Lattice sums and their phase diagram implications for the classical Lennard-Jones model

Frank H. Stillinger
Agere Systems, Murray Hill, New Jersey 07974 and Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544

High-accuracy lattice sums have been evaluated for the Lennard-Jones 12-6 pair potential, without cutoffs, in the close-packed fcc and hcp lattices. The results confirm the small relative stability of hcp at low pressure, and locate precisely the first-order phase transition at zero temperature to the fcc structure. The reduced pressure $p\sigma^3/\epsilon$ at this transition is approximately $878.476\ldots$, with both structures having been compressed to about one-half of their zero-pressure volumes. On account of its lower symmetry compared to fcc, the hcp lattice spontaneously distorts from the ideal close-packed geometry to lower its energy by a tiny amount. For low compressions, this distortion involves expansion within close-packed planes, and shrinkage in the perpendicular stacking direction. However this spontaneous distortion changes sign shortly before reaching the compression required for the hcp–fcc phase transition, vanishing at a volume ratio (compared to zero pressure) of about 0.537. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1394922]

I. INTRODUCTION

Ever since its introduction in 1924, the classical Lennard-Jones (LJ) model has become and has remained a familiar fixture in statistical–mechanical and condensed-matter research activities.[1] This model's extensive published literature includes calculations of gas-phase virial coefficients,[1,2] examination of liquid-phase structural, thermodynamic, and transport properties,[3–6] and determination of melting and freezing behavior.[7–14] Although it was originally (and is still) viewed as a reasonable representation for the pure heavier noble gases Ar, Kr, and Xe, it has been extended to description of mixtures with suitable combining rules for the basic energy and length parameters.[15] One such binary LJ system, patterned originally on the $Ni_{80}P_{20}$ eutectic system,[16] has become a popular classical model for numerical simulation of liquid supercooling and glass formation.[17–20] It is also appropriate to note that the LJ pair potential is frequently invoked as part of more complicated interactions for polyatomic substances,[21,22] which can be interpreted as a measure of the extent to which the original model has become embedded in the research culture.

Kihara and Koba[23] pointed out in 1952 that the stable crystal structure at low temperature and pressure for the one-component LJ model was hexagonal close-packed (hcp), not the face-centered-cubic (fcc) form exhibited by all of the heavier noble gases.[24] The zero-pressure difference in lattice energies favoring hcp over fcc is quite small (fractional difference of order 10^{-4}), but unequivocal. In spite of this discrepancy, and perhaps because the LJ model has been viewed as appropriate and satisfactory for noble gas fluid phases, most published papers that have required consideration of the LJ crystal have assumed that the fcc structure was applicable[7,8,10–14] (but see Ref. 25). We hasten to add, however, that numerical expediency has frequently led to use of a variety of finite-distance cutoff modifications applied to the

infinite-range LJ pair potential,[26] and for at least some of these the dominance of fcc over hcp may be restored. In addition, vibrational degrees of freedom at positive temperatures below the melting point may also influence the relative stability of the lattices.[25]

On account of its great utility and popularity, the LJ model deserves to have precise numerical documentation; this has been our primary motivation for the present work. In pursuit of this aim we are able to extend the conclusions of the under-appreciated paper by Kihara and Koba.[23] The following section describes our numerical method of evaluating the relevant lattice sums to high precision, and presents our results for the ideal (unstrained) fcc and hcp lattices; in particular these calculations indicate that under sufficiently high compression a first-order phase change converts hcp to fcc. Section III examines the occurrence of a spontaneous lowering of the energy of the ideal-structure hcp by homogeneous strain. Finally, Sec. IV summarizes conclusions and raises the issue of hybrid close-packed structures.

II. STRAIN-FREE LATTICES

The classical LJ model is defined by the particle mass m and the potential energy function Φ:

$$\Phi(\mathbf{r}_1\cdots\mathbf{r}_N)=\sum_{i<j} v_{LJ}(r_{ij}), \tag{2.1}$$

$$v_{LJ}(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]. \tag{2.2}$$

The energy and length parameters ϵ and σ are positive; we follow the usual convention that sets these to unity. Our interest focuses on periodic particle arrays that are ultimately infinite in extent, and within which all particles are equivalent. The limiting potential energy per particle ϕ can be expressed in terms of the local coordination geometry as follows:

$$\phi = \lim_{N \to \infty} \Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)/N$$

$$= 2 \sum_{\mu=1}^{\infty} Z_\mu (R_\mu^{-12} - R_\mu^{-6}). \tag{2.3}$$

This last expression isolates the separate contributions to ϕ from the successive shells of neighbors: the μth coordination shell at radial distance R_μ comprises Z_μ neighbors. Tables of the R_μ and Z_μ have been published for the unstrained fcc and hcp lattices.[27]

For both unstrained lattices the nearest-neighbor distance R_1 and the volume per particle v are related, thus

$$R_1(v) = 2^{1/6} v^{1/3}. \tag{2.4}$$

Also, for both unstrained lattices all R_μ^2/R_1^2 are integers.[27] In view of these facts the individual terms in Eq. (2.3) contributing to ϕ scale with v in a simple way. Consequently,

$$\phi^{(x)}(v) = a_{12}^{(x)} v^{-4} - a_6^{(x)} v^{-2}, \tag{2.5}$$

where x denotes fcc or hcp, and where the positive constants $a_{12}^{(x)}$ and $a_6^{(x)}$, respectively, accumulate all terms in Eq. (2.3) with exponents -12 and -6.

Instead of relying on the coordination shell resolution that underlies expression (2.3), we have instead used a numerically more convenient direct summation over lattice locations. This procedure was carried out separately for each of the exponents, at unit density, to evaluate each of the four unstrained-lattice constants $a_n^{(x)}$. The required summations span the arrays of unit cells for each lattice, between finite limits, followed when needed by extrapolation to the infinite-system limit. The fcc lattice contains one particle per unit cell, while the hcp lattice contains two particles per unit cell.[28] Formally, both cases can be expressed by the following multiple sums over integer variables m_1, m_2, m_3, l:

$$a_n^{(x)} = 2 \sum_{m_1} \sum_{m_2} \sum_{m_3} \sum_l |m_1 \mathbf{B}_1 + m_2 \mathbf{B}_2 + m_3 \mathbf{B}_3 + \mathbf{b}_l|^{-n}, \tag{2.6}$$

where the $\mathbf{B}_j$ are the basis vectors of the unit cell array, and the $\mathbf{b}_l$ locate the particles (just one or two in the present circumstance) within the unit cell. One particle is placed at the origin, requiring that the term $m_1 = m_2 = m_3 = 0$, $l = 1$ be excluded from the sum.

Although each of m_1, m_2, and m_3 in principle should run between $-\infty$ and $+\infty$, in practice they are limited to the finite interval $-M$ to $+M$, where we have examined the range $10 \leq M \leq 450$. For the larger exponent 12 both fcc and hcp sums converge rapidly with increasing M to high precision. However for exponent 6 the series converge more slowly, and to attain the necessary precision it was necessary to estimate and include a truncation error that asymptotically is proportional to M^{-3} as $M \to \infty$. It has also been necessary to recognize and to compensate for another source of numerical inaccuracy that would otherwise compromise results for both exponent values 12 and 6. Particularly for large M, the multiple sums include a very large number of very small terms, and if the numerical routine used attempts to add any one of these to a register already containing a partial sum of

TABLE I. Dimensionless properties for the unstrained fcc and hcp lattices in the LJ model.

Property	fcc	hcp
a_{12}	6.065 940 098 27	6.066 146 884 55
a_6	14.453 921 043 5	14.454 897 277 9
$v_{\min}$	0.916 159 770 36	0.916 144 447 85
$\phi(v_{\min})$	−8.610 200 156 43	−8.611 069 732 23
$v_{\inf1}$	1.182 757 177 69	1.182 737 396 41
$\phi(v_{\inf1})$	−7.232 568 131 40	−7.233 298 575 07
$p_{\inf1}$	−6.988 579 148 87	−6.989 401 846 96
v_0	0.460 239 412 615	
$\phi(v_0)$	66.958 995 930 6	
v_{trans}	0.460 238 488 170	0.460 240 337 045
p_{trans}	878.486 276 395	

order unity, the conventional floating-point arithmetic may treat it as zero. Consequently, results were accumulated separately in two floating-point registers according to magnitude (by comparing with 10^{-8}), and only at the end were those two components combined.

Table I presents our results for the unstrained fcc and hcp lattices. In addition to the constants $a_n^{(x)}$, we have included the v and ϕ values at the respective $\phi^{(x)}(v)$ minima and inflection points. The latter locate the states of maximum metastable dilation for the unstrained lattices, i.e., the states beyond which the lattices would spontaneously fracture. Table I also shows the corresponding magnitudes of the isotropic tension at these inflection points:

$$p_{\inf1} = -\phi'(v_{\inf1}). \tag{2.7}$$

The unstrained hcp lattice exhibits greater cohesion (lower ϕ) than fcc at low positive pressure, and under tension. But as noted in Ref. 23, the fractional difference in ϕ values is very small throughout this range. The difference attains its largest magnitude at

$$v = v^* \cong 0.650\ 876\ 819\ 257$$

at which

$$|\Delta \phi| \cong 1.152\ 196\ 37 \times 10^{-3}.$$

Further compression of both lattices causes $\Delta \phi$ to decline in magnitude, and to change sign permanently at

$$v_0 = 2^{-1/2} v^* \cong 0.460\ 239\ 412\ 615,$$

that also appears in Table I. This crossover heralds the existence of a zero-temperature first-order phase transition between the two structures. A double tangent construction for the two $\phi^{(x)}(v)$ curves is necessary to locate the coexisting-phase v values, which bracket v_0; these have also been entered into Table I as $v_{\text{trans}}^{(x)}$, along with the common transition pressure p_{trans}.

Entries in Table I are all dimensionless quantities. Selection of ϵ and σ parameters to approximate a real substance allows conversion to more familiar dimensioned quantities. To the extent that the LJ model applies to the noble gas Ar, the following values can be assigned:[29]

$$\epsilon(\text{Ar}) \cong 120 \text{ K},$$

$$\sigma(\text{Ar}) \cong 3.4 \text{ A}, \tag{2.8}$$

so that the pressure unit becomes

$$\epsilon/\sigma^3 \cong 421.5 \text{ bar.} \tag{2.9}$$

The LJ phase transition pressure p_{trans} thereupon converts to approximately 370.3 kbar for this assignment, and the p_{infl} values translate to about -2946 bar for both lattices.

III. SPONTANEOUS hcp DEFORMATION

The structural relationship between the fcc and hcp lattices is conventionally described in terms of the vertical stacking sequence of close-packed (triangular) particle layers.[30,31] The former is represented symbolically by the sequence $ABCABC\cdots$, because centers of particles in every layer reside directly above those of particles three layers below. By contrast, the latter presents the symbolic pattern $ABABAB\cdots$, with particle centers of any given layer directly above those two levels below. As a result of this stacking distinction, fcc has higher symmetry than hcp. One should note in passing that close-packed crystals of some real substances display structures with longer-period stacking sequences.[31]

The hcp lattice considered in the preceding section was unstrained, i.e., all nearest-neighbor distances were identical, whether the particle pairs involved were in the same close-packed layer, or resided in successive layers. But unlike the fcc case, the lower-symmetry hcp structure does not require this equality, and one cannot rule out *ab initio* the possibility that a spontaneous stacking-direction compression or elongation (at constant v) might lower the cohesive energy ϕ. It is this possibility that we now examine.

Place a Cartesian coordinate system (x,y,z) within the hcp lattice, with origin at any one of the equivalent particles, and oriented so that the z direction is perpendicular to the close-packed layers. That is, the x and y axes are parallel to those layers, and the z axis is their stacking direction. If the lattice-generating basis vectors $\mathbf{B}_j$ and $\mathbf{b}_l$ [Eq. (2.6)] have their z components multiplied by factor $1+u$, while their x and y components are each multiplied by $(1+u)^{-1/2}$, then the volume per particle v will remain unchanged. However the resulting homogeneously strained hcp lattice will have an energy per particle ϕ that varies with the strain variable u. Because the underlying scaling properties still apply in the presence of homogeneous strain, Eq. (2.5) for hcp generalizes simply to

$$\phi^{(\text{hcp})} = a_{12}^{(\text{hcp})}(u)v^{-4} - a_6^{(\text{hcp})}(u)v^{-2}. \tag{3.1}$$

If u is small, we can write

$$\begin{aligned}
a_{12}^{(\text{hcp})}(u) &= a_{12}^{(\text{hcp})}(0)(1+c_1 u + c_2 u^2 + \cdots), \\
a_6^{(\text{hcp})}(u) &= a_6^{(\text{hcp})}(0)(1+d_1 u + d_2 u^2 + \cdots).
\end{aligned} \tag{3.2}$$

The terms linear in u in these last expressions would vanish for the corresponding fcc quantities, owing to the higher symmetry of that lattice.

The hcp lattice sums described in Sec. II have been repeated with small nonzero values of u (± 0.005, ± 0.010), with the results fitted to fourth-order polynomials in u to extract numerical values of the coefficients c_1, c_2, d_1, and d_2. Table II shows the outcome. The fact that the linear

TABLE II. Strain-energy coefficients for the hcp lattice, defined in Eqs. (3.2).

c_1	$-0.000\,730\,439\,75$
c_2	$14.843\,269\,980\,7$
d_1	$-0.001\,265\,116\,45$
d_2	$2.626\,340\,870\,51$

coefficients c_1 and d_1 do not vanish indicates that in fact the hcp lattice can lower its energy by undergoing a spontaneous distortion away from the ideal $u=0$ structure.

Under the assumption (to be justified by results below) that the spontaneous distortion is small, it is proper to retain terms only through quadratic order in u in Eqs. (3.2). The resulting energy minimization problem with respect to u then is trivial. One formally finds the following expressions for $u^*(v)$, the minimizing strain, and for the correspondingly lower energy per particle:

$$u^*(v) = -\frac{N(v)}{2D(v)}, \tag{3.3}$$

$$\phi^{(\text{hcp})}(u^*,v) = \phi(0,v) - \frac{[N(v)]^2}{4D(v)}, \tag{3.4}$$

where we have set

$$N(v) = a_{12}^{(\text{hcp})}(0)c_1 v^{-4} - a_6^{(\text{hcp})}(0)d_1 v^{-2}, \tag{3.5}$$

$$D(v) = a_{12}^{(\text{hcp})}(0)c_2 v^{-4} - a_6^{(\text{hcp})}(0)d_2 v^{-2}. \tag{3.6}$$

These last two quantities have roots, respectively, at the following values of the volume per particle:

$$v_N \cong 0.492\,238\,870\,41, \tag{3.7}$$

$$v_D \cong 1.540\,061\,994\,4. \tag{3.8}$$

The latter of these, v_D, is well beyond the expansion limit $v_{\text{infl}}^{(\text{hcp})}$ reported above in Table I, and therefore has no direct physical significance. The former, v_N, however falls within the physically meaningful range, and according to Eqs. (3.3) and (3.4) is a state in which the spontaneous distortion tendency happens to vanish identically.

The existence of the null-distortion point v_N arises from the fact that the repulsive r^{-12} and the attractive r^{-6} portions of the LJ pair interaction, Eq. (2.2), exert opposing effects on the strain field. The former acts to drive u to positive values and dominates for $v < v_N$, while the latter drives u in the opposite direction and dominates for $v > v_N$. In the high compression limit $v \to 0$, we have the following asymptotes from Eqs. (3.3) and (3.4):

$$u^*(v) \sim 2.460\,508\,208\,8 \times 10^{-5},$$

$$\phi^{(\text{hcp})}(u^*,v) - \phi^{(\text{hcp})}(0,v)$$

$$\sim -5.451\,200\,366\,1 \times 10^{-8} v^{-4}. \tag{3.9}$$

Although the second of these diverges to $-\infty$ in the limit considered, it amounts only to a very small fractional reduction in the divergence to $+\infty$ of the unstrained hcp energy.

The spontaneous-strain reductions in energy at the volumes $v_{min}^{(hcp)}$ and $v_{infl}^{(hcp)}$ reported in Table I are also fractionally very small. Numerical evaluation of expressions (3.3) and (3.4) lead to the following:

$$u^*(v_{min}^{(hcp)}) \cong -9.383\,121\,715\,4 \times 10^{-5},$$

$$\phi^{(hcp)}(u^*, v_{min}^{(hcp)}) - \phi^{(hcp)}(0, v_{min}^{(hcp)})$$

$$\cong -7.271\,048\,697\,8 \times 10^{-7}; \tag{3.10}$$

$$u^*(v_{infl}^{(hcp)}) \cong -2.863\,137\,891\,1 \times 10^{-4},$$

$$\phi^{(hcp)}(u^*, v_{infl}^{(hcp)}) - \phi^{(hcp)}(0, v_{infl}^{(hcp)})$$

$$\cong -1.547\,304\,822\,8 \times 10^{-6}. \tag{3.11}$$

Finally, we note that the common volume at which the fcc and strained hcp energies are equal shifts very slightly downward:

$$v_0(\text{strained}) - v_0(\text{unstrained}) \cong -1.054\,078 \times 10^{-6}, \tag{3.12}$$

while the pressure and the volume change across the first order phase transition change very little from the value indicated by entries in Table I.

IV. CONCLUSIONS AND DISCUSSION

By means of the calculations described above, we have been able to confirm at a substantially higher level of precision the Kihara and Koba conclusion[23] that the strict Lennard-Jones classical model at low pressure prefers by a small energy margin to crystallize in the hexagonal close-packed structure, in preference to the face-centered-cubic alternative. This relative stability persists under substantial compression, but is overturned when the volume per particle has been reduced by approximately a factor of 2 from its zero-pressure value. The face-centered-cubic structure continues to be the stable form under further compression.

We have examined the symmetry-allowed homogeneous distortion phenomenon for the hcp case, verifying that this can produce an enhanced (but still very small) stabilization compared to fcc. Under vanishing external pressure, this distortion compresses the hcp crystal slightly in the plane-stacking direction ($u < 0$), while expanding the two perpendicular in-plane directions equally. However, even this small distortion continuously diminishes in magnitude under compression, vanishing at v_N [Eq. (3.7)], and changing sign thereafter. The hcp state at v_N is immune to spontaneous distortion.

Although the present study has been confined to the classical ground state, vibrational degrees of freedom that are excited at positive temperature are expected to have a substantial influence on the fcc–hcp relative stability. Indeed it has been argued that both harmonic[32] and anharmonic[25] effects can overcome the small energy differences examined carefully herein, conferring stability on the fcc structure throughout most of the temperature–volume plane, and in particular all of the melting line. Furthermore, if the phase diagrams of the helium isotopes He[3] and He[4] are any indication, quantum zero-point motions and/or quantum statistics (Bose–Einstein vs Fermi–Dirac) can also exert profound influences on crystal stability, and bring the body-centered-cubic structure into contention.[33] But however dominating these effects may be in substantial portions of the LJ phase diagram, we stress the point made earlier, that all aspects of this venerable model deserve very careful analysis, specifically including the classical ground state over the entire range of volumes.

Finally, for the classical ground state of the LJ model, we return to the issue of hybrid stacking sequences that interpolate between fcc and hcp extremes.[31] Although it would be difficult to study thoroughly, it would nevertheless be valuable to determine if the narrow first-order transition around v_0 from hcp to fcc actually proceeds through a sequence of intermediate stacking species. Each such species, on account of its reduced symmetry compared to fcc, would be subject to its own spontaneous distortion that lowers energy slightly. Such distortions generally would not be spatially homogeneous as considered in Sec. III above, but instead would vary between planes depending on their stacking type. An extreme version of this transition scenario would entail a continuous transition between the volume limits already identified, with a continuous variation in the proportion of hcp-like and fcc-like planes. Clearly this possibility is beyond the scope of the present study, and will have to be reserved for future consideration.

[1] J. E. Lennard-Jones, Proc. R. Soc. London, Ser. A **106**, 463 (1924).
[2] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
[3] A. Rahman, Phys. Rev. **136**, A405 (1964).
[4] L. Verlet, Phys. Rev. **159**, 98 (1967).
[5] D. Levesque, L. Verlet, and J. Kürkijarvi, Phys. Rev. A **7**, 1690 (1973).
[6] J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).
[7] J.-P. Hansen and L. Verlet, Phys. Rev. **184**, 151 (1969).
[8] W. B. Street, H. J. Ravaché, and R. D. Mountain, J. Chem. Phys. **61**, 1960 (1974).
[9] H. J. Ravaché and R. D. Mountain, J. Chem. Phys. **61**, 1970 (1974).
[10] J. Q. Broughton and G. H. Gilmer, J. Chem. Phys. **79**, 5095 (1983).
[11] S. Nosé and F. Yonezawa, J. Chem. Phys. **84**, 1803 (1986).
[12] D. K. Chokappa and P. Clancy, Mol. Phys. **61**, 597 (1987).
[13] R. Agrawal and D. A. Kofke, Mol. Phys. **85**, 43 (1995).
[14] M. A. van der Hoef, J. Chem. Phys. **113**, 8142 (2000).
[15] See Ref. 2, p. 168.
[16] T. A. Weber and F. H. Stillinger, Phys. Rev. B **32**, 5402 (1985).
[17] W. Kob and H. C. Andersen, Phys. Rev. E **51**, 4626 (1995).
[18] S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature (London) **393**, 554 (1998).
[19] M. Utz, P. G. Debenedetti, and F. H. Stillinger, Phys. Rev. Lett. **84**, 1471 (2000).
[20] L. Angelani, R. DiLeonardo, G. Ruocco, A. Scala, and F. Sciortino, Phys. Rev. Lett. **85**, 5356 (2000).
[21] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983).
[22] B. Smit, S. Karaborni, and J. I. Siepmann, J. Chem. Phys. **102**, 2126 (1995).

[23] T. Kihara and S. Koba, J. Phys. Soc. Jpn. **7**, 348 (1952).

[24] J. Donohue, *The Structures of the Elements* (Krieger, Malabar, FL, 1982), Chap. 2.

[25] Y. Choi, T. Ree, and F. H. Ree, J. Chem. Phys. **99**, 9917 (1993); , Phys. Rev. B **48**, 2988 (1993); S. Somasi, B. Khomani, and R. Lovett, J. Chem. Phys. **113**, 4320 (2000).

[26] See, for example, T.-M. Wu, W.-J. Ma, and S. L. Chang, J. Chem. Phys. **113**, 274 (2000), Eq. (1).

[27] See Ref. 2, pp. 1036–1039.

[28] L. Brilloiun, *Wave Propagation in Periodic Structures* (Dover, New York, 1953), p. 150.

[29] A. Michels, H. Wijker, and H. K. Wijker, Physica (Utrecht) **15**, 627 (1949).

[30] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1956), pp. 35 and 36.

[31] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1960), pp. 404–412.

[32] Z. W. Salsburg and D. A. Huckaby, J. Comput. Phys. **7**, 489 (1971).

[33] See Ref. 24, pp. 13–20.