$$u \geq 3\varphi(a) - 3\int_a^c \min\left\{1, \frac{(\rho_{\rm cp}/\rho) - 1}{(1-\frac{3}{2}\beta_r)\beta_r}\right\}|d\varphi_d(r)|, \quad (31)$$

$$u \leq 3\varphi(a) + 3\int_a^c \min\left\{1, \frac{(\rho_{\rm cp}/\rho) - 1}{(1-\frac{3}{2}\beta_r)\beta_r}\right\}d\varphi_i(r), \quad (32)$$

where $\beta_r = (r/a)^2 - 1$, ρ is the number of particles per unit area, and $\rho_{\rm cp} = 2/a^2\sqrt{3}$ is the value of ρ at close packing.

Proof of the theorem.—Define

$$p(r_2) = \lim_{N\to\infty} P(a, r_2)/N; \qquad (33)$$

then lemma 2 gives

$$p(r_2) \leq 3 \qquad (34)$$

and

$$p(r_2) \geq 3 - 3\frac{(\rho_{cp}/\rho) - 1}{(1-\frac{3}{2}\beta_2)\beta_2}, \qquad (35)$$

where $\beta_2 = (r_2/a)^2 - 1$. Since $p(r_2) \geq 0$, the bound in (35) can be strengthened to

$$p(r_2) \geq 3 - 3\min\left\{1, \frac{(\rho_{cp}/\rho) - 1}{(1-\frac{3}{2}\beta_2)\beta_2}\right\}. \qquad (36)$$

Now the potential energy per particle is, with $c = \frac{1}{2}a\operatorname{cosec}\frac{1}{7}\pi$,

$$u = \int_a^c \varphi(r)dp(r). \qquad (37)$$

Since $p(a) = 0$ and $\varphi(c) = 0$, integration by parts gives

$$u = -\int_a^c p(r)d\varphi(r), \qquad (38)$$

$$u = -\int_a^c p(r)d\varphi_i(r) - \int_a^c p(r)d\varphi_a(r), \qquad (39)$$

using (32). From (34) and (35), (39) yields

$$u \geq -\int_a^c 3\,d\varphi_i(r) + \int_a^c \left[3 - 3\min\left\{1, \frac{(\rho_{cp}/\rho) - 1}{(1-\frac{3}{2}\beta_r)\beta_r}\right\}\right]|d\varphi_a(r)| \qquad (40)$$

$$= -\int_a^c 3\,d\varphi(r) - 3\int_a^c \min\left\{1, \frac{(\rho_{cp}/\rho) - 1}{(1-\frac{3}{2}\beta_r)\beta_r}\right\}|d\varphi_a(r)| \qquad (41)$$

and

$$u \leq -\int_a^c \left[3 - 3\min\left\{1, \frac{(\rho_{cp}/\rho) - 1}{(1-\frac{3}{2}\beta_r)\beta_r}\right\}\right]d\varphi_i(r) + \int_a^c 3\,|d\varphi_a(r)| \qquad (42)$$

$$= -\int_a^c 3\,d\varphi(r) + 3\int_a^c \min\left\{1, \frac{(\rho_{cp}/\rho) - 1}{(1-\frac{3}{2}\beta_r)\beta_r}\right\}d\varphi_i(r) \qquad (43)$$

from which (31) and (32) follow.

It is a simple corollary of this theorem that in the close-packing limit, the energy per particle approaches a close-packing value of $3\varphi(a)$:

$$\lim_{\rho\to\rho_{cp}} u = 3\varphi(a). \qquad (44)$$

The corresponding result for three dimensions, which we believe but cannot prove, would be

$$\lim_{\rho\to\rho_{cp}} u = 6\varphi(a). \qquad (45)$$

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[1]For a good general review, see J. A. Barker and D. Henderson, Rev. Mod. Phys. 48, 587 (1976).

[2]As described by G. Stell, in *Statistical Mechanics*, Modern Theoretical Chemistry Vol. 5, edited by B. Berne (Plenum, New York, 1977), Part A, p. 54, the success of thermodynamic perturbation theories can be understood on the grounds of the linearity of the free energy as a function of $\lambda = \epsilon/kT$ expected for *large* as well as small λ (fixed density) in many systems, and also expected for the high-density limit (fixed λ) considered here.

[3]The one-dimensional result is given by J. M. Kincaid, G. Stell, and C. Hall, J. Chem. Phys. 65, 2161 (1976). The plausibility of the higher-dimensional result is discussed by J. M. Kincaid, G. Stell, and E. Goldmark, J. Chem. Phys. 65, 2172 (1976), as well as in Ref. 2 above.

[4]Although restricted in range, the pair potential we consider here already includes the shouldered-potential and sloped-potential models introduced by Stell and Hemmer to study isostructural phase transitions with ranges relevant to the solid-solid transitions found in Ce, Cs, and their alloys. See P. C. Hemmer and G. Stell, Phys. Rev. Lett. 24, 1284 (1970); G. Stell and P. C. Hemmer, J. Chem. Phys. 56, 4274 (1972); and Ref. 3 above. The narrow-ranged shouldered potential has been the subject of considerable Monte Carlo simulation motivated by this application. See, e.g., P. A. Young and B. J. Alder, Phys. Rev. Lett. 38, 1213 (1977), and J. Chem. Phys. 70, 437 (1979).

[5]L. Fejes Toth, *Regular Figures* (MacMillan, New York, 1964), p. 165.