

## Graham's law of diffusion: Quantum analogy and non-ideality<sup>†</sup>

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**Abstract.** We focus attention on two equivalent forms of Graham's law of diffusion that is valid for an ideal gas mixture. This equivalence is shown to be lost by the empirical equations of state in presence of an attractive nonideality. The modified forms are noted. We then construct a simple quantum mechanical model to simulate these results and obtain a one-to-one correspondence. We see how these equations of interest may be extended to  $D$ -dimensions. By employing the quantum model, we next observe the equivalence of the results found above with those obtained via statistical mechanics. As an added advantage, we demonstrate that the virial theorem for confined quantum stationary states retains its validity in the statistical domain too, though here the averaging scheme is correspondingly different.

**Keywords.** Graham's law; nonideality; confined quantum system; statistical mechanics, quantum thermodynamics.

### 1. Introduction

Graham's law of diffusion is well-known. It states that the rates of diffusion  $R_G$  of different gases in a mixture satisfy the proportionality  $R_G \propto (P/d)^{1/2}$ , where  $P$  is the gas pressure and  $d$  the density. An equivalent expression in terms of temperature  $T$  and molar mass  $M$  is also available in the form  $R_G \propto (T/M)^{1/2}$ . For gas mixtures in thermal equilibrium, therefore, the rates of diffusion of different components are inversely related to the square roots of their molar masses. Isotopic separation turns out to be an important application of this tenet.

The law is simple and useful. There are, nevertheless, three important assumptions in the above statement of the law. First, we consider the process to be too slow to affect the equilibrium distribution. Secondly, we disregard the fact that the system is open. Thirdly, we neglect any interparticle interaction. It is this last point that we like to concentrate on.

In phenomenological equations of state for real gases, we usually take care of repulsion among the particles through a hard-sphere model. This is basically a mechanical size effect. One avoids penetra-

tions among the particles and thus the notion of an 'excluded volume' appears. On the other hand, attraction is dealt with more carefully and elaborately. It is also directly linked with a reduction of pressure at the walls. An added advantage is that, while the role of size is difficult to decipher in the quantum domain, the attractive force can be modelled in a very rational manner. So, we shall mainly focus attention on this part of the interaction.

Considerable recent attention has been paid to quantum-mechanical analogs of several macroscopic processes and concepts. The primary motivation has been provided by Bender *et al*<sup>1</sup> who defined quantum isothermal and adiabatic processes, and next proceeded to define<sup>2</sup> entropy and temperature in the quantum domain. They employed the particle-in-a-box (PB) model to arrive at the quantum analogs. We later extended<sup>3,4</sup> their analysis to include some effect of nonideality. Work along this direction of quantum thermodynamics is continuing.<sup>5</sup> An interesting point in this context is that, one has to enclose the system in finite boundaries to define the pressure.<sup>1,6</sup> This naturally takes us to studies on confined systems, another important area of current concern. An exhaustive review of early works on such systems may be found from Fröman *et al*.<sup>7</sup> Interesting works of more chemical relevance include studies on confined H atom,<sup>8</sup> H<sub>2</sub> molecule,<sup>9</sup> H<sub>2</sub><sup>+</sup> ion, He

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atom and quantum dot,<sup>10</sup> etc. Physical effects at the boundaries<sup>11</sup> of enclosed quantum systems have been investigated in a variety of ways. Mostly, simple potentials are chosen. Among others, the Woods–Saxon potential has received some attention.<sup>12</sup> However, the oscillator problem has turned out to be the most favourite choice.<sup>3,4,13–18</sup> Apart from purely numerical works<sup>13</sup> on confined systems, a confined 1-*D* oscillator has been found to be efficient in furnishing energy eigenvalues of near-exact quality<sup>14</sup> when confinement is gradually withdrawn. Pedagogic works concentrate on force<sup>15</sup> and view it as a two-mode system<sup>16</sup> to introduce an ‘oblique’ basis for computations. In case of *D*-dimensional oscillators of this type, one looks for degeneracies<sup>17</sup> and fractional dimensions.<sup>18</sup> Studies on chemical potentials of fermionic and bosonic confined systems<sup>19</sup> form yet another class of endeavour. We have seen earlier<sup>4</sup> how the virial theorem<sup>20</sup> (VT) and Hellmann–Feynman theorem<sup>21</sup> (HFT) help in such situations. Indeed, the modification of the VT under confinement is of very general interest.<sup>22</sup> However, to the best of our knowledge, the implications of nonideality on Graham’s law have not been explored so far. Therefore, it will be worthwhile to investigate it in some detail here, both from macroscopic and microscopic standpoints. This would enrich our understanding of the correspondence between quantum concepts and the empirical classical notions. The behaviour of confined systems will also be consolidated. Additionally, one may appreciate the importance of the VT and the HFT, as applicable to confined systems, again in the present case.

In view of the aforesaid discussion, purpose of the present endeavour is to highlight the effect of introducing an attractive nonideality in Graham’s law of diffusion. This will be explored via three routes, viz. the phenomenological equations, the quantum models and statistical mechanics. As we shall see, there exist a few nice correspondences among the outcomes of these approaches.

## 2. Phenomenological outcomes

We consider first the case of Graham’s law of effusion. The volume of a gas effusing out in time  $\delta t$  through a hole of cross sectional area  $\delta A$  is equivalent to the volume swept out by the particles during this time. Assuming that no collision occurs within  $\delta t$ , the result is given by the concerned area times the average velocity along a particular direction.<sup>23</sup> We thus have

$$\delta V_e / \delta t = \delta A c_a / 4, \quad (1)$$

where  $c_a$  is the average speed. A similar relation for diffusion holds, the only difference being that here we have a number of such holes and hence

$$\delta V_d / \delta t = (c_a / 4) \sum_j \delta A_j. \quad (2)$$

Thus, for a given container, we have the following rate expression in either case:

$$R_G = \delta V / \delta t \propto c_a. \quad (3)$$

Let us remember at this point that

$$c_a \propto \langle c^2 \rangle^{1/2}. \quad (4)$$

Since the gas is in thermal equilibrium at temperature  $T$ , the equipartition principle applies to the situation, yielding

$$\frac{1}{2} m \langle c^2 \rangle = \frac{3}{2} \kappa T. \quad (5)$$

From (5), one obtains

$$\langle c^2 \rangle = 3\kappa T / m = 3RT / M, \quad (6)$$

where  $M$  is the molar mass of the constituent of the gas. Using (3), (4) and (6), we thus get

$$R_G \propto (T/M)^{1/2}. \quad (7)$$

For an ideal gas, on the other hand, the standard equation

$$PV = \frac{1}{3} mN \langle c^2 \rangle, \quad (8)$$

holds, with  $N$  defining the total number of particles. This leads to

$$P/d = \langle c^2 \rangle / 3. \quad (9)$$

Coupling (3), (4) and (9), it follows that

$$R_G \propto (P/d)^{1/2}. \quad (10)$$

Note that (7) and (10) constitute the traditional Graham’s law and they are entirely equivalent.

However, we shall see below that this equivalence is lost once we go over to *real* gases.

Consider, for the sake of simplicity, a real gas with *only* attractive force. We take first the case of a van der Waals gas for which one finds

$$P\bar{V} + a/\bar{V} = RT, \quad (11)$$

where  $\bar{V}$  is the molar volume. This leads to

$$P/d = RT/M - ad/M^2. \quad (12)$$

A similar result follows for the Dieterici equation of state that starts with

$$Pe^{a/RT\bar{V}}\bar{V} = RT, \quad (13)$$

yielding

$$P/d = (RT/M)e^{-ad/MRT}. \quad (14)$$

For  $ad \ll MRT$ , one obtains the same result as (12). But, more important is to note that, in both the cases, we observe the inequality

$$P/d < RT/M, \quad (15)$$

as (12) and (14) reveal. On the other hand, putting (6) in (9), the equality  $P/d = RT/M$  follows for the ideal gas model. The two observations may be coupled by writing

$$P/d \leq RT/M. \quad (16)$$

In (16), the equality applies to the ideal gas case only. An alternative is to proceed via the speed. To this end, we notice that, by virtue of (6), the inequality (15) leads to

$$P/d < \langle c^2 \rangle / 3. \quad (17)$$

But, we already noted that (9) is obeyed for an ideal gas. Now, if we concentrate on the observations (9) and (17), respectively applicable to ideal and real gases, the net result can be cast in the form of the following inequality:

$$P/d \leq \langle c^2 \rangle / 3. \quad (18)$$

The equality in (18) holds again only for an ideal gas. Indeed, we shall see below that such a relation

is obeyed in the quantum domain too. Let us, however, highlight here the point that (5) continues to be true *even when the gas becomes nonideal*. Thus, a study of Graham's law leads us to an important result: (7) is obeyed for real gases, but (10) is not. This loss of equivalence has not been noted before. We shall here concentrate on this point in the course of discussion on nonideality.

It will be useful for the future to look at the forms of a few equations with some greater degree of generality. So, we specifically remark here on the form of (16) or (18) for a  $D$ -dimensional *ideal* gas. From  $P\bar{V} = RT$  and  $M\langle c^2 \rangle / 2 = DRT/2$ , the latter being a consequence of the equipartition principle that retains its validity even when nonideality is present, we obtain

$$P/d = \langle c^2 \rangle / D. \quad (19)$$

It is clear that the other relation,

$$P/d = RT/M, \quad (20)$$

does *not* depend on dimensionality.

### 3. Quantum models

The PB model has long been used to describe ideal gases. The philosophy has been analysed in considerable detail on several occasions.<sup>24</sup> However, in a quantum-mechanical context, the temperature  $T$  does not enter the discussion in a natural way. So, on the way to extend the PB model to real gases, we concentrate on (18), rather than (16). This is because,  $\langle c^2 \rangle$  is directly linked with the average kinetic energy  $\langle T \rangle$  and this is well-defined in the quantum domain.

#### 3.1 The ideal case

We first consider a particle in a 1- $D$  box of length  $L$ . The energy eigenvalues are given by

$$E_n = n^2 h^2 / (8mL^2). \quad (21)$$

The pressure is defined by the relation  $P = -\partial E_n / \partial L$  to yield

$$P = n^2 h^2 / (4mL^3), \quad (22)$$

and this gives

$$PL = 2E_n = 2 \frac{1}{2} m \langle u^2 \rangle, \quad (23)$$

with  $u$  as the velocity along  $x$  direction, whereby

$$P/d = \langle u^2 \rangle, \quad (24)$$

follows. Let us note that it agrees well with (19) when we put  $D = 1$ .

For a particle confined in a 3- $D$  box of lengths  $L_x$ ,  $L_y$  and  $L_z$ , respectively along  $x$ ,  $y$  and  $z$  directions, with  $\nu = L_x L_y L_z$ , we would likewise have  $P = -\partial E_n / \partial \nu = -(\partial E_n / \partial L_x)(\partial L_x / \partial \nu) = -(\partial E_n / \partial L_y)(\partial L_y / \partial \nu)$ , etc. Thus, one obtains

$$P = \frac{n_x^2 h^2}{4mL_x^3} \frac{1}{L_y L_z} = \frac{n_y^2 h^2}{4mL_y^3} \frac{1}{L_x L_z} = \frac{n_z^2 h^2}{4mL_z^3} \frac{1}{L_x L_y}. \quad (25)$$

From (25), we get

$$3P\nu = 2E_n = 2 \frac{1}{2} m \langle c^2 \rangle. \quad (26)$$

It gives us directly

$$P/d = \langle c^2 \rangle / 3, \quad (27)$$

that agrees with (9). Indeed, by following the same procedure in  $D$  dimensions with  $\nu$  as the hyper-volume, one is easily led to the quantum analog of (19).

A simpler way to obtain the above result proceeds by taking the volume of the container  $\nu$  as  $L^3$ . Then, we define the pressure by

$$P = -\partial E_n / \partial \nu = -(\partial E_n / \partial L)(\partial L / \partial \nu) = n^2 h^2 / (12mL^5). \quad (28)$$

This leads to

$$P\nu = \langle p^2 \rangle / 3m, \quad (29)$$

where  $p$  is the momentum of the particle. This again shows

$$P/d = \langle c^2 \rangle / 3, \quad (30)$$

similar to (9) and (27).

In arriving at results (27) or (30), we deliberately employed the symbol  $\nu$  for the volume. The reason is that, here a single particle is involved and it occupies the whole space. Conventionally,  $N$  particles are kept in the volume  $V$ .

### 3.2 The real case

To account for the loss of ideality, we need to introduce a potential inside the container that the particle will feel. This means, we do not have a free particle in  $(-L/2, L/2)$  now. Instead, some potential field, symbolized by  $V(x)$ , is present. So, we define our system in this new situation by the Hamiltonian

$$H = -d^2/dx^2 + V(x). \quad (31)$$

Next, we confine the system in the specified region  $(-L/2, L/2)$ . This amounts to the modification

$$H_T = -\frac{d^2}{dx^2} + V(x) + \lim_{M \rightarrow \infty} \left( \frac{4x^2}{L^2} \right)^M. \quad (32)$$

Thus, the effect of confinement is naturally taken care of via the last term in (32). In other words, we may pretend that our system Hamiltonian now contains an auxiliary potential that is denoted by, say,  $V_1(x)$ , defined by the last term. This makes the subsequent manipulations easy. For example, by employing the VT to the total Hamiltonian  $H_T$ , we obtain

$$2\langle T \rangle_n = \left\langle x \frac{dV}{dx} \right\rangle_n + \left\langle x \frac{dV_1}{dx} \right\rangle_n. \quad (33)$$

On the other hand, employing the HFT on (32), we find

$$\frac{dE_n}{dL} = \left\langle \frac{dV_1}{dL} \right\rangle_n = -\frac{1}{L} \left\langle x \frac{dV_1}{dx} \right\rangle_n. \quad (34)$$

Combining (33) and (34), we obtain the following final expression for the VT in case of a confined system:

$$2\langle T \rangle_n = \left\langle x \frac{dV}{dx} \right\rangle_n - L \frac{dE_n}{dL}. \quad (35)$$

The auxiliary potential  $V_1(x)$  does not show up here. It is an advantage. However, the last term in (35) involves *pressure*. This term enters the expression because of confinement. This is why, (35) becomes crucial in discussions on confined systems. The extension to higher dimensions is pretty straightforward.

### 3.3 Attractive non-ideality

In modelling cases of an attractive non-ideality, we assume the presence of a potential that would somehow reduce the probability of finding the particle near the walls of the container. In one dimension, this is satisfied by simple potentials of the form  $x^{2J}$ ,  $J = 1, 2$ , etc. This ensures an inward attraction, much

like the 'a' constant in the empirical equations of state like (11) and (13). In the quantum case, however, the virial theorem requires that (35) should be true, as shown above. Rearranging (35), we obtain

$$PL = 2\langle T \rangle - \left\langle x \frac{dV}{dx} \right\rangle. \quad (36)$$

Clearly, with  $V(x) \sim x^{2J}$ , the second term at the right side of (36) is positive definite. Noting that in 1-D, we have  $\langle T \rangle = m\langle u^2 \rangle / 2$ , it follows from (36) that

$$PL < m\langle u^2 \rangle. \quad (37)$$

Thus, we obtain

$$P/d < \langle u^2 \rangle. \quad (38)$$

This inequality is the 1-D equivalent of (17). This may be contrasted with the equality in (24) for the ideal case.

Confining attention to 3-D, we rewrite (35) as

$$\begin{aligned} & - \left( L_x \frac{\partial E_n}{\partial L_x} + L_y \frac{\partial E_n}{\partial L_y} + L_z \frac{\partial E_n}{\partial L_z} \right) \\ & = 2(\langle T_x \rangle_n + \langle T_y \rangle_n + \langle T_z \rangle_n) - \langle r \cdot \nabla V \rangle_n. \end{aligned} \quad (39)$$

Following the definitions and usage that has been used previously in arriving at (25), we now see that the left side of (39) becomes

$$- \left( L_x \frac{\partial E_n}{\partial L_x} + L_y \frac{\partial E_n}{\partial L_y} + L_z \frac{\partial E_n}{\partial L_z} \right) = 3P\nu. \quad (40)$$

Therefore, keeping it in mind that the second factor at the right side of (39) is positive definite and that

$$\langle T \rangle = \langle T_x \rangle + \langle T_y \rangle + \langle T_z \rangle = m\langle c^2 \rangle / 2, \quad (41)$$

we arrive at the inequality

$$P/d < \langle c^2 \rangle / 3. \quad (42)$$

This is the quantum-mechanical analog of (17). Now, coupled with (27), (42) yields the inequality that is the microscopic equivalent of (18).

For a  $D$ -dimensional system, the left side of (39) becomes  $DP\nu$ . The second term at the right side is again positive definite. Naturally, we then have

$$DP\nu < m\langle c^2 \rangle, \quad (43)$$

and hence

$$P/d < \langle c^2 \rangle / D. \quad (44)$$

The quantum analog of (19) is easy to get (see the discussion below (27)) for the ideal case. However, here (44) shows an inequality owing to non-ideality.

#### 4. Statistical mechanics

In this section, we first take the simplest potential of the variety  $V(x) \sim x^{2J}$  and proceed to estimate the pressure as well as the average energy. Then, we can check our results against those found via the quantum model and the phenomenological equations. The effect of other potentials of the same attractive nature will be transparent at the subsequent stage. Thus, we hope to extract some general features of the whole endeavour.

##### 4.1 The harmonic potential in one-dimension

Let us consider the PB system in  $(-L/2, L/2)$  and study the effect of the potential  $\lambda x^2$  on the energy levels and hence the partition function. Here  $\lambda$  acts as a perturbation parameter. The overall Hamiltonian is given by

$$H = -\nabla^2 + \lambda x^2 + \lim_{M \rightarrow \infty} \left( \frac{4x^2}{L^2} \right)^M. \quad (45)$$

The energy levels  $E_n$  of this system can be expanded as

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (46)$$

where

$$E_n^{(0)} = \frac{n^2 h^2}{8mL^2}, \quad (47)$$

$$E_n^{(1)} = \frac{L^2}{12} - \frac{L^2}{2\pi^2 n^2}, \quad (48)$$

$$E_n^{(2)} = -\frac{mL^6}{4h^2 n^2} \left( \frac{7}{45} + \frac{10}{3} \frac{1}{\pi^2 n^2} + O(1/n^4) \right), \quad (49)$$

etc. Let us note that series (46) is convergent. Indeed, it has to converge at large  $L$  because then the

left side would basically correspond to the energy of the harmonic oscillator. This is indeed the basis of the work of ref. 14. With this assurance, we now proceed to write the partition function  $Z$  as

$$\begin{aligned} Z &= \sum_{n=1}^{\infty} \exp[-E_n/kT] \quad (50) \\ &= \sum_{n=1}^{\infty} \exp[-(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots)/kT]. \\ &\approx \sum_{n=1}^{\infty} \exp[-E_n^{(0)}/kT] \exp[-\lambda E_n^{(1)}/kT] \exp[-\lambda^2 E_n^{(2)}/kT]. \end{aligned}$$

For small  $\lambda$ , one can expand the last two exponentials to obtain

$$\begin{aligned} Z &\approx \sum_{n=1}^{\infty} \exp[-E_n^{(0)}/kT] [1 - \lambda E_n^{(1)}/kT + \dots] \\ &\quad [1 - \lambda^2 E_n^{(2)}/kT + \dots] \end{aligned}$$

Now, for simplicity, we retain terms up to first order in  $\lambda$  only. This yields

$$Z \approx \sum_{n=1}^{\infty} \exp[-E_n^{(0)}/kT] [1 - \lambda E_n^{(1)}/kT]. \quad (51)$$

To explicitly work out, we now put the energy expressions from (47) and (48). Thus,

$$\begin{aligned} Z &\approx \sum_{n=1}^{\infty} \exp\left[-\frac{n^2 h^2}{8mL^2 kT}\right] \\ &\quad \left(1 - \lambda \frac{L^2}{12kT} + \lambda \frac{L^2}{2\pi^2 n^2 kT}\right). \quad (52) \end{aligned}$$

One has to separate here two different types of terms:

$$\begin{aligned} Z &\approx \left(1 - \lambda \frac{L^2}{12kT}\right) \sum_{n=1}^{\infty} \exp\left[-\frac{n^2 h^2}{8mL^2 kT}\right] \\ &\quad + \left(\lambda \frac{L^2}{2\pi^2 kT}\right) \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-\frac{n^2 h^2}{8mL^2 kT}\right]. \quad (53) \end{aligned}$$

We now define

$$\lambda_d = \frac{h}{\sqrt{2\pi mkT}}, \quad (54)$$

where  $\lambda_d$  is the thermal de Broglie wavelength. Since we consider here a set of  $N$  non-interacting particles confined in a one-dimensional box of length  $L$ , there are two dimensionless parameters which define the thermodynamic and the classical limits. These are respectively given by  $L/\lambda_d$  and  $n\lambda_d$ , where  $n = N/L$  is the number density, so that  $n^{-1}$  signifies the mean separation between particles. The thermodynamic limit is obtained under the condition  $L/\lambda_d \gg 1$ . If this is satisfied, the energies of the particles can be approximated as continuously distributed. The classical limit is obtained by requiring that  $n\lambda_d \ll 1$ . In this limit, quantum correlation is insignificant and one can safely use the Maxwell-Boltzmann statistics. Anyway, we now go back to (54) and employ the thermodynamic limit, i.e.  $\lambda_d/L \rightarrow 0$ . Under this limit, the first sum can be integrated (see, e.g. ref. 25 for a discussion on this point) to yield  $L/\lambda_d$ , while the second one can be approximated by  $\pi^2/6$ . Thus, we arrive at

$$\begin{aligned} Z &\approx \left(1 - \lambda \frac{L^2}{12kT}\right) \frac{L}{\lambda_d} + \left(\lambda \frac{L^2}{2\pi^2 kT}\right) \frac{\pi^2}{6} \\ &= \left(1 - \frac{\lambda L^2}{12kT}\right) \frac{L}{\lambda_d} + \frac{\lambda L^2}{12kT}. \end{aligned}$$

However, the second term at the right side of the above equation is negligible compared to the first one. So, we may go one step further to retain the most significant contribution to the partition function:

$$Z \approx \left(1 - \frac{\lambda L^2}{12kT}\right) \frac{L}{\lambda_d}. \quad (55)$$

In (55), the first term refers to the pure PB model and the  $\lambda$ -dependent part accounts for the *primary* non-ideality correction factor. This is the simplest possible form for the partition function that one can use profitably.

From (55), one can quickly estimate the quantities of interest. We find

$$\ln Z = \ln\left(1 - \frac{\lambda L^2}{12kT}\right) + \ln \frac{L}{\lambda_d},$$

that can be further approximated to

$$\ln Z = \ln \frac{L}{\lambda_d} - \lambda \frac{L^2}{12kT} + O(\lambda^2), \quad (56)$$

so that we keep consistently terms up to first order in  $\lambda$  only. We now define the pressure by the standard equation

$$P = - \left( \frac{\partial A}{\partial L} \right)_T = - \frac{\partial}{\partial L} (-NkT \ln Z), \quad (57)$$

that gives, from (56), the relation

$$P = \frac{NkT}{L} \left( 1 - \frac{\lambda L^2}{6kT} \right). \quad (58)$$

On the other hand, the average energy is obtained from the relation

$$\langle E \rangle = NkT^2 \frac{\partial \ln Z}{\partial T}. \quad (59)$$

Employing (56) here, we obtain

$$\langle E \rangle = NkT^2 \left( \frac{1}{2T} + \frac{\lambda L^2}{12kT^2} \right). \quad (60)$$

In (60), the first term arises from the kinetic energy part while the second one accounts for the potential energy contribution. Thus, (60) may be rewritten as

$$\langle E \rangle = \frac{NkT}{2} + \frac{N\lambda L^2}{12} = \langle T \rangle + \langle V \rangle. \quad (61)$$

Note that the averages in (59)–(61) now refer to statistical averages. Rearranging (58), we use (61) to find

$$PL = NkT - \frac{N\lambda L^2}{6} = 2\langle T \rangle - 2\langle V \rangle. \quad (62)$$

The result (62) is very relevant in the present context. With  $d = Nm/L$  in 1-dimension, we note that it yields directly the inequality

$$P/d < kT/m. \quad (63)$$

This provides the statistical support to (15) in 1-D. In case of ideality, we put  $\lambda = 0$  in (62) to obtain the

statistical equivalent of (16) as well. Also, using  $kT = m\langle u^2 \rangle$ , we obtain

$$P/d < \langle u^2 \rangle, \quad (64)$$

which is the statistical analog of (38). Further, since  $V(x) = \lambda x^2$ , we can rewrite (62) in the form

$$PL = 2\langle T \rangle - \left\langle x \frac{dV}{dx} \right\rangle. \quad (65)$$

This equation, we happily note, resembles *exactly* the quantum-mechanical VT for confined systems, as given by (35), but here with *statistical* averaging.

#### 4.2 Other potentials and higher dimensions

The two key points mentioned above, viz. obtaining the statistical equivalents of (15) and (17), which follow from the empirical equations of state, and demonstrating that the quantal VT is valid in the statistical domain too, retain their validity in other potentials and in higher dimensions as well.

Consider first the 3-D extension of the results presented in subsection 4.1. We have in this case, by virtue of the approximation (55),

$$Z_{3D} = Z_x Z_y Z_z \approx \left( 1 - \frac{\lambda L_x^2}{12kT} \right) \left( 1 - \frac{\lambda L_y^2}{12kT} \right) \left( 1 - \frac{\lambda L_z^2}{12kT} \right) \frac{L_x L_y L_z}{\lambda_d^3}. \quad (66)$$

Approximating further [see (56)], one finds

$$\ln Z_{3D} = \ln \frac{V}{\lambda_d^3} - \frac{\lambda}{12kT} (L_x^2 + L_y^2 + L_z^2) + O(\lambda^2). \quad (67)$$

The work function  $A$  takes then the form

$$A = -NkT \ln Z_{3D} = -NkT \ln \frac{V}{\lambda_d^3} + \frac{\lambda N}{12} (L_x^2 + L_y^2 + L_z^2) + O(\lambda^2). \quad (68)$$

From (68), one gets the pressure as

$$P = - \left( \frac{\partial A}{\partial V} \right)_T = \frac{NkT}{V} - \frac{\lambda N}{12} \frac{\partial}{\partial V} (L_x^2 + L_y^2 + L_z^2). \quad (69)$$

This finally leads us to

$$P = \frac{NkT}{V} - \frac{\lambda N}{6V}(L_x^2 + L_y^2 + L_z^2). \quad (70)$$

The average energy likewise starts from

$$\langle E \rangle = NkT^2 \frac{\partial \ln Z_{3D}}{\partial T}, \quad (71)$$

to yield finally

$$\begin{aligned} \langle E \rangle &= \frac{3}{2}NkT + \frac{\lambda N}{12}(L_x^2 + L_y^2 + L_z^2) \\ &= (\langle T_x \rangle + \langle T_y \rangle + \langle T_z \rangle) + (\langle V_x \rangle + \langle V_y \rangle + \langle V_z \rangle). \end{aligned} \quad (72)$$

Rearranging (70) and making use of (72), we then obtain

$$3PV = 2(\langle T_x \rangle + \langle T_y \rangle + \langle T_z \rangle) - \langle r \cdot \nabla V \rangle. \quad (73)$$

Coupling (39) and (40), we notice that (73) is the 3-D equivalent of (35) that is valid in the statistical domain. Additionally, we see clearly from (70) that (63) is true. It is also notable from (73) that (44) is obeyed here.

If we employ, for example, the perturbation  $\lambda x^4$  instead of  $\lambda x^2$  in (45), the corrections (48) and (49) would change. However, one may notice that only the  $n$ -independent term finally survives in (55). To be explicit, (55) now takes the form

$$Z \approx \left(1 - \frac{\lambda L^4}{80kT}\right) \frac{L}{\lambda_d}. \quad (74)$$

From here, one can work out and check that all our findings like (63) to (65) retain their validity. This reflects the generality of our endeavour. Further, the Helmholtz free energy, correct up to first order, can now be calculated from (74) as

$$A^{(0)} + A^{(1)} = -kT \ln \left( \frac{L}{\lambda_d} \right) + \lambda \frac{L^4}{80}. \quad (75)$$

This agrees with the result obtained by Callen<sup>26</sup>. Additionally, we may check that the Bogoliubov inequality [see ref 26] here becomes

$$A \leq -kT \ln \left( \frac{L}{\lambda_d} \right) + \lambda \frac{L^4}{80}. \quad (76)$$

The inequality states that the sum of all higher order corrections would be positive, so that the right hand side of (76) becomes an upper bound to the Helmholtz potential. The length  $L$  of the box has not yet been chosen. Clearly, the best approximation is obtained by making the upper bound of  $A$  as small as possible. Thus, we choose  $L$  so as to minimize  $A$ , which then becomes the best available approximation to the Helmholtz free energy of the system. This leads to

$$L = \left( \frac{20kT}{\lambda} \right)^{1/4}. \quad (77)$$

This result determines the optimum size of a square-well potential with which to approximate the thermal properties of the system, and it determines the corresponding approximate Helmholtz potential. For a system of  $N$  identical but distinguishable particles, (75) can be used to calculate the pressure, correct up to first order, and it turns out to be

$$P = \frac{NkT}{L} \left[ 1 - 20 \frac{\lambda L^4}{kT} \right]. \quad (78)$$

Here the interesting point is that, for the optimal size of the square well (77), the resultant pressure disappears. This refers to the thermodynamic equilibrium.

## 5. Conclusions

Our purpose has been to investigate how far the proportionality of  $P/d$  and  $T/M$  retains its validity for gaseous systems in presence of nonideality. We have chosen Graham's law of diffusion as a physical process that employs it directly. A quantum model to simulate the case of an attractive nonideality has been put forward and analysed. The chief results are as follows:  $P/d \leq \langle c^2 \rangle / D$  and  $P/d \leq RT/M$ . They are found to agree well with those obtained from phenomenological equations of state. To provide a more concrete basis, we have next proceeded to check our conclusions via statistical mechanics, using the same quantum model in the course of constructing the partition function. A weakly perturbed system has shown the correctness of all our previous findings. The proper reduction to the ideal case has always been shown to be maintained. Additionally, our analysis has revealed that the VT for confined quantum systems, which is known to be valid only for

stationary states, remains intact in the statistical domain too, with statistical averaging of the quantities concerned. We hope to examine this part in a more general manner in future studies.

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