

Self-diffusivity as a function of density and temperature in crystalline solids and compensating rules for self-diffusion parameters in carbon subgroup crystals

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The self-diffusion coefficient of crystalline solids as a function of density and temperature may derive from thermodynamics concepts and an earlier elastic thermodynamic point defect model [Varotsos and Alexopoulos, *Phys. Rev. B* **15**, 4111 (1977); *Phys. Rev. B* **18**, 2683 (1978)]. Compensation laws ruling self-diffusion parameters in carbon-subgroup crystals obtained from theoretical calculations are predicted, as well. © 2010 American Institute of Physics. [doi:10.1063/1.3467203]

Analytic functions that scale diffusivity in ultraviscous liquids (which constitute an exceptional state of matter, characterizing “solids that flow”¹) with respect to density were derived recently.^{2,3} The scope was to understand why dynamic quantities scale with density and temperature in ultraviscous liquids, which are characterized by a strong temperature dependence of the activation enthalpy (fragile liquids). These efforts were based on thermodynamical concepts and an earlier thermodynamic elastic model (the so-called cBΩ model⁴) that correlates the Gibbs energy for activation with the isothermal bulk modulus, combined with specific characteristics of the ultraviscous state. Inspired by the above-mentioned approach, diffusivity vs density and temperature function for crystalline solids are derived in the present work. A pressure dependent diffusivity equation is modified through an equation of state, the cBΩ model and proper temperature dependence for the Gibbs activation energy to a density and temperature function.

The mechanism of self-diffusion in crystals of the carbon subgroup C (diamond), Si, Ge α-Sn, and Pb remains a matter of ongoing investigation.⁵ These crystals have very large Debye temperature (i.e., for diamond, $\Theta_D=2246$ K), making quantum effects appreciably important even at room temperature. Self-diffusion calculations were recently reported in carbon-subgroup crystals by Magomedov.⁶ An expression for the self-diffusion coefficient as a function of density ρ and temperature was proposed; i.e., $D(\rho, T) = D_d(\rho)\chi(\rho, T)$, where $D_d(\rho)$ is a function of the correlation factor, the inter-atomic spacing, the pack-density of atoms and the Debye temperature and $\chi(\rho, T)$ is the fraction of atoms having kinetic energy above a threshold value required to diffuse. In this paper, we shall show that diffusivity functions versus density and temperature mentioned in Ref. 6 result independently from fundamental thermodynamic concepts and the so-called cBΩ elastic point defect model.⁴ The parameters of the diffusivity versus density and temperature equations are correlated with physical quantities of the crystal, which vary slightly with pressure. Compensation laws relating self-diffusion entropy and enthalpy as well as self-

diffusion entropy and volume observed in Ref. 6 are direct consequences of the cBΩ model.

Starting from the definition of the isothermal bulk modulus, as follows:

$$B \equiv -(\partial P / \partial \ln V)_T, \quad (1)$$

and recalling that the density is $\rho \equiv m/V$, we get the following:

$$B = (\partial P / \partial \ln \rho)_T. \quad (2)$$

To a first approximation, we assume that:

$$B(P) = B_0 + (\partial B / \partial P)_T P, \quad (3)$$

where B_0 denotes the zero (ambient) pressure value of the bulk modulus and $(\partial B / \partial P)_T$ is assumed to be (to a first approximation) roughly constant. Equations (2) and (3) merge to give the following:

$$\left(\frac{\partial P}{\partial \ln \rho} \right)_T = B_0 + (\partial B / \partial P)_T P. \quad (4)$$

By integrating over pressure and density, we get the following the so-known Murnaghan equation of state (EOS):

$$\rho^{*(\partial B / \partial P)_T} = 1 + \frac{(\partial B / \partial P)_T}{B_0} P, \quad (5)$$

where ρ^* denotes furthermore the reduced density with respect with its value at ambient (zero) pressure.

The activation volume controls the pressure evolution of the diffusivity $\nu^{\text{act}} \equiv (\partial g^{\text{act}} / \partial P)_T$, where g^{act} denotes the Gibbs free energy for diffusion the compressibility of the activation volume is generally defined as $\kappa^{\text{act}} \equiv -(\partial \ln \nu^{\text{act}} / \partial P)_T$,⁴ and can be positive, negative, or zero.

A general equation for self-diffusion describing monovacancy mechanism for the three cubic Bravais lattices is as follows:

$$D(P, T) = \lambda \alpha^2 \nu \exp(-g^{\text{act}}/kT), \quad (6)$$

where D is the diffusion coefficient, λ is a geometrical factor, α is the interatomic spacing, ν is the vibrational frequency of the diffusing species (and related with the phonon frequency involved in the diffusion process), and k is the Boltzmann's constant. For a single mechanism of diffusion $g^{\text{act}} = g^{\text{m}} + g^{\text{f}}$, where g^{m} and g^{f} denote the free energy for migration and

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formation of vacancies, respectively; i.e., g^{act} describes both the motion of carriers and the changes of their concentration induced by temperature and pressure variation. Differentiating Eq. (6) with respect to pressure and considering that pressure does not modify the geometrical factor λ , we get the following:

$$\left(\frac{\partial \ln D}{\partial P}\right)_T = -\frac{v^{\text{act}}(P)}{kT} + \frac{1}{B(P)}\left(\gamma_G - \frac{2}{3}\right), \quad (7)$$

where γ_G is the Grüneisen parameter. In the present work, we assume that $B(P)$ is linear. If v^{act} is constant (i.e., $\kappa^{\text{act}}=0$), Eq. (7) yields a reduced diffusivity D^* [which is the diffusivity $D(P)$ reduced to the ambient (zero) pressure diffusivity value], as follows:

$$\ln D^*(P) = -\frac{v^{\text{act}}}{kT}P + \left(\gamma_G - \frac{2}{3}\right)\frac{1}{(\partial B/\partial P)_T} \ln \left[1 + \frac{(\partial B/\partial P)_T P}{B_0} \right]. \quad (8a)$$

If $v^{\text{act}}(P)$ has a constant (positive) compressibility κ^{act} we have $v^{\text{act}}(P) = v_0^{\text{act}} \exp(-\kappa^{\text{act}}P)$. For the case $\kappa^{\text{act}}P \ll 1$, the latter reduces to: $v^{\text{act}}(P) \equiv v_0^{\text{act}}(1 - \kappa^{\text{act}}P)$. Thus, from Eq. (7), we get the following:

$$\ln D^*(P) = -\frac{v_0^{\text{act}}}{kT}P + \left(\frac{v_0^{\text{act}}\kappa^{\text{act}}}{2kT}\right)P^2 + \left(\gamma_G - \frac{2}{3}\right)\frac{1}{(\partial B/\partial P)_T} \ln \left[1 + \frac{(\partial B/\partial P)_T P}{B_0} \right]. \quad (8b)$$

Alternatively, we may assume that κ^{act} depends on pressure and consider that $1/\kappa^{\text{act}}(P) = B(P)$, i.e., the bulk modulus of the activation volume $B^{\text{act}}(P) \equiv 1/\kappa^{\text{act}}(P)$ has the same pressure dependence as that of the “total” bulk modulus $B(P)$: $1/\kappa^{\text{act}}(P) \equiv B^{\text{act}}(P) = B_0 + (\partial B/\partial P)_T P$. Within this condition, Eq. (7) reduces to the following:

$$\ln D^*(P) = -\frac{v_0^{\text{act}}B_0}{kT[(\partial B/\partial P)_T - 1]} \left\{ \left[1 + \frac{(\partial B/\partial P)_T P}{B_0} \right]^{1 - [(\partial B/\partial P)_T]^{-1}} - 1 \right\} + \left(\gamma_G - \frac{2}{3}\right)\frac{1}{(\partial B/\partial P)_T} \ln \left[1 + \frac{(\partial B/\partial P)_T P}{B_0} \right]. \quad (8c)$$

We note that $D^*(P)$ is dimensionless and denotes the diffusivity reduced to its zero pressure value D_0 . Pressure transforms to reduced density ρ^* (i.e., the density reduced to its ambient pressure value) through Eq. (4). Equations (8a)–(8c) can be rewritten, respectively:

$$\ln D^*(\rho^*, T) = -\frac{v_0^{\text{act}}B_0}{kT(\partial B/\partial P)_T} (\rho^{*(\partial B/\partial P)_T} - 1) + \left(\gamma_G - \frac{2}{3}\right)\frac{1}{(\partial B/\partial P)_T} \ln \rho^{*(\partial B/\partial P)_T}, \quad (9a)$$

$$\ln D^*(\rho^*, T) = -\frac{v_0^{\text{act}}B_0}{kT(\partial B/\partial P)_T} (\rho^{*(\partial B/\partial P)_T} - 1) + \left(\frac{v_0^{\text{act}}B_0}{2kT(\partial B/\partial P)_T^2}\right) (\rho^{*(\partial B/\partial P)_T} - 1)^2 + \left(\gamma_G - \frac{2}{3}\right)\frac{1}{(\partial B/\partial P)_T} \ln \rho^{*(\partial B/\partial P)_T}, \quad (9b)$$

and

$$\ln D^*(\rho^*, T) = -\frac{v_0^{\text{act}}B_0}{kT[(\partial B/\partial P)_T - 1]} [\rho^{*(\partial B/\partial P)_T} - 1] + \left(\gamma_G - \frac{2}{3}\right)\frac{1}{(\partial B/\partial P)_T} \ln \rho^{*(\partial B/\partial P)_T}. \quad (9c)$$

While Eq. (9a) is based on the assertion that $\kappa^{\text{act}}=0$, Eq. (9b) derives from Eq. (8b) under the condition that κ^{act} is of the order of the inverse of material’s isothermal bulk modulus and was set roughly equal to $1/B_0$. Equation (9c) stems from Eq. (8c) assuming that $1/\kappa^{\text{act}}(P) \equiv B^{\text{act}}(P) = B_0 + (\partial B/\partial P)_T P$.

Varotsos and Alexopoulos suggested that the bulk modulus is the elastic quantity that controls activation and established proportionality between activation Gibbs free energy and bulk modulus (cB Ω model).^{7–10} Experimental results on many different types of materials indicate that the bulk modulus manifests a migration process rather than shear modulus.^{11,12} According to the following so-called cB Ω model:^{7–10}

$$g^{\text{act}} = cB\Omega, \quad (10)$$

where c is practically constant⁹ and Ω denotes the mean atomic volume. Note that the validity of Eq. (10) has been checked at ambient pressure in a wide range of solids extending from silver halides¹³ to rare gas solids,¹⁴ in ionic crystals under gradually increasing uniaxial stress¹⁵ in which electric signals are emitted before fracture (in a similar fashion as the electric signals detected before earthquakes^{16–19}), as well as in disordered polycrystalline materials.²⁰ Recently, diffusivity-density equations describing scaling of the dynamic properties of ultraviscous liquids based on thermodynamic concepts and the cB Ω model were reported.^{2,3} Differentiating Eq. (10) with respect to pressure we get the following:

$$v^{\text{act}} = B^{-1}[(\partial B/\partial P)_T - 1]g^{\text{act}}. \quad (11)$$

The Gibbs activation energy is a decreasing function of temperature, in general. Recall that $g^{\text{act}} \equiv h^{\text{act}} - Ts^{\text{act}}$, where h^{act} and s^{act} denote the activation enthalpy and entropy respectively. $g^{\text{act}}(T) = f(T)T$, where $f(T)$ is an adjustable function. Thermodynamics demand a significant increase in h^{act} and s^{act} with temperature. The excessive fall of g^{act} is due to an increasing difference between h^{act} and s^{act} .²¹ The latter aspect underlies the temperature variation in self-diffusivity parameters calculated for carbon sub-group crystals.⁶ Subsequently, at zero pressure, Eq. (11) is rewritten as the following:

$$\frac{v_0^{\text{act}}B_0}{kT} \approx f(T)[(\partial B/\partial P)_T - 1]. \quad (12)$$

Introducing the latter relation into Eqs. (9a)–(9c) we get the following:

$$\ln D^*(\rho^*, T) = -\frac{f(T)[(\partial B/\partial P)_T - 1]}{(\partial B/\partial P)_T}(\rho^{*(\partial B/\partial P)_T} - 1) + \left(\gamma_G - \frac{2}{3}\right) \frac{1}{(\partial B/\partial P)_T} \ln \rho^{*(\partial B/\partial P)_T}, \quad (13a)$$

$$\ln D^*(\rho^*, T) = -\frac{f(T)[(\partial B/\partial P)_T - 1]}{(\partial B/\partial P)_T}(\rho^{*(\partial B/\partial P)_T} - 1) + \left(\frac{f(T)[(\partial B/\partial P)_T - 1]}{2(\partial B/\partial P)_T^2}\right)(\rho^{*(\partial B/\partial P)_T} - 1)^2 + \left(\gamma_G - \frac{2}{3}\right) \frac{1}{(\partial B/\partial P)_T} \ln \rho^{*(\partial B/\partial P)_T}, \quad (13b)$$

and

$$\ln D^*(\rho^*, T) = -f(T)[\rho^{*(\partial B/\partial P)_T-1} - 1] + \left(\gamma_G - \frac{2}{3}\right) \frac{1}{(\partial B/\partial P)_T} \ln \rho^{*(\partial B/\partial P)_T}. \quad (13c)$$

The above three equations correlate the (reduced) self-diffusion coefficient with (reduced) density and temperature (the dependence upon temperature is expressed through the function $f(T)$, which is material dependent). The parameters determining Eqs. (13a)–(13c) are negligibly dependent on pressure. Thus, diffusivity isobars obtained at various pressure values collapse on a common (master) curve when expressed as a function of density and temperature. It seems that the aforementioned representation reveals a scaling behavior of the diffusivity versus density and temperature, which is a novel idea in the field of transport in crystalline solids.

An alternative straightforward route toward diffusivity versus density and temperature function in crystalline solids through the cB Ω model is presented in the next: Eq. (7) [again, $B(P)$ is roughly linear and the resulting EOS is that given by Eq. (5)] combined with a couple of the cB Ω formulas Eqs. (10) and (11), yields the following:

$$\ln D^*(P) = -c \int_0^P \frac{[(\partial B/\partial P)_T - 1]\Omega(P)}{kT} dP + \left(\gamma_G - \frac{2}{3}\right) \frac{1}{(\partial B/\partial P)_T} \ln \left[1 + \frac{(\partial B/\partial P)_T}{B_0} P\right]. \quad (14)$$

However, $\Omega = F_{\text{APF}} \rho_{\text{at}}^{-1}$, where F_{APF} is the atomic packing factor (which is assumed to be constant) and ρ_{at} denotes here the atomic density. Thus, Eq. (14) yields the following:

$$\ln D^*(\rho_{\text{at}}^*, T) = -\frac{cF_{\text{APF}}B_0}{kT}(\rho_{\text{at}}^{*(\partial B/\partial P)_T-1} - 1) + \left(\gamma_G - \frac{2}{3}\right) \frac{1}{(\partial B/\partial P)_T} \ln \rho_{\text{at}}^{*(\partial B/\partial P)_T}, \quad (15)$$

where ρ_{at}^* denotes the atomic density reduced to its ambient (zero) pressure value. It is worth noticing that the latter derivation is based on the cB Ω model and the concept of the atomic packing fraction; neither the pressure dependence of v^{act} nor the temperature dependence of g^{act} [expressed through the $f(T)$ function] are required.

The calculations of Magomedov⁶ reveal two compensation laws, as follows:

- (i) The self diffusion entropy s^{act} is proportional to the activation enthalpy h^{act} , and,
- (ii) The self-diffusion entropy s^{act} is linear with the activation volume v^{act} .

Within the frame of the cB Ω model s^{act} and h^{act} are interconnected through:²²

$$\frac{s^{\text{act}}}{h^{\text{act}}} = -\frac{\beta B + (\partial B/\partial T)_P}{B - T\beta B + (\partial B/\partial T)_P} \equiv \mathfrak{R}, \quad (16)$$

where β denotes the volume thermal expansion coefficient. The compensation rule (i) is actually that predicted by the cB Ω model (i.e., $s^{\text{act}} = \mathfrak{R}h^{\text{act}}$). Furthermore, by dividing a couple of equations derived from the cB Ω model¹¹ by differentiation of Eq. (10) in respect to temperature and pressure, as follows:

$$s^{\text{act}} = -c\Omega[\beta B + (\partial B/\partial T)_P],$$

$$v^{\text{act}} = c[(\partial B/\partial P)_T - 1]\Omega,$$

we get the following:

$$\frac{s^{\text{act}}}{v^{\text{act}}} = -\frac{\beta B + (\partial B/\partial T)_P}{(\partial B/\partial P)_T - 1} \equiv \mathfrak{R}'. \quad (17)$$

The compensation law (ii) observed by Magomedov is that predicted by the cB Ω model through Eq. (17) (i.e., $s^{\text{act}} = \mathfrak{R}'v^{\text{act}}$). These laws, stemming from the cB Ω model, have been experimentally tested for diamond,¹² lead (see Ref. 4, pp. 99–194 and 275), white tin (see Ref. 4, pp. 232–238 and 280) and may probably apply to the carbon subgroup.

¹J. Dyre, *Rev. Mod. Phys.* **78**, 953 (2006).

²A. N. Papathanassiou, *Phys. Rev. E* **79**, 032501 (2009).

³A. N. Papathanassiou and I. Sakellis, *J. Chem. Phys.* **132**, 154503 (2010).

⁴P. A. Varotsos and K. D. Alexopoulos, in *Thermodynamics of Point Defects and Their Relation with Bulk Properties*, edited by S. Amelinckx, R. Gevers, and J. Nihoul (North-Holland, Amsterdam, 1986), pp. 126–127.

⁵K. T. Koga and M. J. Walter, *Phys. Rev. B* **72**, 024108 (2005).

⁶M. N. Magomedov, *Semiconductors* **44**, 271 (2010).

⁷P. Varotsos, *Phys. Rev. B* **13**, 938 (1976).

⁸P. Varotsos, W. Ludwig, and K. Alexopoulos, *Phys. Rev. B* **18**, 2683 (1978).

⁹P. Varotsos, *J. Appl. Phys.* **101**, 123503 (2007).

¹⁰P. A. Varotsos and K. D. Alexopoulos, in *Thermodynamics of Point Defects and Their Relation with Bulk Properties*, edited by S. Amelinckx, R. Gevers, and J. Nihoul (North-Holland, Amsterdam, 1986), pp. 269–306.

¹¹P. Varotsos and K. Alexopoulos, *Phys. Status Solidi B* **110**, 9 (1982).

¹²P. Varotsos, *Phys. Rev. B* **75**, 172107 (2007).

¹³P. Varotsos and K. Alexopoulos, *J. Phys. Chem. Solids* **39**, 759 (1978).

¹⁴P. Varotsos and K. Alexopoulos, *Phys. Rev. B* **30**, 7305 (1984).

¹⁵P. Varotsos, N. Sarlis and M. Lazaridou, *Phys. Rev. B* **59**, 24 (1999).

¹⁶P. Varotsos, N. V. Sarlis, E. S. Skordas, and M. S. Lazaridou, *Phys. Rev. E* **71**, 011110 (2005).

¹⁷P. A. Varotsos, N. V. Sarlis, E. S. Skordas, H. K. Tanaka, and M. S. Lazaridou, *Phys. Rev. E* **73**, 031114 (2006).

¹⁸P. A. Varotsos, N. V. Sarlis, E. S. Skordas, H. K. Tanaka, and M. S. Lazaridou, *Phys. Rev. E* **74**, 021123 (2006).

¹⁹P. Varotsos, K. Eftaxias, M. Lazaridou, G. Antonopoulos, J. Makris, and J. P. Polyannakis, *Geophys. Res. Lett.* **23**, 1449 (1996).

²⁰P. A. Varotsos and K. Alexopoulos, *Phys. Rev. B* **24**, 904 (1981).

²¹P. Varotsos and K. Alexopoulos, *J. Phys. C* **12**, L761 (1979).

²²P. A. Varotsos and K. D. Alexopoulos, in *Thermodynamics of Point Defects and Their Relation with Bulk Properties*, edited by S. Amelinckx, R. Gevers, and J. Nihoul (North-Holland, Amsterdam, 1986), p. 163.