Necessary Conditions on Radial Distribution Functions

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Certain necessary conditions must be met by any function introduced to serve as a radial distribution function of a uniform N-particle system. One large class of necessary conditions is based on the statement that the expectation value of a potential energy (for an arbitrary potential function between pairs of particles) cannot fall below the classical minimum potential energy of the system. To convert this statement into a family of useful inequalities, we have evaluated the classical potential energies of close-packed crystals for a linear combination of Yukawa and Coulomb two-particle interactions. The numerical evaluation of lattice sums is performed by two procedures: (1) direct summation over the lattice (suitable for short-range potentials), and (2) an adaptation of the Ewald summation procedure suitable for long-range potentials. Results are given for the Coulomb and Yukawa potentials and also for the potentials $1/r(r+a)$ and $1/r(r+a)^2$. Two simple approximate forms are developed both giving close lower bounds on the classical potential energy of interacting particles forming a regular crystalline lattice.

1. INTRODUCTION

A GENERAL problem in the quantum theory of many-particle systems is the characterization of admissible density matrices and distribution functions.[1,2]. One aspect of this problem is the development of necessary conditions on the radial distribution function of an extended uniform system.[2,3] In this study we determine a family of necessary conditions based on the evaluation of the minimum classical potential energy of a system of particles interacting in pairs through a linear combination of Coulomb and Yukawa potentials. To begin, the physical system is specified as N particles in a cubical box of volume Ω subject to the limiting process $N, \Omega \to \infty$, while $\rho = N/\Omega$ is held constant. The given Hamiltonian operator H and periodic boundary conditions complete the specification. Let $\psi(1, 2, \cdots, N)$ represent a normalized trial function subject to the constraint $\mathbf{P}\psi = 0$ (an eigenstate of the center-of-mass momentum with the eigenvalue $\mathbf{P}' = 0$). The two-particle distribution function $p^{(2)}(1, 2)$ for the pure state represented by ψ is the positive definite form

$$p^{(2)}(1, 2) = N(N-1)\int |\psi|^2\, dv_{3\cdots N}, \qquad (1)$$

the integration including summation over all discrete (spin and iso-spin) coordinates when these are present. The radial distribution function $g(r)$ is introduced by writing $p^{(2)}(1, 2) = \rho^2 g(r_{12})$ and neglecting the slight dependence of $p^{(2)}$ on the direction of $\mathbf{r}_{12}$. The condition $\mathbf{P}' = 0$ has the consequence that $p^{(2)}(1, 2)$ is a function of $\mathbf{r}_{12}$ only. This can be seen by expressing ψ as a $3N$-dimensional Fourier series (periodic in the fundamental cube).

Let $\mathbf{k}$ represent an allowed wave vector defined by the periodic boundary condition. For $k \neq 0$, the liquid structure function is defined as a positive definite form by

$$\begin{aligned} S(k) &= \frac{1}{N}\int |\psi|^2 \left|\sum_l e^{i\mathbf{k}\cdot\mathbf{r}_l}\right|^2 dv_{12\cdots N} \\ &= 1 + \frac{\rho^2}{N}\int g(r_{12}) e^{i\mathbf{k}\cdot\mathbf{r}_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2 \\ &= 1 + \rho\int [g(r) - g(\infty)] e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}. \qquad (2) \end{aligned}$$

The third line of Eq. (2) involves the asymptotic limit of $g(r)$ as $r \to \infty$ and $N \to \infty$. The proof that $g(\infty) = 1$, or more precisely $\lim_{N\to\infty} |N[1 - g(\infty)]| \ll 1$, can be developed by relating $S(k)$ in a qualitative manner to fluctuations in the number of particles found in a suitably defined half space within Ω.[4] A more precise derivation follows from three well-known sum rules[5] which have the consequence, $S(k) \leq \hbar k/2mC$ (here C is the velocity of 1st sound at absolute zero and N is assumed infinite). Thus the sum rules imply

$$\lim_{k\to 0}\,[\lim_{N\to\infty} S(k)] = 0. \qquad (3)$$

Equation (1) imposes the normalization condition

$$\frac{\rho}{\Omega}\int [g(r_{12}) - 1]\, d\mathbf{r}_1\, d\mathbf{r}_2 = -1 \qquad (4)$$

or

$$\rho\int [g(r) - g(\infty)]\, d\mathbf{r} + N[g(\infty) - 1] = -1. \qquad (5)$$

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[1] A. J. Coleman, Rev. Mod. Phys. 35, 690 (1963).
[2] C. Garrod and J. K. Percus, J. Math. Phys. 5, 1756 (1964).
[3] M. Yamada, Progr. Theoret. Phys. (Kyoto) 25, 579 (1961).
[4] E. Feenberg, in *Lectures in Theoretical Physics* (University of Colorado Press, Boulder, Colorado, 1965), Vol. VIIC.
[5] P. J. Price, Phys. Rev. 94, 257 (1954).

Equations (2), (3), and (5) require

$$\lim_{N\to\infty} |N[1 - g(\infty)]| = 0. \tag{6}$$

Through the sum rules, this argument involves the restriction that ψ is the correct ground-state eigenfunction ψ_0. The fluctuation argument establishes the less precise result

$$\lim_{N\to\infty} |N[1 - g(\infty)]| \ll 1,$$

but requires only that ψ exhibit reasonably well the essential physical structure expected of the ground-state eigenfunction when the interactions are strongly repulsive for small separations of the particles.

The relation[6,7]

$$S(k) = \hbar k/2mC, \quad k \ll \rho^{\frac{1}{3}} \tag{7}$$

is expected to hold in liquid He^4. This behavior has implications for the manner in which $g(r)$ approaches its asymptotic value as r increases without limit. Equation (2) with $g(\infty) = 1$ can be expressed in the equivalent form

$$S(k) = 4\pi\rho \int_0^\infty \left(\frac{\sin kr}{kr} - 1\right)[g(r) - 1]r^2\, dr$$
$$= \frac{4\pi\rho}{k^3}\int_0^\infty \left(\frac{\sin x}{x} - 1\right)\left[g\left(\frac{x}{k}\right) - 1\right]x^2\, dx. \tag{8}$$

The correct dependence on k as $k \to 0$ occurs only if

$$\overline{g(r)} \simeq 1 - b/r^4, \quad r \gg \bar{\rho}^{\frac{1}{3}}, \tag{9}$$

the bar denoting an average over a small range of r values ($\delta r \sim \bar{\rho}^{\frac{1}{3}}$). Introducing Eq. (7) into Eq. (8) for $k \ll \rho^{\frac{1}{3}}$, we find

$$\frac{\hbar k}{2mc} = 4\pi\rho b k \int_0^\infty \left(1 - \frac{\sin x}{x}\right)\frac{dx}{x^2} \tag{10}$$

and[4,8]

$$b = \frac{\hbar}{2\pi^2\rho m c}. \tag{11}$$

A broad class of necessary conditions on $g(r)$ are defined by the statement[2]

$$N(N-1)\int |\psi|^2 v(\mathbf{r}_1, \mathbf{r}_2)\, dv_{12\cdots N} \geq \min \sum_{i\neq j} v(\mathbf{R}_i, \mathbf{R}_j), \tag{12}$$

in which $v(\mathbf{R}_i, \mathbf{R}_j)$ is a real integrable function and the points $\mathbf{R}_1, \mathbf{R}_2, \cdots$ are all distinct, all located within Ω (or on the boundary of Ω), and otherwise arbitrary. Equation (12) implies

$$\rho^2 \int g(r_{12})\, v(\mathbf{R}_1, \mathbf{R}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \geq \min \sum_{i\neq j} v(\mathbf{R}_i, \mathbf{R}_j) \tag{13}$$

and also

$$\rho^2 \int [g(r_{12}) - 1] v(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \geq \min \left[\sum_{i\neq j} v(\mathbf{R}_i, \mathbf{R}_j) - \rho^2 \int v(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'\right]. \tag{14}$$

These inequalities can be given an immediate physical interpretation. Suppose $v(\mathbf{r}_1, \mathbf{r}_2) = v(r_{12})$ is a potential between particles at points $\mathbf{r}_1$ and $\mathbf{r}_2$, Eqs. (12) and (13) state that the expectation value of

$$V = \sum_{i<j} v(R_{ij})$$

with respect to the normalized state function ψ exceeds the minimum possible value of V (assumed to exist for a definite configuration $\mathbf{R}_1, \mathbf{R}_2, \cdots$). Suppose further that $\int v(\mathbf{R}_i - \mathbf{r})\, d\mathbf{r}$ is independent of the location of $\mathbf{R}_i$ except for points in a negligible fraction of the total volume near the surface; then the left- and right-hand members of Eq. (14) represent two ways of computing the potential energy (doubled) of a system of particles immersed in a uniform charged background of equal total strength and opposite sign. The energy expended to assemble the background charge against the interaction is included. Here we postulate that $-\rho v(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}'$ is the potential energy of a particle at $\mathbf{r}$ interacting with the uniform background charge in the volume element $d\mathbf{r}'$. The corresponding potential for the mutual interaction of charges in elements $d\mathbf{r}_1$ and $d\mathbf{r}_2$ is $\rho^2 v(r_{12})\, d\mathbf{r}_1\, d\mathbf{r}_2$.

Results for the Coulomb potential $v(r) = 1/r$ are known from calculations of the minimum potential energy of a system of electrically charged particles.[9,10] In this case Eq. (14) reduces to the explicit form[11]

$$4\pi\rho \int_0^\infty [1 - g(r)] r\, dr \leq 1.792\left(\frac{4\pi\rho}{3}\right)^{\frac{1}{3}}, \tag{15}$$

or, in conjunction with the normalization condition on $g(r)$,

$$\int_0^\infty [1 - g(r)] r\, dr \left[\int_0^\infty [1 - g(r)] r^2\, dr\right]^{-\frac{2}{3}} \leq \frac{1.792}{3^{\frac{1}{3}}} = 1.243. \tag{16}$$

The object of the present study is to derive additional relations of the above type employing the Yukawa potential and linear combinations of Yukawa potentials:

$$v(r) = \sum_l C_l \frac{e^{-\mu_l r}}{r} \tag{17}$$

and

$$v(r) = \int_0^\infty C(\mu) \frac{e^{-\mu r}}{r}\, d\mu. \tag{18}$$

2. EVALUATION OF LATTICE SUMS INVOLVING THE YUKAWA POTENTIAL

The analysis begins with the classical potential energy

$$V(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N) = \frac{1}{2}\sum_{i\neq j} \frac{e^{-\mu R_{ij}}}{R_{ij}} + \tfrac{1}{2}\rho^2 \int \frac{e^{-\mu|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' - \sum_i \rho \int \frac{e^{-\mu|\mathbf{R}_i - \mathbf{r}|}}{|\mathbf{R}_i - \mathbf{r}|}\, d\mathbf{r}, \tag{19}$$

[6] R. P. Feynman and M. Cohen, Phys. Rev. **102**, 1189 (1956).
[7] K. Huang and A. Klein, Ann. Phys. (N.Y.) **30**, 203 (1964).
[8] J. E. Enderby, T. Gaskell, and N. H. March, Proc. Phys. Soc. (London) **85**, 217 (1965).
[9] E. P. Wigner, Trans. Faraday Soc. **34**, 678 (1938).
[10] K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).
[11] E. Feenberg, J. Math. Phys. **6**, 658 (1965).

TABLE I. Lattice energies for the Yukawa potential.

$\beta = \mu r_s$	Lattice type	$-\frac{2r_s}{N}E_a^*$	$-\frac{2r_s}{N}V_a^*$	$-\frac{2r_s}{N}V_b$	$-\frac{2r_s}{N}V_c$	$-\frac{2r_s}{N}V$
	sc			−0.0535	−0.0470	1.7606
0.0	bcc	1.8000	1.8611	−0.0363	−0.0331	1.7917
	fcc			−0.0367	−0.0328	1.7916
	hcp					
	sc			−0.0500	−0.0455	1.31339
0.5	bcc	1.3578	1.4089	−0.0340	−0.0317	1.34334
	fcc			−0.0344	−0.0313	1.34326
	hcp					1.34320
	sc			−0.0409	−0.0401	0.96817
1.0	bcc	1.0215	1.0492	−0.0281	−0.0281	0.99341
	fcc			−0.0283	−0.0275	0.99340
	hcp					0.99335
	sc			−0.0293	−0.0326	0.71112
1.5	bcc	0.7709	0.7731	−0.0204	−0.0225	0.73028
	fcc			−0.0206	−0.0222	0.73035
	hcp					0.73032
	sc			−0.0186	−0.0244	0.52478
2.0	bcc	0.5860	0.5677	−0.0131	−0.0167	0.53805
	fcc			−0.0132	−0.0164	0.53816
	hcp					0.53814
	sc			−0.0105	−0.0169	0.39174
2.5	bcc		0.4191	−0.0075	−0.0115	0.40024
	fcc			−0.0076	−0.0113	0.40036
	hcp					0.40035

* These are independent of lattice type.

in which $\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N$ are a set of lattice points occupying the entire box. One point coincides with the origin at the center. Calculations are made for (i) $\mu > 0$ and $\mu\Omega^{\frac{1}{3}} \gg 1$ and (ii) $\mu = 0$. The first condition is permitted by the limiting process Ω, $N \to \infty$, subject to ρ held constant for any $\mu > 0$. Thus for $\mu > 0$ the formula for V may be simplified to

$$V(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N) = \tfrac{1}{2}N\left[\sum_j{}' \frac{e^{-\mu R_j}}{R_j} - \frac{4\pi\rho}{\mu^2}\right] \quad (20)$$

the primed summation excluding $R_j = 0$.

The direct evaluation of the sum in Eq. (20) is feasible when $\mu\bar{\rho}^{\frac{1}{3}}$ is sufficiently large (calculations have been made for $\mu\bar{\rho}^{\frac{1}{3}} \geq 0.8$). Also a close lower bound on $V(R_1, \cdots, R_N; \mu)$ can be derived by a simple argument based on the physical picture of N-point charges immersed in a uniform background charge of equal total strength but with opposite sign. Each point charge can be pictured at the center of its own s sphere of radius $r_s = (3/4\pi\rho)^{\frac{1}{3}}$. Adjacent s spheres overlap slightly, but in the following nonrigorous argument the overlap is disregarded. Since the conclusions are verified by accurate numerical calculations, the lack of rigor does not matter. In terms of the s spheres the energy of the system can be split into two parts: the self energy E_a of the charges within the N s spheres and the interaction energy E_b of these spheres.[9] As shown in Appendix A, E_a is easily computed [Eq. (A3)] and E_b is found to be positive. The inference appears safe that E_a is a lower bound to the energy $V(R_1, \cdots, R_N; \mu)$. This is confirmed by the explicit computation shown in Table I.

Ewald's summation procedure[12] is easily adapted to the Yukawa potential and offers the advantage of rapid convergence for small μ. It also provides a simple approximate formula giving a moderately close rigorous upper limit on the lattice sum.

The derivation of the Ewald form is given in Appendix B. Some essential information on the basis vectors (in both lattice and dual spaces) and the numerical values of certain derived quantities are listed in Table II. This information is needed to connect the mathematical analysis with the numerical

TABLE II. Basis vectors and nearest-neighbor distance.

Lattice type	sc	fcc	bcc
$\mathbf{a}_1$	$\rho^{-\frac{1}{3}}(1,0,0)$	$(2\rho)^{-\frac{1}{3}}(1,1,0)$	$(4\rho)^{-\frac{1}{3}}(1,1,-1)$
$\mathbf{a}_2$	$\rho^{-\frac{1}{3}}(0,1,0)$	$(2\rho)^{-\frac{1}{3}}(0,1,1)$	$(4\rho)^{-\frac{1}{3}}(-1,1,1)$
$\mathbf{a}_3$	$\rho^{-\frac{1}{3}}(0,0,1)$	$(2\rho)^{-\frac{1}{3}}(1,0,1)$	$(4\rho)^{-\frac{1}{3}}(1,-1,1)$
$\mathbf{b}_1$	$\rho^{\frac{1}{3}}(1,0,0)$	$(\rho/4)^{\frac{1}{3}}(1,1,-1)$	$(\rho/2)^{\frac{1}{3}}(1,1,0)$
$\mathbf{b}_2$	$\rho^{\frac{1}{3}}(0,1,0)$	$(\rho/4)^{\frac{1}{3}}(-1,1,1)$	$(\rho/2)^{\frac{1}{3}}(0,1,1)$
$\mathbf{b}_3$	$\rho^{\frac{1}{3}}(0,0,1)$	$(\rho/4)^{\frac{1}{3}}(1,-1,1)$	$(\rho/2)^{\frac{1}{3}}(1,0,1)$
R_n^*	$\rho^{-\frac{1}{3}}$	$2^{\frac{1}{6}}\rho^{-\frac{1}{3}} = 1.12\rho^{-\frac{1}{3}}$	$\sqrt{3}(4\rho)^{-\frac{1}{3}} = 1.09\rho^{-\frac{1}{3}}$

* Nearest-neighbor distance.

[12] P. P. Ewald, Ann. Physik **54**, 519, 557 (1917).

evaluation for simple cubic, face-centered cubic, and body-centered cubic lattices.

The results of Appendix B can be summarized in the formulas

$$V = V_a + V_b + V_c,$$
$$\frac{2}{N} V_a = -\frac{2x_0}{\sqrt{\pi}} \exp\left[-\left(\frac{\mu}{2x_0}\right)^2\right] + \mu\left[1 - E\left(\frac{\mu}{2x_0}\right)\right] + \frac{4\pi\rho}{\mu^2}\left[\exp\left[-\left(\frac{\mu}{2x_0}\right)^2\right] - 1\right],$$
$$\frac{2}{N} V_b = \pi\rho \sum_{\mathfrak{p}\neq 0} \frac{\exp\left[-\frac{1}{x_0^2}(\pi^2 h_{\mathfrak{p}}^2 + \frac{1}{4}\mu^2)\right]}{\pi^2 h_{\mathfrak{p}}^2 + \frac{1}{4}\mu^2}, \tag{21}$$
$$\frac{2}{N} V_c = \sum_{\mathfrak{l}\neq 0} \frac{1}{2R_{\mathfrak{l}}}\left\{e^{-\mu R_{\mathfrak{l}}}\left[1 - E\left(x_0 R_{\mathfrak{l}} - \frac{\mu}{2x_0}\right)\right] + e^{\mu R_{\mathfrak{l}}}\left[1 - E\left(x_0 R_{\mathfrak{l}} + \frac{\mu}{2x_0}\right)\right]\right\}.$$

Both V_b and V_c are positive valued functions; consequently, $V_a < V$ supplies a lower limit on V independent of the lattice type. We choose x_0 to make V_a as large as possible, thus simultaneously minimizing the contributions from $V_b + V_c$. The maximum occurs at $x_0 = \pi^{\frac{1}{2}}\rho^{\frac{1}{3}}$, independent of μ, and has the value

$$V_{a,\max} = -N\rho^{\frac{1}{3}}[1/2p^2 + (1 - 1/2p^2)e^{-p^2} - \pi^{\frac{1}{2}}pE(p)], \tag{22}$$

with

$$p = \mu/2\pi^{\frac{1}{2}}\rho^{\frac{1}{3}} = \mu r_s/6^{\frac{1}{3}}\pi^{\frac{1}{6}} = 0.4547\mu r_s. \tag{23}$$

Numerical results for V and the several partial V's appear in Table I as functions of the parameter $\beta = \mu r_s$ and the lattice type. Some results for the hexagonal close-packed lattice are included.

To introduce these results into Eq. (14) let

$$U(\beta) \equiv -\frac{2r_s}{N} \min\,[V(R_1, \cdots R_N; \mu)], \tag{24}$$

then

$$(4\pi\rho)^{\frac{2}{3}} \int_0^\infty [1 - g(r)] \frac{e^{-\mu r}}{r} r^2\, dr \leq \frac{1}{3^{\frac{1}{3}}} U(\beta). \tag{25}$$

The normalization condition can be used to convert Eq. (25) into

$$\int_0^\infty [1 - g(r)] \frac{e^{-\mu r}}{r} r^2\, dr \left[\int_0^\infty [1 - g(r)] r^2\, dr\right]^{-\frac{2}{3}} \leq \frac{1}{3^{\frac{1}{3}}} U(\beta). \tag{26}$$

Equations (25) and (26) remain valid for linear combinations of Yukawa potentials as in Equations (17) and (18) subject to the constraint $C_l \geq 0$ or $C(\mu) \geq 0$. In particular, the distribution $C(\mu) = e^{-\mu a}$ produces a potential intermediate between the inverse distance and the inverse square of the distance:

$$v_1(r) = 1/r(r + a). \tag{27}$$

Equation (25) is replaced by

$$(4\pi\rho)^{\frac{1}{3}} \int_0^\infty [1 - g(r)] \frac{1}{r(r + a)} r^2\, dr \leq \frac{1}{3^{\frac{2}{3}}} U_1\left(\frac{a}{r_s}\right), \quad U_1(x) = \int_0^\infty e^{-\beta x} U(\beta)\, d\beta, \tag{28}$$

and Eq. (26) by

$$\int_0^\infty [1 - g(r)] \frac{1}{r(r + a)} r^2\, dr \left[\int_0^\infty [1 - g(r)] r^2\, dr\right]^{-\frac{1}{3}} \leq \frac{1}{3^{\frac{2}{3}}} U_1\left(\frac{a}{r_s}\right). \tag{29}$$

The process of using one potential to generate another can be continued in many ways. In particular, the relation

$$v_2(r) = -\frac{d}{da} \frac{1}{r(r + a)} = \frac{1}{r(r + a)^2} \tag{30}$$

leads to

$$\int_0^\infty [1 - g(r)] \frac{1}{r(r + a)^2} r^2\, dr \leq \tfrac{1}{3} U_2\left(\frac{a}{r_s}\right),$$
$$U_2(x) = -\frac{d}{dx} U_1(x) = \int_0^\infty \beta e^{-\beta x} U(\beta)\, d\beta. \tag{31}$$

Numerical results for $U_1(\beta)$ and $U_2(\beta)$ appear in Table III. These functions are represented quite well by the simple formulas

$$U_1(x) \simeq f(x), \quad U_2(x) \sim -\frac{d}{dx} f(x),$$
$$f(x) = \frac{3.49}{1 + 1.948x} + \frac{x \ln x}{1 + 19.33x - 20.33x^3}. \tag{32}$$

Equation (16) is recovered from Eq. (28) by letting $a \to \infty$; this yields

$$\lim_{x\to\infty} x\, U_1(x) = 1.792 \tag{33}$$

in agreement with the limiting value given by the interpolation formula of Eq. (32).

TABLE III. Lattice energies for the potentials v_1 and v_2 (bcc or fcc).

$x = a/r_s$	$U_1(x)$	$U_2(x)$
0.0	3.490	∞
0.25	2.308	3.06
0.50	1.718	1.55
0.75	1.382	1.00
1.00	1.160	0.78
1.50	0.878	0.46
2.00	0.704	0.29
2.50	0.590	0.19
3.00	0.514	0.13
4.00	0.402	0.08

A qualitative summary of the results in Table 1 is contained in the statement that the bcc structure has the lowest energy for small β and the fcc for large β with the crossover near $\beta = 1$. The fcc and hcp structures are remarkably close in energy.

3. THE ABSOLUTE MINIMUM POTENTIAL ENERGY

Some information is available on the stability of these structures against small deformations. All potentials considered here are positive-valued, monotonic decreasing functions of r with positive second derivatives. These properties occur as a special case under the general stability condition found by Born[13,14] for small, slowly varying disturbances. Powers[15] showed that Born's conditions are sufficient to ensure stability against arbitrary small disturbances subject to the limitation that only nearest neighbors need be included in evaluating lattice sums. For the Yukawa potential this means $\beta = \mu r_s \gg 1$.

For $\beta = 0$ stability is proved by the actual numerical evaluation of the frequency spectrum.[16] In this case the fixed background charge (not present in the analysis of Born and Powers) is essential for stability.[17] In general ($\beta \neq 0$), the background charge contributes to stability by generating a restoring force for arbitrary small displacements of the particles from the lattice sites. Since stability is assured at $\beta = 0$ (more generally $\beta \ll 1$) and at $\beta \gg 1$, the smallness of the energy range covered by the three close-packed structures is, in itself, strong evidence for all values of β that the most stable close-packed structure either (i) realizes the configuration for the absolute energy minimum, or (ii) possesses an energy very close to the absolute minimum.

In any event the minimum computed energy establishes a safe upper limit on the allowed value of the integral occurring in Eq. (25); safe in the sense that one does not hesitate to discard any trial function $g(r)$ which violates the inequality. This is enough to make the inequality useful. Applications have been made in theoretical studies of liquid helium[18] and of an alpha-particle model of low-density nuclear matter.[19]

[13] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1962), p. 142.

[14] A. A. Maradudin, E. W. Montroll, and G. W. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963).

[15] S. C. Powers, Proc. Cambridge Phil. Soc. **38**, 62 (1942).

[16] C. B. Clark, Phys. Rev. **109**, 1133 (1958).

[17] E. W. Kellerman, Phil. Trans. Roy. Soc. (London) **238**, 513 (1940).

[18] W. E. Massey, Ph.D. thesis, Washington University (1966); Phys. Rev. **151**, 153 (1966).

[19] J. W. Clark and T. P. Wang, Ann. Phys. (N.Y.) **40**, 127 (1966).

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APPENDIX A. LOWER BOUND ON $V(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N; \mu)$

The self-energy E_a of an s sphere, a uniformly charged sphere plus a point charge at the center, contains two parts: the self energy E_{a1} of the uniform charge, and the interaction energy E_{a2} between the point charge and the uniform charge density. Direct calculation yields

$$E_{a1} = \frac{1}{2}\left(\frac{3}{4\pi r_s^3}\right)^2 \int_{\substack{r_1<r_s\\ r_2<r_s}} \frac{e^{-\mu r_{12}}}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2 = \frac{3}{r_s}\int_0^1 e^{-2\mu r_s x}(2x - 3x^2 + x^4)\, dx, \tag{A1}$$

$$E_{a2} = -\frac{3}{4\pi r_s^3}\int_0^{r_s} e^{-\mu r} 4\pi r\, dr, \tag{A2}$$

and

$$E_a = N(E_{a1} + E_{a2}) = N\frac{3}{r_s}\left[\frac{3}{4\beta^5}(1 - \beta^2 - \tfrac{2}{3}\beta^3) - \frac{3}{4\beta^5}(1+\beta)^2 e^{-2\beta} + \frac{e^{-\beta}}{\beta^2}(1+\beta)\right] \tag{A3}$$

with $\beta = \mu r_s$.

The result for the Coulomb potential[20] is obtained in the limit of $\beta \to 0$:

$$\lim_{\beta\to 0} E_a = -N\frac{9}{10 r_s}. \tag{A4}$$

Next, we demonstrate that the interaction energy E_b of the s spheres is positive. It is well known that a spherically symmetric distribution of electric charge produces the same potential outside the distribution as if all the charge were concentrated at the center. A closely related conclusion actually holds also for the Yukawa potential. In fact, an elementary computation yields the potential produced by an s sphere (for definiteness, let the uniform charge be positive) at distance $r > r_s$ from its center as

$$V(r) = F(\beta)(e^{-\mu r}/r) \tag{A5}$$

with

$$F(\beta) = (3/\beta^2)(\cosh\beta - \beta^{-1}\sinh\beta) - 1 > 0. \tag{A6}$$

At all points outside the sphere, the charge distribution can be replaced by a point charge of strength $F(\beta)$ at the center. If one replaces all the s spheres by point charges of the same strength, clearly then $E_b > 0$.

As a further check, we observe that $F(\beta)$ increases monotonically as a function of β. We then expect a larger discrepancy in approximating the minimum

[20] E. P. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934).

potential energy by E_a as β increases. This is indeed the case as seen from Table I.

APPENDIX B. EWALD PROCEDURE FOR THE YUKAWA POTENTIAL

The Ewald procedure involves two transformations.[12] The first is based on the integral

$$\frac{2}{\pi^{\frac{1}{2}}}\int_0^\infty e^{-(Rx-\mu/2x)^2}\,dx = \left(\frac{2\mu}{\pi R}\right)^{\frac{1}{2}}\int_0^\infty e^{-\frac{1}{2}\mu R(y-1/y)^2}dy. \tag{B1}$$

A change of variable $y = e^\theta$ yields $dy = d\sinh\theta + d\cosh\theta$; since $\sinh\theta$ is an odd function of θ the integral reduces to $1/R$. Consequently,

$$\frac{e^{-\mu R}}{R} = \frac{2}{\pi^{\frac{1}{2}}}\int_0^\infty e^{-(R^2x^2+\mu^2/4x^2)}\,dx. \tag{B2}$$

Equations (20) and (B2) combine to give

$$\frac{2V}{N} + \frac{4\pi\rho}{\mu^2} = \frac{2}{\pi^{\frac{1}{2}}}\int_0^\infty \sum_j{}' e^{-R_j^2x^2-\mu^2/4x^2}\,dx. \tag{B3}$$

Next, the range of integration is split into two, $0 \le x \le x_0$ and $x_0 < x < \infty$ with x_0 to be determined. Equation (23) assumes the form

$$\frac{2V}{N} + \frac{4\pi\rho}{\mu^2} = \frac{2}{\pi^{\frac{1}{2}}}\int_{x_0}^\infty \sum_j{}' e^{-R_j^2x^2-\mu^2/4x^2}\,dx + \frac{2}{\pi^{\frac{1}{2}}}\int_0^{x_0}\sum_j e^{-R_j^2x^2-\mu^2/4x^2}\,dx - \frac{2}{\pi^{\frac{1}{2}}}\int_0^{x_0} e^{-\mu^2/4x^2}\,dx. \tag{B4}$$

Also

$$\frac{2}{\pi^{\frac{1}{2}}}\int_0^{x_0} e^{-\mu^2/4x^2}\,dx = \frac{\mu}{\pi^{\frac{1}{2}}}\int_{\mu/2x_0}^\infty e^{-y^2}\frac{dy}{y^2} = \frac{2}{\pi^{\frac{1}{2}}}x_0e^{-(\mu/2x_0)^2} - \mu 1 - E(\mu/2x_0)], \tag{B5}$$

$$\begin{aligned}\frac{2}{\pi^{\frac{1}{2}}}\int_{x_0}^\infty e^{-R^2x^2-(\mu/2x)^2}\,dx &= 2\left(\frac{\mu}{2\pi R}\right)^{\frac{1}{2}}e^{-\mu R}\int_{y_0}^\infty e^{-\frac{1}{2}\mu R(y-1/y)^2}\,dy\\ &= 2\left(\frac{\mu}{2\pi R}\right)^{\frac{1}{2}}e^{-\mu R}\left[\int_{\theta_0}^\infty e^{-2\mu R(\sinh\theta)^2}\,d\sinh\theta + \int_{\theta_0}^\infty e^{-2\mu R((\cosh\theta)^2-1)}\,d\cosh\theta\right]\\ &= \frac{1}{2R}\left[e^{-\mu R}\{1 - E(Rx_0 - \mu/2x_0)\} + e^{\mu R}\{1 - E(Rx_0 + \mu/2x_0)\}\right].\end{aligned} \tag{B6}$$

In Eqs. (B5) and (B6), $E(x)$ denotes the error function [defined for negative x by the relation $E(x) = -E(-x)$].

The remaining integral over the range $0 \le x \le x_0$ is evaluated by a theta-function transformation. Three linearly independent lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are determined by the condition that all lattice points are generated by the linear combinations

$$\mathbf{R}_l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3, \quad l_i = 0, \pm1, \cdots. \tag{B7}$$

Here the j subscript is replaced by the descriptive vector $\mathbf{l}$. The dual vectors

$$b_1 = \frac{a_2\times a_3}{A},\quad b_2 = \frac{a_3\times a_1}{A},\quad b_3 = \frac{a_1\times a_2}{A}, \tag{B8}$$

with $A = a_1\cdot(a_2\times a_3) = 1/\rho$, satisfy the conditions

$$a_i\cdot b_j = \delta_{ij},\quad b_1\cdot(b_2\times b_3) = 1/A = \rho. \tag{B9}$$

The dual vector space contains all vectors

$$\mathbf{h}_p = p_1\mathbf{b}_1 + p_2\mathbf{b}_2 + p_3\mathbf{b}_3,\quad p_i = 0, \pm1, \cdots. \tag{B10}$$

The required transformation,[12]

$$\sum_{\mathbf{l}} e^{-R_l^2x^2} = \frac{\pi^{\frac{3}{2}}\rho}{x^3}\sum_{\mathbf{p}} e^{-(\pi/x)^2h_p^2} \tag{B11}$$

converts a slowly converging sum for x either very small or very large into an equivalent rapidly converging sum. Now

$$\begin{aligned}\frac{2}{\pi^{\frac{1}{2}}}\int_0^{x_0}\sum_{\mathbf{l}} e^{-R^2x^2-(\mu/2x)^2}\,dx &= 2\pi\rho\int_0^{x_0}\sum_{\mathbf{p}} e^{-[\pi^2h_p^2+(\mu/2)^2]/x^2}\frac{dx}{x^3}\\ &= \pi\rho\sum_{\mathbf{p}}\frac{e^{-[\pi^2h_p^2+(\mu/2)^2]/x_0^2}}{\pi^2h_p^2+(\mu/2)^2}.\end{aligned} \tag{B12}$$

These results are combined in Eq. (21) of the text and used to determine the best value of x_0.