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Entropic approach to Brownian movement

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A diffusional driving force, called the radial force, which is responsible for the increase with time of the scalar separation between a fixed point and a particle undergoing three-dimensional Brownian motion, is derived using Boltzmann's equation. The radial force is used to derive several results from the classical theory of Brownian motion, namely Einstein's $\langle x^2 \rangle = 2Dt$ equation and the expression for the one-dimensional harmonic oscillator. The radial force concept is then extended to establish a thermodynamic criterion for the occurrence of a melting transition in a liquid whose particles attract one another by means of centrally symmetric forces. The theory, when applied to the alkali halide and alkaline-earth oxide molten salts, accurately predicts the observed melting temperatures. The definition of the dielectric constant used in the ionic salt fusion theory also provides a basis for understanding molten salt surface tensions. Finally, the radial force is used to demonstrate that an ideal rubber network is not prone to collapse into a state having zero volume.

INTRODUCTION

Brownian movement is traditionally discussed in terms of either (i) the solution to a diffusion equation¹ or (ii) the Langevin equation.² These approaches are equivalent and lead to a description of single-particle behavior in terms of probability distribution functions of laboratory-fixed coordinates.

Here, the behavior of a single Brownian particle in three dimensions will be described using the statistical mechanical concept of entropy. The thermodynamic independent variable is the *scalar* separation r between the particle and a point which is fixed in the laboratory coordinate system. The description of the particle's entropy in terms of r leads to the concept of a radial force; indeed this force can also be established without explicitly using entropic considerations. The radial force f_r is the basis for all of the work presented in this paper.

The radial force is used to derive several well-known equations in the theory of Brownian motion: $\langle x^2 \rangle = 2Dt$, which relates average particle location to time for a free particle and $\langle x^2 \rangle = kT/a$, which relates average particle location to the spring constant a for a particle bound to a harmonic oscillator. These derivations demonstrate that our approach yields results identical to those obtained using traditional methods.^{1,2}

The radial force leads naturally to the concept of a melting transition in liquids composed of hard-sphere particles which attract one another by means of radially symmetric forces. In the molten alkali halide and alkaline-earth oxide salts, the use of a Coulombic attractive electrical force between oppositely charged particles produces a relationship among melting temperature, ionic radii, and heat of fusion, which agrees very well with experiment. In addition, an expression for the surface tension is formulated for these molten salts in terms of their ionic radii and heats of fusion.

The radial force is used to provide a novel perspective on the nature of the ideal rubber network. The traditional statistical-mechanical theory views the undeformed network

as being prone to collapse because of nonvanishing elastic forces which attempt to bring all the crosslink junctions together at a common point.³ It is shown here how the radial force, acting between any pair of junctions, opposes the tendency of the Gaussian network chains to collapse.

ORIGIN OF THE RADIAL FORCE

Consider a fixed point and a Brownian particle in a liquid which, at a given instant, are separated by a *scalar* distance r . An observer on the particle, who keeps his eyes fixed on the point, will note that r gradually increases with time as a consequence of three-dimensional Brownian motion. He may, therefore, postulate the existence of a diffusional driving force responsible for increasing r in his frame of reference. If the particle is a distance r away from the fixed point, the magnitude of f_r can be calculated by considering the particle to have an entropy S based on the number of configurations, W , associated with r . At low density, W is proportional to $4\pi r^2$. Using Boltzmann's equation

$$S = k \ln W \quad (1)$$

and the thermodynamic relationship between the radial force and the entropy⁴,

$$f_r = T \left(\frac{\partial S}{\partial r} \right)_T = 2kT/r, \quad (2)$$

a relationship between the radial force, the absolute temperature, and the separation is obtained. f_r acts along the line connecting the point and the particle.

f_r can be obtained by differentiating the chemical potential μ of the particle with respect to r .⁵ The volume element associated with the particle is the volume of a spherical shell of thickness Δr ,

$$f_r = - \left(\frac{\partial \mu}{\partial r} \right)_T = - \frac{kT}{c} \frac{\partial c}{\partial r} = 2kT/r. \quad (3)$$

The particle concentration associated with r is the number

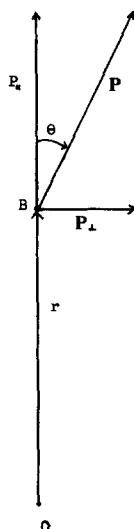


Fig. 1. Resolution of the instantaneous momentum of particle *B* with respect to the radius vector *r* is depicted.

of particles (one in this case) divided by the volume element or $c(r) = 1/(4\pi r^2 \Delta r)$.

That f_r can be expressed in terms of an energy divided by r suggests an analogy with centrifugal force. Figure 1 shows particle *B* a distance r away from a fixed point *O*. Brownian motion causes *B* to move about randomly relative to *O* by means of small bursts of momentum $\mathbf{p} = m\mathbf{v}$, where m is the mass of the particle and \mathbf{v} is its instantaneous velocity. \mathbf{p} can be resolved into a component parallel to \mathbf{r} , p_{\parallel} , and a component perpendicular to \mathbf{r} , p_{\perp} . p_{\perp} may be viewed as giving rise to a centrifugal force f_c of magnitude $mv^2(\sin^2\theta)/r$. The directional average of f_c is

$$\langle f_c \rangle = \frac{1}{4\pi} \int f_c du = \frac{2m\bar{v}^2}{3r} = \frac{2kT}{r} = f_r, \quad (4)$$

where $m\bar{v}^2 = 3kT$ and $du = \sin\theta d\theta d\phi$. The directional average of p_{\parallel} is zero.

Finally, the ideal gas law also serves as a basis for perceiving the radial force. For one particle in a sphere of radius r , the pressure \mathcal{P} exerted by the particle on the surface is

$$\mathcal{P} = \frac{1kT}{V} = \frac{3kT}{4\pi r^3} = \frac{f_s}{A} = \frac{f_s}{4\pi r^2}, \quad (5)$$

since $V = 4\pi r^3/3$ and \mathcal{P} is force f_s per area A . Therefore, $f_s = 3kT/r$, which is a factor of 3/2 larger than f_r because components of particle momenta which are parallel to the radius vector contribute to f_s but cancel one another with respect to f_r as was shown in the previous example.

BROWNIAN MOTION

Consider the motion of a particle with respect to a fixed point in a solvent of viscosity η . On the average, the particle undergoes no radial acceleration; thus f_r must be balanced by the viscous drag f_v , arising from the viscosity of the solvent. f_v is given by Stokes's law, $f_v = f_0 dr/dt$, where f_0 takes the form $f_0 = 6\pi R\eta$ for a spherical particle of radius R . f_0 is known as the friction factor for the solvent.⁶ Since f_r and f_v are both functions of the fluctuating variable r , at constant time t , it is necessary to equate their ensemble-average values: $\langle f_r \rangle = \langle f_v \rangle$. The justification for associating a force with a given r and then averaging lies in the assumption that a particle undergoes an enormous number

of collisions with solvent particles before r changes appreciably.² The differential equation to be solved is

$$2kT \left\langle \frac{1}{r} \right\rangle = f_0 \frac{d\langle r \rangle}{dt}. \quad (6)$$

The averages are performed at constant t using the three-dimensional probability distribution $P(r)$, where

$$P(r) = 4q^{-3}\pi^{-1/2}r^2 \exp(-r^2q^{-2}).$$

$P(r)dr$ is the probability that a particle, which undergoes a large number of collisions in time t , will be located between r and $r + dr$.⁵ $q(t)$ is the most probable value of r . One has $\langle r^2 \rangle = 3q^2/2$, $\langle r \rangle = 2\pi^{-1/2}q$, and $\langle 1/r \rangle = 2\pi^{-1/2}/q$.

The resulting differential equation of radial motion is

$$q dq = 2D dt, \quad (7)$$

where D the diffusion coefficient is given⁶ by $D = kT/f_0$. The solution to Eq. (7) is $q^2 = 4Dt$; the constant of integration is zero since initial conditions require that q be zero when t is zero. Since $q^2 = 2\langle r^2 \rangle/3 = 2\langle x^2 \rangle$, the desired result follows:

$$\langle x^2 \rangle = 2Dt. \quad (8)$$

The harmonic oscillator problem is treated by considering the particle to be attached to one end of a spring of force constant a . The other end is attached to the fixed point in such a way as to permit free rotation about the point in three dimensions. The Hooke's law force on the particle is $f_h = ar$ and would keep the particle at the fixed point ($r = 0$) were it not for the opposing radial force. Thus one has $\langle f_h \rangle = \langle f_r \rangle$:

$$a\langle r \rangle = 2kT\langle 1/r \rangle \quad (9)$$

or $q^2 = 2kT/a = 2\langle x^2 \rangle$. Finally, the classical result for the average particle position as a function of the force constant is obtained,²

$$\langle x^2 \rangle = kT/a. \quad (10)$$

The reason why $P(r)$ can be used in the calculation of average values for the Brownian oscillator is that the averages here are taken over the Boltzmann distribution of energies, $\exp[-E(r)/kT]$, where $E(r) = ar^2/2 - kT \ln r^2 + \text{const}$. The first term is the spring energy and the next two terms come from the integration of $2kT/r$. Thus the distribution becomes proportional to $r^2 \exp(-ar^2/2kT)$, which is formally similar to the radial distribution function $P(r)$.

STATISTICAL THERMODYNAMICS OF MOLTEN SALTS MELTING TRANSITION

If two spherical Brownian particles attract one another by means of a radially symmetric force, there must exist a temperature T_m below which the attractive force is greater than f_r when r is equal to their distance of closest approach, s (sum of their respective radii). T_m , the melting temperature, is that temperature at which the dominant attractive force quenches the Brownian movement and the material solidifies. In ordinary liquids, the attractive forces between the particles are electrical. One system wherein the electrical force may assume a particularly simple form is the fused alkali halides and the alkaline-earth oxides. Here the dominant interaction is given by Coulomb's law,⁷

$$f_e = Z_+Z_-e^2/D_0r^2, \quad (11)$$

Z_+e and Z_-e are the charges on the cation and anion, respectively, and D_0 is the static macroscopic dielectric constant of the melt at T_m . In the subsequent discussion, the ions are regarded as charged hard spheres; the interionic pair potential energy U is

$$U(r) = \infty \quad r < s \\ = Z_+Z_-e^2/D_0r \quad r \geq s. \quad (11')$$

Following Ref. 7, the molten salt is assumed to consist of sharply delineated spherical cavities, in the dielectric continuum, outside of which the dielectric constant is everywhere D_0 , the macroscopic value. However, here we do not restrict the dielectric constant to the "optical" value D_∞ (square of the fused salt refractive index at optical frequencies) because the spatial location of the ions themselves as well as their orbital electron polarizabilities can contribute to the total polarization. This positional contribution is analogous to the orientational polarization of dipoles in a "Debye" dielectric. Thus our D_0 will exceed D_∞ .

The magnitude of D_0 is estimated as follows. A mole of crystalline salt, surrounded by a large evacuated container, is transformed to gaseous ions which fill the container. The energy required for this process is the crystal lattice energy ΔH_1 . In another identical container a mole of crystalline salt is surrounded by additional molten salt at temperature T_m ; the molten salt fills the container. The crystal is melted by supplying an amount of energy equal to the heat of fusion ΔH_f ; the resulting ions diffuse throughout the existing melt of dielectric constant D_0 . ΔH_1 may be estimated by applying Eq. (11) (with $D_0 = 1$) to each ion pair as the ions are separated to a great distance.⁸ The fusion process is analogous to that described for the lattice energy, with the exception that the ions are separated in a medium of dielectric constant D_0 rather than in a vacuum. Thus the work for each ion pair is reduced by a factor of D_0 in the fusion process or in total, $\Delta H_f = \Delta H_1/D_0$.

Application of the melting criterion that f_e and f_r be equal when r is equal to the sum s of the anionic and cationic radii, yields the equation

$$T_m = Z_+Z_-e^2/2ksD_0. \quad (12)$$

The effect of pressure P on T_m follows at once from this hard sphere model. From Eq. (12), $T_m = c\Delta H_f$, where c

is independent of the pressure. Differentiation of T_m with respect to P at constant entropy yields a form of the Clapeyron equation

$$\left(\frac{\partial T_m}{\partial P}\right)_S = c\Delta V_f = T_m\Delta V_f/(\Delta H_f), \quad (13)$$

where ΔV_f is the volume change associated with the fusion process.

Table I presents a comparison between the experimentally observed and calculated melting temperatures for some of the alkali halides and alkaline-earth oxides. The members of the halide and oxide series not depicted also show reasonable agreement between the observed and calculated temperatures with the exception of four compounds whose measured heats of fusion are suspect.

SURFACE TENSION

A somewhat crude definition of the surface tension is the energy required to create an ion vacancy (hole) divided by the surface area of the hole. We regard a hole as being a permanent vacancy created adjacent to a given anion or cation. Thus to create a hole next to a given ion, an ion of opposite charge must be removed to infinity. The energy required for this process is $Z_+Z_-e^2/(sD_0)$. $s/2$ is the average of the anion and cation radii; the average surface area is πs^2 . The surface tension γ is given by

$$\gamma = Z_+Z_-e^2/\pi s^3D_0. \quad (14)$$

Table II lists the calculated and observed surface tensions for some typical salts at their respective melting temperatures. It should be noted that the D_0 values used in calculating γ were obtained by using observed melting temperatures and solving Eq. (12) for D_0 . The agreement between observed and calculated surface tensions is surprisingly good and lends additional credence to our definition of the dielectric constant.

RUBBER ELASTICITY

In most statistical mechanical treatments of ideal rubberlike elasticity (entropic effects only), a "phantom network" forms the conceptual point of departure in describing the properties of the network.^{3,9} The phantom network has been characterized by Flory³ as follows: "A phantom net-

Table I. Comparison between the calculated and observed melting temperatures for some selected ionic salts.

Salt	s^a (Å)	ΔH_1^b (kcal/mole)	ΔH_f^a (kcal/mole)	$T_m(\text{lit.})^a$ (K)	$T_m(\text{calc.})$ (K)	% Difference
LiF	1.96	240	6.47	1121	1149	2.5
NaBr	2.90	175	6.24	1020	1027	0.7
NaI	3.11	164	5.64	933	924	-1.0
KCl	3.14	165	6.34	1043	1023	-2.0
RbF	2.84	182	6.15	1068	994	-6.9
CsI	3.85	139	5.64	899	881	-2.0
MgO	2.05	960 ^c	18.5	3173	3142	-.98
SrO	2.53	804 ^c	16.7 ^b	2703 ^b	2744	1.5

^a Reference 11.

^b Reference 12.

^c Calculated from $\Delta H_1 = (2320/s)(1 - 0.311/s)$ with s in Å (Ref. 8).

Table II. Comparison between the calculated and observed surface tensions for some selected salts at their respective melting temperatures.

Salt	γ (lit.) ^a (dyne/cm)	γ (calc.) (dyne/cm)
LiF	251	256
NaCl	116	123
NaI	88	84
KBr	89	82
RbCl	98	80
CsF	105	93
CsI	75	53
CaO	555	438

^a Reference 11.

work is expressly defined as a hypothetical one whose chains may move freely through one another; the chains act exclusively by introducing a force that is proportional to the distance between each pair of junctions so connected." This force F acting between the junctions of Gaussian chains is given by the equation

$$F = -2kTb^2\mathbf{r}. \quad (15)$$

\mathbf{r} is the instantaneous vector end-to-end separation and

$$b^2 = (3/2)\langle \mathbf{r} \cdot \mathbf{r} \rangle^{-1}.$$

It follows that such a network has an intrinsic tendency to collapse. Again this tendency has been aptly described³: "However, the phantom network is an intrinsically formless object whose configuration function reaches a maximum when the network shrinks to a point." The single-chain configuration function Ω corresponds to an ideal

$$\Omega \propto b^3\pi^{-3/2}\exp(-b^2r^2). \quad (16)$$

Gaussian chain whose ends are attached to the network at the "crosslink" junction points. In a "real" network based on carbon atoms the junction points have either three or four chains radiating from them.

Here, we regard the undeformed rubber network junction points as ideal gas particles which attract one another by means of a Hooke's law force where a , the force constant, is $a = 2kTb^2$ [see Eq. (15)]. b is a function of the number of links between the two junction points connected by the given Gaussian chain. The junctions do not undergo a spontaneous collapse because their "gas pressure" opposes any action tending to lower the "gas volume" of the junction points. Specifically, the radial force acting between any two points opposes the Hookean force given in Eq. (15) resulting in an equilibrium described by Eq. (9). From Eq. (10) one has

$$\langle r^2 \rangle / 3 = kT / 2kTb^2 \quad \text{or} \quad \langle r^2 \rangle = 3 / 2b^2, \quad (17)$$

which is the standard statistical result for the mean-squared end-to-end distance in a Gaussian chain.^{2,3,9} We have shown that the tendency of an undeformed ideal rubber network to collapse is removed if one allows for the three-dimensional Brownian motion of the junction points.

As shown in a previous publication⁴ and from the above considerations, the net force contribution from a given chain acting on a junction point is

$$f_{\text{net}} = -2kT(b^2r - 1/r). \quad (18)$$

The most interesting property of this equation is that f_{net} vanishes when the magnitude of \mathbf{r} , r , is equal to $1/b$ rather than when $r = 0$.

It will be shown¹⁰ how Eq. (18) leads to a new equation of state for a bulk ideal rubber undergoing uniaxial elongation. For extension ratios β in the region $1 \leq \beta \leq 3$, the retractive force is predicted to be nearly proportional to $T(\beta - 1)$ rather than proportional to $T(\beta - \beta^{-2})$ as in the traditional theory.^{3,9} This has some interesting implications with respect to the role of entanglement slippage in real rubber networks undergoing deformation.

CONCLUSION

The second law of thermodynamics implies that two Brownian particles, which are initially close to one another, will experience an increase in their *scalar* separation with time. Using intuitive arguments based on macroscopic statistical mechanics, we have derived a radial force responsible for this radial diffusion process. This novel approach was shown to yield two results of the classical theory of Brownian motion: Einstein's well-known equation for particle migration and the equation for the harmonic oscillator. A thermodynamic theory of melting based on the radial force was formulated and was successfully applied to the alkali halide and alkaline-earth oxide salts. The definition of the dielectric constant required in the theory of fusion also provided a satisfactory method of estimating surface tensions for these salts. Finally, it was shown that an ideal (point masses) rubber network can exist in three dimensions without collapsing into a state of zero volume.

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