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ABSTRACT

This paper applies the Poisson Sum Formula to the problem of summing pairwise interactions between an "observer" molecule and a semi-infinite regular array of solid state molecules. The transformed sum is often much more rapidly convergent than the original sum and forms a Fourier series in the solid surface coordinates. The method is applicable to a variety of solid state structures and functional forms of the pairwise potential. As an illustration of the method, the electric field above the (100) face of the CsCl structure is calculated and compared to earlier results obtained by direct summation.

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I. INTRODUCTION

In treating the interaction of atoms and molecules with crystalline solids it is often assumed that the total interaction is just the sum of the pairwise interactions between the "colliding" molecule and each of the solid state molecules. Such a treatment requires the evaluation of the sum of those interactions over all the molecules in the solid lattice.

These lattice sums are often slowly converging especially for the long range part of the potential, and therefore direct summation, although often used in conjunction with integration,[1] is not a very attractive method even with high speed computers due to the purely numerical nature of the results.

This paper develops an approach to the evaluation of lattice sums based on the Poisson sum formula.[2] Basically, the Poisson sum formula analytically transforms the sum of pair potentials into a sum of their Fourier transforms. Since the Fourier transform of a diffuse function is, in general, sharp, the Poisson sum formula is expected to improve the convergence of the long range part of the potential especially. Because of the rapid convergence usually available with this method, only a few terms in the transformed sum need be retained to produce an accurate potential.

In addition, this method, which is applicable to a variety of structures and potentials, produces a Fourier series in the solid surface coordinates. This is true even when the sum is truncated after a finite number of terms. Thus, only the dependence of the potential on the distance from the surface needs to be treated numerically.

Other analytic treatments of lattice sums yield results equivalent to the present treatment based on the Poisson sum formula.[3] The advantage of the present development is that it makes connection with the large body of mathematical literature on the convergence of the Poisson sum.

In the next section we shall outline the basic method using the Poisson sum formula. Since Steele, who uses an approach equivalent to the one used here, has given a large catalogue of potentials for various lattices, we shall limit our applications to the calculation of the electric field above the (100) face of the CsCl-type structure.

In Section III, we shall show that the electrostatic potential for this lattice diverges, but the field does not. The only previous evaluation of the field is the direct-summation results of Orr. We shall show that some of these results are in error by a larger amount than was originally estimated.

II. METHOD

Consider a semi-infinite lattice ($z \leq 0$) of points whose xy plane is shown in Fig. 1. Let $\underset{\sim}{\ell}_1$ and $\underset{\sim}{\ell}_2$ denote the surface lattice vectors and let ϕ be the angle between them. The vector $\underset{\sim}{\tau} = k\underset{\sim}{\ell}_1 + \ell\underset{\sim}{\ell}_2$ (k, ℓ integer) denotes the origin of a surface unit cell. Suppose there are N atoms per unit cell and let $\underset{\sim}{\tau}_n(m)$ be the vector from the origin of any surface unit cell in the m-th layer to the n-th atom in that cell.

Suppose we wish to sum a function u (such as a pair potential) over all the atoms in the lattice. This requires summing over all of the $\underset{\sim}{\tau}$'s (or alternatively, all of the k's and ℓ's) and all of the layers, m . At an arbitrary point above the lattice (x,y,z), such a sum can be written as

$$V(x,y,z) = \sum_{k=-\infty}^{\infty} \sum_{\ell=-\infty}^{\infty} \sum_{m=0}^{\infty} \sum_{n=1}^{N} u[\underset{\sim}{\tau}-\underset{\sim}{\tau}_0+\underset{\sim}{\tau}_n(m),z_m] \tag{1}$$

where $\underset{\sim}{\tau}_0 = x^*\underset{\sim}{\ell}_1 + y^*\underset{\sim}{\ell}_2$ (with $x^* \equiv x/\ell_1$ and $y^* \equiv y/\ell_2$) is the observer's lateral displacement from the surface origin and z_m is the perpendicular distance to the m+1 layer. For example, if the layers are regularly spaced at a distance ℓ_3 , then $z_m = \ell_3(m+z^*)$ with $z^* \equiv z/\ell_3$.

The Poisson sum formula[2a] can be adapted to two dimensions to give*

$$V(x,y,z) = \frac{1}{A} \sum_{p=-\infty}^{\infty} \sum_{q=-\infty}^{\infty} \sum_{m=0}^{\infty} \sum_{n=1}^{N} e^{i\underset{\sim}{g}\cdot(\underset{\sim}{\tau}_0-\underset{\sim}{\tau}_n(m))}\, U(\underset{\sim}{g},z_m) \tag{2}$$

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* For typographical reasons, both $\underset{\sim}{g}$ and $\underset{\sim}{g}$ will be used to denote the reciprocal lattice vector as defined in Eq. (3).

where $A = \ell_1 \ell_2 \sin\phi$, the area of the surface unit cell, and

$$U(\underset{\sim}{g}, z_m) = \int u(\underset{\sim}{\tau}, z_m)\, e^{i\underset{\sim}{g}\cdot\underset{\sim}{\tau}}\, d\underset{\sim}{\tau} ,$$

the Fourier transform of u . Here $\underset{\sim}{g}$ takes on all the characteristics of the usual reciprocal lattice vector; that is,

$$\underset{\sim}{g} = 2\pi p\, \underset{\sim}{g}_1 + 2\pi q\, \underset{\sim}{g}_2 \qquad (p,q \text{ integer}) \tag{3}$$

with

$$\underset{\sim}{\ell}_i \cdot \underset{\sim}{g}_j = \delta_{ij} .$$

The length of $\underset{\sim}{g}$ is given by

$$g = \frac{2\pi}{\sin\phi} \{ (\frac{p}{\ell_1})^2 + (\frac{q}{\ell_2})^2 - \frac{2pq \cos\phi}{\ell_1 \ell_2} \}^{1/2} . \tag{4}$$

In order to apply this technique to the evaluation of the potential energy above a crystalline lattice, a few assumptions are made regarding the pair potential u .

Assume the pair potential $u(\underset{\sim}{\tau}, z_m)$ can be written as $u(\underset{\sim}{\tau}, z_m) = C\, f(\underset{\sim}{\tau}, z_m)$ where C is some constant characteristic of a particular interaction pair, while f is a general function independent of the types of atoms giving rise to the potential. If we define

$$F(\underset{\sim}{g}, z_m) = \int f(\underset{\sim}{\tau}, z_m)\, e^{i\underset{\sim}{g}\cdot\underset{\sim}{\tau}}\, d\underset{\sim}{\tau} \tag{5a}$$

and

$$\alpha_{\underset{\sim}{g},m} = e^{i\underset{\sim}{g}\cdot\underset{\sim}{\tau}_0} \sum_{n=1}^{N} e^{-i\underset{\sim}{g}\cdot\underset{\sim}{\tau}_n(m)} \tag{5b}$$

we can write the potential as

$$V(x,y,z) = \frac{C}{A} \sum_{\underset{\sim}{g}} \sum_{m=0}^{\infty} \alpha_{\underset{\sim}{g},m} F(\underset{\sim}{g},z_m) \tag{6}$$

where the sum over $\underset{\sim}{g}$ has been used to denote the double sum over p and q. Note that $\alpha_{\underset{\sim}{g},m}$ is dependent only on the physical arrangement of the lattice molecules and independent of the form of the pair potential. This means that $\alpha_{\underset{\sim}{g},m}$ needs to be calculated only once for any given type of lattice. Further, assume that f is just a function of the distance between the observer and the lattice atom; that is, $f = f[(\tau^2+z_m^2)^{1/2}]$. This considerably simplifies the Fourier transform:

$$F(g,z_m) = \int_0^{2\pi} \int_0^{\infty} f(\tau,z_m) e^{ig\tau\cos\theta} \, \tau d\tau \, d\theta = 2\pi \int_0^{\infty} J_0(g\tau) \, f(\tau,z_m) \, \tau d\tau \, . \tag{7}$$

A particularly useful form of the pair potential is the inverse power law, which will be denoted $u_s(\underset{\sim}{\tau},z_m) = C^{(s)} f_s(\underset{\sim}{\tau},z_m) = C^{(s)} R^{-s} = C^{(s)} (\tau^2+z_m^2)^{-1/2 s}$, and for which we can write

$$F_s(g,z_m) = 2\pi \int_0^{\infty} J_0(g\tau)[\tau^2+z_m^2]^{-1/2 s} \, \tau d\tau \, .$$

This is a standard integral which has the value[4]

$$F_s(g,z_m) = \frac{2\pi}{\Gamma(1/2 s)} \left(\frac{g}{2z_m}\right)^{1/2 s-1} K_{1/2 s-1}(g z_m) \tag{8}$$

with

$$\lim_{g \to 0} F_s(g,z_m) = \frac{2\pi}{(s-2)} z_m^{-(s-2)} \qquad (s > 2) \, , \tag{9}$$

where $\Gamma(x)$ is the Gamma function and $K_\nu(z)$ is a modified Bessel function. For half integer orders $K_{\nu+1/2}(z)$ takes the form $K_{\nu+1/2}(z) = P_\nu(z)(\pi/2z)^{1/2}\, e^{-z}$ where $P_0(z) = 1$ and

$$P_\nu(z) = \sum_{r=0}^{\nu} \frac{(\nu+r)!}{r!\,(\nu-r)!} (2z)^{-r}$$

in general. The term with $\underset{\sim}{g} = 0$, denoted V_0, is generally treated separately. For most lattices $\alpha_{0,m}$ is independent of m, so that

$$V_0 = \frac{C}{A}\alpha_0 \sum_{m=0}^{\infty} \lim_{\underset{\sim}{g} \to 0} F(\underset{\sim}{g}, z_m) , \tag{10}$$

or in the case of an inverse power law where the layers are spaced at intervals of ℓ_3, (9) and (10) give

$$V_0^{(s)} = \frac{2\pi C^{(s)}\alpha_0}{(s-2)A\ \ell_3^{s-2}} \sum_{m=0}^{\infty} (m+z^*)^{-(s-2)} = \frac{2\pi C^{(s)}\alpha_0}{(s-2)A\ \ell_3^{s-2}} \zeta(s-2;z^*) , \tag{11}$$

where $z^* = z/\ell_3$, and ζ is the generalized Riemann zeta function. A potential can be constructed from (5b) and (6), using either (7) or (8) if the pair potential is chosen to be an inverse power law. Similarly, a supplementary equation, (10) or (11), can be used to yield the dominant term in the transformed sum. In the next section, the CsCl structure will be considered.

III. CsCl STRUCTURE

To apply the results of the previous section to the (100) face of CsCl type structures, we note that the lattice consists of two interpenetrating simple cubic lattices of opposite charge. The surface unit cell and other cell parameters for the simple cubic lattice are shown in Fig. 2.

To calculate the electric potential above such a surface we need to sum the pair potential $u_1 = \pm|\varepsilon|/R$ over the simple cubic lattices of positive and negative ions (ε is the unit of electronic charge). In the notation of the previous section $C^{(1)} = \pm|\varepsilon|$ depending the charge of the ion lattice, and $f_1 = R^{-1}$ so that by (8) and the relation $K_{-\nu}(x) = K_{\nu}(x)$, $F_1 = (2\pi/g)e^{-gz_m}$. If we assume the surface layer is composed of positive ions and that the origin of the coordinate system is taken at one of these ions, then the origin of the lattice of negative ions will be located at $(-\frac{1}{2}a, -\frac{1}{2}a, -\frac{1}{2}a)$. The electric potential is given by (6), for which the sum on m can be done explicitly to give

$$V(x^*,y^*,z^*) = \frac{2\pi|\varepsilon|}{a^2} \sum_{\underset{\sim}{g}} \frac{[1+(-)^{p+q+1} e^{-\frac{1}{2}ag}]}{g(1-e^{-ag})} e^{-agz^*} \cos 2\pi px^* \cos 2\pi qy^*$$

with $x^* = x/a$, $y^* = y/a$, $z^* = z/a$. This sum diverges because of the term $\underset{\sim}{g} = 0$. This term appears because individual layers of the CsCl structure are not electroneutral. However, as it is the electric field and its gradient which interact with the multipole moments (permanent and induced) of the colliding molecule, the potential itself is not needed.

Since the singular term has no (x,y,z)-dependence, the components of the electric field can be calculated by differentiating this potential. The z-component of the field above the lattice is

$$E_z(x^*,y^*,z^*) = \frac{2\pi|\varepsilon|}{a^2} \sum_{\underset{\sim}{g}\neq 0} \frac{[1+(-)^{p+q+1}\, e^{-\frac{1}{2}ag}]}{(1-e^{-ag})}\, e^{-agz^*} \cos 2\pi p x^* \cos 2\pi q y^* . \tag{12}$$

This sum does converge and has been evaluated for several distances above two different sites: (a) directly above a surface ion; (b) above the center of a surface unit cell. Table I shows the results of using (12), taking terms with $\sqrt{p^2+q^2} \leq 15$, and those of Orr,[1a] obtained by directly summing R^{-3} for the nearest 88-96 ions and approximating the remainder by integration. The direct summation results were estimated to be in error by only 0.5% while the present results indicate a much larger error in those earlier calculations. Of course the direct summation results could be improved by summing over more ions, but there is little reason to extend this type of calculation when a more rapidly convergent method is available.

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TABLE I. Electric field (z-component) above the (100) face of a semi-infinite CsCl type crystal in units of $2\pi|\varepsilon|/a^2$, where ε is the unit of electronic charge and a is the lattice constant. Site (a) is directly above a surface ion; (b) is above the center of a surface lattice square. Surface layer composed of positive ions.

	$z^* \equiv z/a$	Orr[1a]	Present Work
Site (a)			
	0.5	0.259	0.24315
	0.6	0.118	0.11958
	0.7	0.064	0.06035
	0.8	0.032	0.03095
	0.9	0.019	0.01604
	1.0	0.011	0.00837
	1.1	---	0.00440
	1.2	0.005	0.00232
Site (b)			
	0.1	---	-0.86
	0.2	-0.580	-0.583
	0.3	-0.326	-0.368
	0.4	-0.230	-0.225
	0.5	-0.144	-0.1333
	0.6	-0.072	-0.0768
	0.7	-0.048	-0.0434
	0.8	-0.027	-0.0241
	0.9	---	-0.0133
	1.0	-0.006	-0.0073

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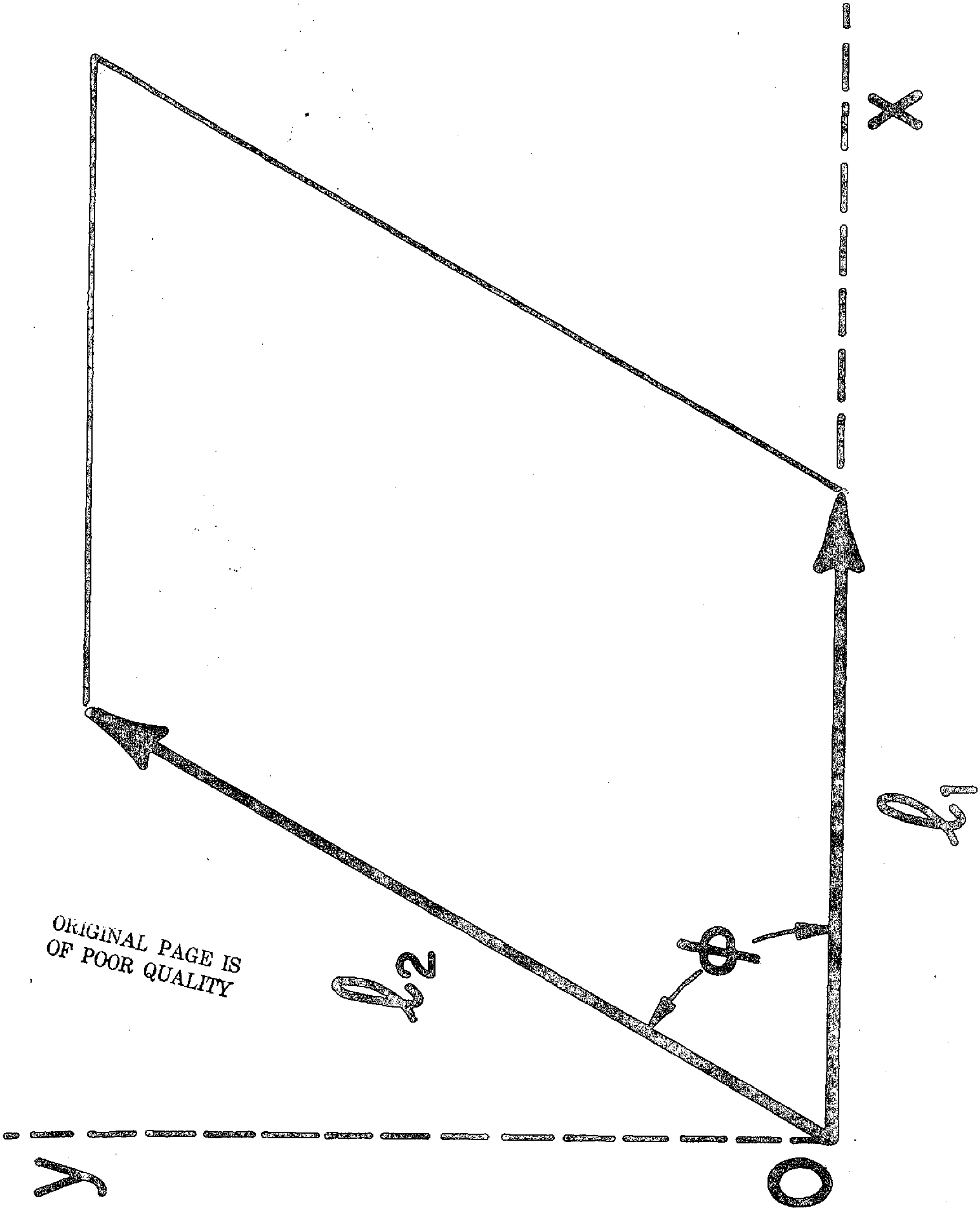
FIGURE CAPTIONS

Figure 1 A generalized surface unit cell.

Figure 2 Surface unit cell and parameters for simple cubic lattice. There is one atom per unit surface cell ($N = 1$) located at the cell origin ($\underset{\sim}{\tau}_1 = 0$) . Here

$\ell_1 = \ell_2 = \ell_3 = a$; $A = a^2$; $g = (2\pi/a)\sqrt{p^2+q^2}$;

$\alpha_{g,m} = \cos 2\pi p x^* \cos 2\pi q y^*$.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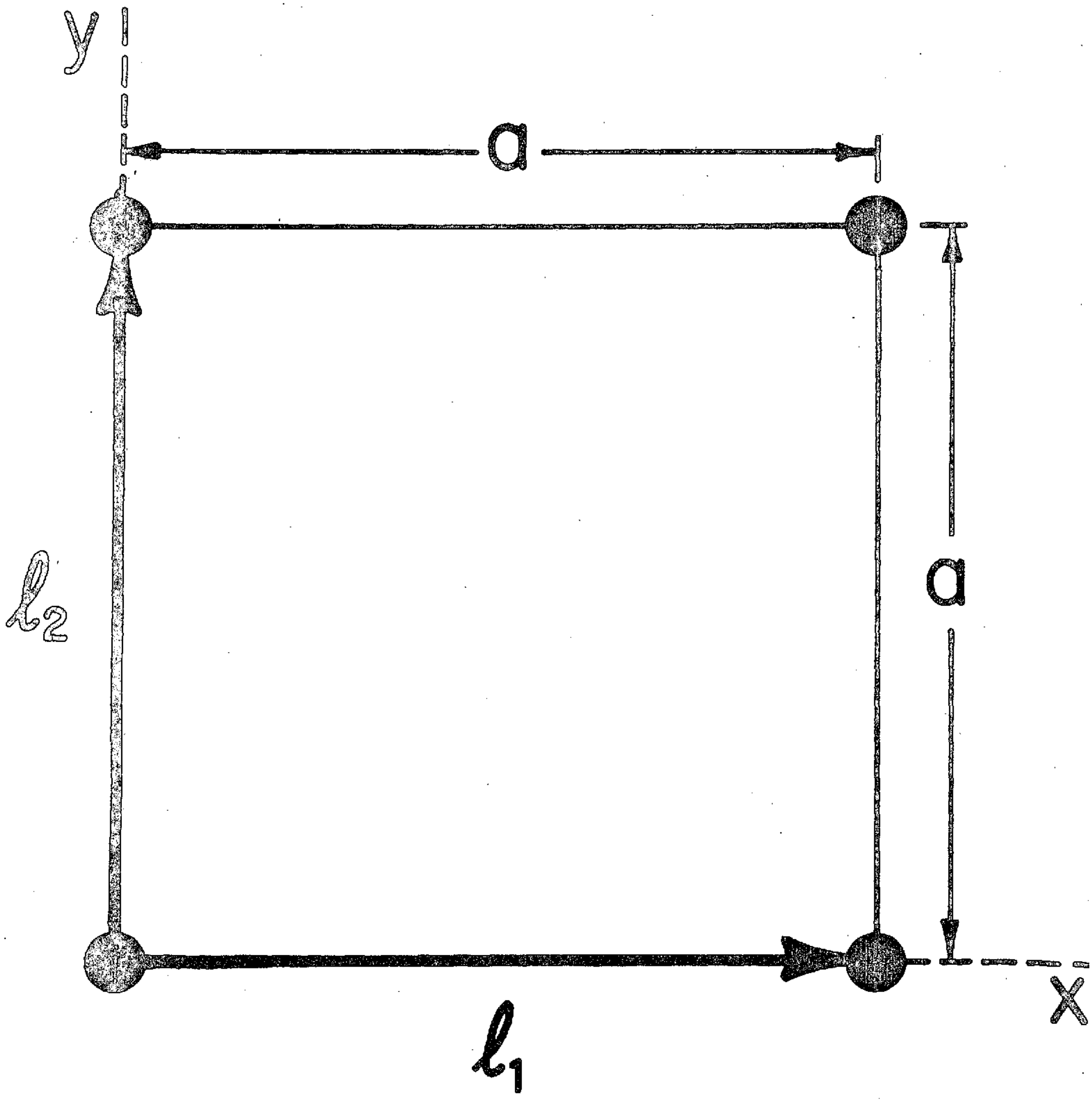
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