$\text{MAXWELL} \underset{t \to \infty}{\to} \text{BOLTZMANN}$

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Joel Lamar Davis, Jr.

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$$\text{MAXWELL} \xrightarrow[t \to \infty]{} \text{BOLTZMANN}$$

Approved:

R. F. Fox, Chairman

J. Ford

H. A. Gersch

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SUMMARY

In this thesis, exact results are obtained for the time evolution of the phase space distribution in several specific situations. The tools of operator calculus are applied to the Liouville equation and the time evolution of the system calculated for a noninteracting, ideal gas, an ideal gas interacting with an external potential, and an ideal gas interacting with an external potential and immersed in a Brownian fluid. It is shown that an equilibrium is reached by each of these systems and the nature of that equilibrium is explored. In the first two cases equilibrium is reached by the contracted, spatial distribution which is obtained by integrating the full phase space distribution with respect to its momentum variables. It is shown that, if the initial distribution is Maxwellian in momentum, the contracted, spatial distribution for the first system becomes a uniform distribution while, for the second system, the contracted, spatial distribution goes to an equilibrium which is not a Boltzmann distribution although it has something of a Boltzmann character. In the case of the third system, the phase space distribution is shown to go to a Maxwell-Boltzmann distribution. In each of these cases, not only is the final equilibrium calculated but some of the details of the approach to equilibrium are revealed.

CHAPTER I

INTRODUCTION

This thesis is concerned with the time evolution of the phase space distribution for classical mechanical systems. The tools of operator calculus, which were originally shown to be useful during the development of quantum electrodynamics, are used in the approach to this problem. The calculations contained in this thesis should strengthen the impression that such tools are also useful in analyzing non-quantum mechanical problems. With these tools, exact results are obtained for the time evolution of the phase space distribution in several specific situations.

Although the dynamical description of the full phase space distribution time evolution is time reversal invariant, a contracted, spatial distribution may exhibit time irreversible behavior. In particular, the object of study in much of this thesis is the time evolution of the contracted, spatial distribution which is obtained by integrating the full phase space distribution with respect to its momentum variables. The asymptotic, $t\to\infty$, form of the contracted, spatial distribution is studied under the condition that the full phase space distribution is characterized, initially, by a momentum distribution which is Maxwellian and an arbitrary distribution in position space. The act of contraction creates a spatial distribution which is time irreversible. This contracted, spatial distribution approaches an asymptotic equilibrium which exhibits the form of a Boltzmann spatial distribution. For this reason this work has been entitled Maxwell $\xrightarrow[t\to\infty]{}$ Boltzmann.

Chapter II of the thesis is devoted to the study of the problem just described in the special case of the ideal gas. This problem is easily shown to be equivalent to the study of one particle in one dimension, and has been studied previously by other researchers using methods more traditional in classical mechanics.[1,2] This problem is presented in order to exhibit, in the simplest context, the contraction of a phase space distribution, and the special role which is played by the condition that the full phase space distribution at the initial time is Maxwellian in momentum. It is this Maxwellian momentum distribution that allows the integral over momentum, which produces the contracted, spatial distribution, to be performed. In this special case, the contracted, spatial distribution becomes, asymptotically in time, uniform spatially. This is, of course, the Boltzmann distribution in the absence of any potentials.

In Chapter III, this kind of analysis is continued with the added complication that the ideal gas is in the presence of an external potential field. This complication requires the introduction of more sophisticated operator calculus techniques. This occurs because the Liouville equation for this case,

$$\frac{\partial}{\partial t} D(r,p,t) = \left(- \frac{p}{m} \frac{\partial}{\partial r} + \frac{dU(r)}{dr} \frac{\partial}{\partial p}\right) D(r,p,t), \tag{1}$$

involves a differential operator for the phase space evolution, $- \frac{p}{m} \frac{\partial}{\partial r} + \frac{dU(r)}{dr} \frac{\partial}{\partial p}$, which is comprised of two non-commuting pieces. Nevertheless, the operator calculus techniques permit the time evolution of the contracted, spatial distribution for this problem to be rendered in the form of an explicit series expansion, each term of which can be analyzed. Asymptotically in time a contracted, spatial distribution is obtained which separates, in a natural way, into a sum of two power series. The first series is shown to be identical with a power series expansion of the Boltzmann, spatial distribution,

$$\frac{1}{Q} \exp[-\beta U(r)], \text{ where } \beta = \frac{1}{k_B T} \text{ and } Q = \int_0^L \exp[-\beta U(r)]dr, \tag{2}$$

in powers of β. The proof of this identity involves an intricate combinatorial identity, some of the details of which have been relegated to the Appendices. The second series in the asymptotic result is comprised of complicated "correction" terms which modify the Boltzmann distribution series, and together these two series provide the equilibrium solution. Because, initially, the Maxwellian momentum distribution is parameterized by the temperature, T, and the asymptotic Boltzmann spatial distribution is parameterized by the same temperature, the "correction" series was conjectured to give rise to a renormalized temperature, T'. On physical grounds this might be expected because the redistribution in an external potential will change the temperature of the system when its time evolution is energy conserving, as is the case here. Up to order β^2 in our β series, the renormalization procedure succeeds, but at order β^3 this approach fails. To confirm the general formulae, a check of internal consistency is carried out at the end of section III. This check shows that the formalism is correct and that a true Boltzmann distribution is not obtained, asymptotically in time, even though the contracted, spatial distribution goes to an equilibrium.

In Chapter IV a successful attempt is made to circumvent the difficulty that arose in the form of a "correction" series. Because the difficulty in the special case analyzed in Chapter III resulted from energy conservation, the analysis of a modified Liouville equation,

$$\frac{\partial}{\partial t} D(r,p,t) = \left(-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU(r)}{dr}\frac{\partial}{\partial p} - \frac{\partial}{\partial p}\left[-\frac{\alpha}{m}p + \tilde{F}(t)\right]\right)D(r,p,t), \tag{3}$$

in which $\tilde{F}(t)$ is a stochastic force, and α is a damping parameter, is attempted. The stochastic properties of $\tilde{F}(t)$ are those of Brownian motion, and the autocorrelation function for $\tilde{F}(t)$ is related to α by the Einstein relation. These "Brownian" forces have been introduced to provide a phenomenological description of an ideal gas of particles in an external potential, and immersed in a fluid of other particles which exhibit their presence only through these "Brownian" forces. If a momentum distribution which is initially Maxwellian is perturbed momentarily into a non-Maxwellian state, these "Brownian" forces are known to cause relaxation back to the Maxwellian momentum distribution. In addition the relaxation guarantees that the temperature remains essentially constant. Of course, these "Brownian" forces are not conservative forces, but conservative time evolution has already been analyzed and its consequences described in section III.

The analysis in this "Brownian" case requires still more sophisticated operator identities, but, remarkably enough, the analysis is tractable in closed form. The contracted, spatial distribution is found to approach the Boltzmann distribution asymptotically in time, and the "correction" series is found to vanish. Again, some of the intricate details of the proofs are found in the appendices.

The last special case, analyzed in Chapter IV, is related to an earlier analysis by Kramers[3] of a similar system. Kramers then applied his results to the analysis of chemical reaction rates. The analysis presented in Chapter IV might also be applied to physical problems, such as the interaction of molecules immersed in a solvent. The molecules would be presumed to interact through some force law, but the solvent molecules would be treated as only producing "Brownian" forces acting upon the solute molecules. The consequences of this kind of approach remain to be explored.

CHAPTER II

IDEAL GAS

The system studied in this section is an ideal gas contained in a cube of side L. This gas is assumed to be composed of particles which do not interact with each other. The Hamiltonian for such a system is given by $\sum_j \frac{||p_j||^2}{2m}$ where j is the particle index. Since the Hamiltonian is separable, both with respect to particle index and with respect to cartesian coordinate, the problem factors and the solution to the three dimensional N-body problem is reduced to the product of solutions of one body, one dimensional problems. Thus, the problem studied in this section is that of one particle in a one dimensional box, [0,L].

The complete description of this system is provided by its phase space distribution, D(r,p,t), the evolution of which is given by the Liouville equation,

$$\frac{\partial}{\partial t} D(r,p,t) = -iL\, D(r,p,t), \tag{4}$$

where
$$-iL = -\frac{p}{m}\frac{\partial}{\partial r}\ . \tag{5}$$

The wall reflections do not appear explicitly because periodic boundary conditions are used. This is a modified problem which is, in a sense, equivalent.[4,5] A contracted, spatial distribution is defined as

$$R(r,t) = \int_{-\infty}^{\infty} D(r,p,t)dp \tag{6}$$

where D(r,p,t) is the solution to Eq. (4). Formally, this solution is given by

$$D(r,p,t) = \exp[-itL] \;\; D(r,p,0) \tag{7}$$

where D(r,p,0) is the initial phase space distribution. In the introduction it is stated that the initial conditions which are used in this analysis are a Maxwellian momentum distribution and an arbitrary spatial distribution. This corresponds to

$$D(r,p,0) = R(r,0)W_m(p) \tag{8}$$

where $W_m(p)$ is a Maxwellian momentum distribution,

$$W_m(p) = \left(\frac{\beta}{2\pi m}\right)^{1/2} \exp\left[-\frac{\beta p^2}{2m}\right], \tag{9}$$

and R(r,0) is the initial spatial distribution. In order to use the evolution operator, exp(-itL), from Eq. (7) the initial spatial distribution is Fourier analyzed

$$R(r,0) = \sum_k L^{-1/2} C_k \, e^{i\frac{2\pi}{L}kr}, k = 0, \pm1, \pm2, \ldots . \tag{10}$$

Thus, the contracted, spatial distribution can be written as

$$R(r,t) = \sum_k L^{-1/2} C_k \int_{-\infty}^{\infty} dp \, \exp[- \frac{tp}{m} \frac{\partial}{\partial r}]\exp[i \frac{2\pi}{L} kr]W_m(p). \tag{11}$$

It is easily seen, by expanding the exponential, that

$$\exp[a \frac{\partial}{\partial r}] \exp[br] = \exp[ab]\exp[br]. \tag{12}$$

Using Eq. (12) in Eq. (11), one has

$$R(r,t) = \sum_k L^{-1/2} C_k \exp[i \frac{2\pi}{L} kr] \int_{-\infty}^{\infty} dp \, \exp[-it \frac{p}{m} \frac{2\pi}{L} k]W_m(p). \tag{13}$$

The integral in Eq. (13) may be done by elementary methods.(6) This is due in a large part to the Gaussian nature of the integral. The result obtained contains terms which damp to zero as the square of t increases,

$$R(r,t) = \sum_k L^{-1/2} C_k \exp[i \frac{2\pi}{L} kr]\exp[- \frac{1}{2\beta m}(\frac{2\pi}{L})^2 k^2 t^2]. \tag{14}$$

The object of study in this analysis is the long time limit of R(r,t), the contracted, spatial distribution. One sees that

$$\lim_{t\to\infty} \exp[-\frac{1}{2\beta m}(\frac{2\pi}{L})^2 k^2 t^2] = \delta(k) \tag{15}$$

where

$$\delta(k) = \begin{cases} 0 & k \neq 0 \\ 1 & k = 0 \end{cases} \tag{16}$$

and where $\delta(k)$ is called the Kronecker delta symbol. Therefore in the long time limit one has

$$\lim_{t\to\infty} R(r,t) = L^{-1/2} C_o. \tag{17}$$

Normalization of the initial distribution requires

$$\int_o^L R(r,0)dr = 1 \tag{18}$$

and therefore $\sum_k L^{-1/2} C_k \int_o^L \exp[i \frac{2\pi}{L} kr]dr = L^{1/2} C_o = 1.$ (19)

From Eq. (17) and Eq. (19), one finally has

$$\lim_{t\to\infty} R(r,t) = L^{-1/2} C_o = L^{-1}. \tag{20}$$

Thus, one sees that in the long time limit the contracted, spatial distribution for this system approaches the uniform distribution. Since this is the Boltzmann distribution in the absence of potentials, one might suppose that the contracted, spatial distribution for an ideal gas in the presence of an outside potential would also approach a Boltzmann distribution.

It should be noted that the use of the Maxwellian momentum distribution is not crucial to the result which was obtained, Eq. (20). If one substitutes any square integrable momentum distribution for $W_m(p)$ in equation (13) and takes the long time limit of that equation, then a simple application of the Riemann-Lebesgue lemma gives the result obtained in Eq. (20).* The analysis was developed in the more restricted manner to elucidate the methods which will be used in later sections.

*In his treatment of this problem (Ref. 1) Grad's approach was essentially a proof of the Riemann-Lebesgne lemma.

CHAPTER III

IDEAL GAS IN THE PRESENCE OF AN EXTERNAL POTENTIAL

In this section the analysis of the ideal gas is extended to the effect the action of conservative forces has upon the equilibrium reached by the contracted, spatial distribution. Since the equilibrium reached in the absence of any forces was a Boltzmann distribution, a Boltzmann distribution may also be approached in the present case. There is more to the matter than just the Boltzmann distribution, however. A Boltzmann distribution, $\exp(-\beta U(r))$, is characterized by the potential, $U(r)$, which is assumed to be arbitrary, and β, which in the case of a Maxwell-Boltzmann distribution is a measure of the average kinetic energy of the gas particles. In the present case, the phase space distribution, at the initial time, is assumed to have a Maxwellian momentum distribution. This distribution is parameterized in terms of such a β, which is a measure of the initial average kinetic energy of the particle. Should one expect that the average kinetic energy of the particle would remain unchanged under the action of conservative forces? Indeed one should not. If the contracted spatial distribution approaches a Boltzmann distribution one would expect to find a new parameter, β'. Next, bearing in mind these arguments, the analysis of this system is performed.

Time Evolution of the Contracted, Spatial Distribution

The Liouville equation which governs the time evolution of this system is

$$\frac{\partial}{\partial t} D(r,p,t) = (-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU(r)}{dr}\frac{\partial}{\partial p}) D(r,p,t) \tag{21}$$

and has a solution given by

$$D(r,p,t) = \exp(-\frac{pt}{m}\frac{\partial}{\partial r} + \frac{tdU(r)}{dr}\frac{\partial}{\partial p}) D(r,p,0). \tag{22}$$

The contracted, spatial distribution is given by

$$R(r,t) = \int_{-\infty}^{\infty} \exp(-\frac{pt}{m}\frac{\partial}{\partial r} + \frac{tdU(r)}{dr}\frac{\partial}{\partial p}) D(r,p,0)dp. \tag{23}$$

In Chapter II, the evolution operator, exp(-itL), acted only on the initial spatial distribution and the results could be resummed to an exponential form. This method can not be applied in the present case because the two parts of the Liouville operator do not commute. Nevertheless, the action of the two parts may be separated by means of a disentanglement theorem.[7,8] This theorem allows R(r,t) to be written in terms of an infinite series; each term of which may be solved.

Introduction of the Disentanglement Theorem

If A and B are noncommuting differential operators, then

$$\exp[is(A+B)] =$$

$$\exp[isA]\underset{\leftarrow}{T}\exp[i\int_0^s \exp(-is'A)B\exp(is'A)ds'] \tag{24}$$

where, for an operator, O(s), which does not commute with itself at different times,

$$\underset{\leftarrow}{T}\exp[\int_0^s O(s')ds'] =$$

$$1 + \sum_{N=1}^{\infty}\int_0^s ds_1\int_0^{s_1} ds_2 \ldots \int_0^{s_{N-1}} ds_N\, O(s_1)O(s_2)\ldots O(s_N). \tag{25}$$

This identity is proved in Appendix I.

Series Expansion of the Contracted, Spatial Distribution

Using Eq. (23) and Eq. (24), one has

$$R(r,t) = \int_{-\infty}^{\infty} dp\, \exp[-\frac{tp}{m}\frac{\partial}{\partial r}]\, \underset{\leftarrow}{T}\exp[\int_0^t ds$$
$$\exp[\frac{s'p}{m}\frac{\partial}{\partial r}]\,\frac{dU(r)}{dr}\,\frac{\partial}{\partial p}\,\exp[-\frac{s'p}{m}\frac{\partial}{\partial r}]]R(r,0)W_m(p) \tag{26}$$

or

$$R(r,t) = R_0 + \sum_{N=1}^{\infty} R_N \tag{27}$$

where

$$R_0 = \int_{-\infty}^{\infty} dp \ \exp[-\frac{tp}{m}\frac{\partial}{\partial r}] \ R(r,0)W_m(p) \tag{28}$$

and

$$R_N = \int_{-\infty}^{\infty} dp \ \exp[-\frac{tp}{m}\frac{\partial}{\partial r}]$$
$$[\prod_{i=1}^{N} \int_{o}^{s_{i-1}} ds_i \ \exp[\frac{s_i p}{m}\frac{\partial}{\partial r}] \ \frac{dU(r)}{dr} \frac{\partial}{\partial p} \exp[-\frac{s_i p}{m}\frac{\partial}{\partial r}]]R(r,0)W_m(p). \tag{29}$$

In Eq. (29), $S_o = t$ and the larger i terms are to the right in the product, $\prod_{i=1}^{N}$. As the series, Eq. (27), is analyzed it is found that a power series in the parameter β is produced. This power series separates, in a natural way, into two power series in β. The first of these two power series is shown to be equal to a Boltzmann distribution in the original parameter β. In light of the previous arguments, the second of the two power series is interpreted to be a correction reflecting the conservation of energy.

In Chapter II the technique used in analyzing the action of operators such as $\exp(\frac{tp}{m}\frac{\partial}{\partial r})$ depended intimately on Fourier analyzing the r dependent terms. Since the same techniques are used in the present calculation, the potential is also Fourier analyzed.

$$U(r) = \sum_k L^{-1/2} \hat{U}(k) \exp[i \tfrac{2\pi}{LM} kr] \qquad k = 0, \pm 1, \pm 2 \ldots \tag{30}$$

It should be noted at this point that this Fourier analysis will not, in general, produce a "nice" spectrum of values for $\hat{U}(k)$. This will not prove to be an impediment, however, in that no arguments will be made requiring $\hat{U}(k)$ to become small for large values of k.

Analysis of the Part of R(r,t) Which is Shown to Approach A Boltzmann Distribution in the Original Parameter β

Normalization requirements on the original distribution, Eq. (18), imply that the first term in the Fourier expansion of R(r,0) is L^{-1}. Thus, each term R_N contains within it a term B_N, where

$$B_N = L^{-1} \int_{-\infty}^{\infty} dp \exp[-\tfrac{tp}{m}\tfrac{\partial}{\partial r}] \prod_{i=1}^{N} \int_{o}^{s_{i-1}} ds_i \exp[\tfrac{s_i p}{m}\tfrac{\partial}{\partial r}] \frac{dU(r)}{dr}\frac{\partial}{\partial p}\exp[-\tfrac{s_i p}{m}\tfrac{\partial}{\partial r}] W_m(p). \tag{31}$$

Using Eq. (12), Eq. (30), and $\alpha = \frac{2\pi}{Lm}$, B_N may be written

$$B_N = L^{-\frac{N+2}{2}} \sum_{k_N} \sum_{k_{N-1}} \cdots \sum_{k_1} \hat{U}(k_N)\hat{U}(k_{N-1}) \cdots \hat{U}(k_1)(i\alpha m)^N$$

$$k_N k_{N-1} \cdots k_1 \exp[i\alpha m r \sum_{i=1}^{N} k_i] \int_{-\infty}^{\infty} dp \int_{o}^{t} ds_1 \int_{o}^{s_1} ds_2 \cdots \int_{o}^{s_{N-1}} ds_N$$

$$\exp[i\alpha p(s_1-t) \sum_{i=1}^{N} k_i] \frac{\partial}{\partial p} \exp[i\alpha p(s_2-s_1) \sum_{i=1}^{N-1} k_i] \frac{\partial}{\partial p} \cdots$$

$$\exp[i\alpha p \ (s_N-s_{N-1})k_1] \frac{\partial}{\partial p} W_m(p). \qquad (32)$$

Integration by parts is performed N times over the variable p and the result is

$$B_N = L^{-\frac{N+2}{2}} (i\alpha m)^N \ [\prod_{i=1}^{N} \sum_{k_i} k_i\hat{U}(k_i)\exp[i\alpha m r k_i]] \int_{-\infty}^{\infty} dp \int_{o}^{t} ds_1 \cdots \int_{o}^{s_{N-1}} ds_N$$

$$(i\alpha)^N[(s_1-t)(\sum_{\ell=1}^{N} k_\ell)][(s_1-t)k_N + (s_2-t)(\sum_{\ell=1}^{N-1} k_\ell)]$$

$$[(s_1-t)k_N + (s_2-t)k_{N-1} + (s_3-t)(\sum_{\ell=1}^{N-2} k_\ell)] \cdots [(s_1-t)k_N +$$

$$(s_2-t)k_{N-1} + \cdots + (s_N-t)k_1]\exp[i\alpha p[(s_1-t)k_N + \cdots +$$

$$(s_N-t)k_1]] \ W_m(p). \qquad (33)$$

Changing variables, $x_i = (s_1-t)$, and performing the integral over the p variable, one has

$$B_N = L^{-\frac{N+2}{2}}(i\alpha m)^N[\prod_{i=1}^{N} \sum_{k_i} k_i\hat{U}(k_i)\exp[i\alpha mrk_i]] \int_{-t}^{o} dx_1 \ldots \int_{-t}^{x_{N-1}} dx_N$$

$$(i\alpha)^N[x_1 \sum_{\ell=1}^{N} k_\ell]\ldots[x_1k_N+x_2k_{N-1} + \ldots + x_Nk_1]$$

$$\exp[-\alpha^2 \frac{m}{2\beta} [x_1k_N + \ldots + x_Nk_1]^2]. \tag{34}$$

The integral over the variable x_N is now easily performed. The integral which results from evaluating at the limit $x_N = -t$ is difficult and will not be considered at this time. Later in the thesis, the first several terms in the series expansion of R(r,t) will be calculated including these terms. However, the integral which results from evaluating at the limit $x_N = x_{N-1}$ is easily done. This process of dropping the terms resulting from evaluation of the integrals at the lower limits is continued until the integral over x_1 is performed. At this point the results from evaluating at both limits are kept and one has

$$L^{-\frac{N+2}{2}}(-\alpha^2m)^N[\prod_{i=1}^{N} \sum_{k_i} k_i\hat{U}(k_i)\exp[i\alpha mrk_i]](\frac{\beta}{-\alpha^2m})^N$$

$$\frac{1}{k_1}\frac{1}{k_1+k_2} \cdots \frac{1}{\sum_{\ell=1}^{N} k_\ell} \exp[-\alpha^2 \frac{m}{2\beta} x_1^2 (\sum_{\ell=1}^{N} k_\ell)^2]\Big|_{-t}^{o}. \tag{35}$$

This form has implied exclusions. In carrying out each integration it was implicitly assumed that the sum, $\sum_{\ell=1}^{N-j} k_\ell$, which appeared was zero. Therefore the possibility of any sum, $\sum_{\ell=1}^{N-j} k_\ell$, being zero must be excluded. Also, the factor, $k_1 k_2 \ldots k_N$, prohibits any k_i from being zero. Thus, in the long time limit, term (35) may be written as

$$L^{-1} K_N'(r)\beta^N \tag{36}$$

where $K_N'(r) =$

$$L^{-\frac{N}{2}} \prod_{\ell=1}^{N} \sum_{k_\ell} \hat{U}(k_\ell)\exp[i\alpha m r k_\ell] \frac{k_\ell}{\sum_{j=1}^{\ell} k_j} (1-\delta(\sum_{j=1}^{\ell} k_j))(1-\delta(k_j)). \tag{37}$$

This part, term (37), of the long time limit of R(r,t) is a Boltzmann distribution. This is a remarkable statement. Only upon closest examination does term (37) reveal itself to be a Boltzmann distribution. In order to prove this statement one needs a power series in β which is equivalent to a Boltzmann distribution.

Series Expansion of the Boltzmann Distribution.

Theorem 1. The series expansion of the Boltzmann distribution is given by

$$\frac{1}{Q} \exp[-\beta U(r)] = L^{-1} \sum_{N=o}^{\infty} K_N(r)\beta^N \tag{38}$$

where

$$K_N(r) = \frac{(-1)^N}{N!} \sum_{m=o}^{N} \frac{N!}{(N-m)!m!} [U(r)-\overline{U(r)}]^{N-m}$$

$$\sum_{\substack{\text{Partitions}\\ \text{of } m}} \prod_{\ell=1}^{m} \frac{p!m!(-1)^p}{m_\ell!(\ell!)^{m_\ell}} [\overline{[U(r)-\overline{U(r)}]^\ell}]^{m_\ell}. \tag{39}$$

In Eq. (39), $\overline{g(r)} = L^{-1} \int_o^L g(r)\, dr$ for any function $g(r)$, and the symbol $\sum_{\substack{\text{Partitions}\\ \text{of } m}}$ is the sum over all partitions of m into smaller integers with multiplicity, m_ℓ, such that

$$m = \sum_{\ell=1}^{m} \ell m_\ell \quad \text{and} \quad p = \sum_{\ell=1}^{m} m_\ell .$$

In the future, this summation symbol is used without explanation. Theorem 1 is proved in Appendix II. In order to show that term (37) is a Boltzmann distribution, one must show $K_N(r) = K'_N(r)$ or term (37) equals term (39).

Proof of the Boltzmann Term. In this proof the method of induction is used. To start with, the first several terms of each series are examined.

$$K_1(r) = -1 \sum_{m=o}^{1} \frac{1}{(1-m)!m!} [U(r)-\overline{U(r)}]^{1-m}$$

$$\sum_{\substack{\text{Partitions}\\ \text{of } m}} \prod_{\ell=1}^{m} \frac{p!m!(-1)^p}{m_\ell!(\ell!)^{m_\ell}} [\overline{[U(r)-\overline{U(r)}]^\ell}]^{m_\ell} \tag{40}$$

$$K_1(r) = -[U(r)-\overline{U(r)}] + \overline{[U(r)-\overline{U(r)}]} = -U(r)+\overline{U(r)} \tag{41}$$

$$K_1'(r) = (-1)L^{-1/2} \sum_{k_1} \hat{U}(k_1)\exp[i\,\tfrac{2\pi}{L}\,rk_1](1-\delta(k_1)) \tag{42}$$

$$K_1'(r) = -U(r) + \overline{U(r)} \tag{43}$$

$$K_2(r) = 1/2[U(r)-\overline{U(r)}]^2 - 1/2\ \overline{[U(r)-\overline{U(r)}]^2} \tag{44}$$

$$K_2'(r) = L^{-1} \sum_{k_1}\sum_{k_2} \hat{U}(k_1)\hat{U}(k_2)\exp[i\,\tfrac{2\pi}{L}\,r(k_1+k_2)]\frac{k_2}{k_1+k_2}$$

$$(1-\delta(k_1+k_2))\ (1-\delta(k_1))(1-\delta(k_2)) \tag{45}$$

$K_2'(r)$ does not appear to equal $K_2(r)$. However, $K_2'(r)$ would be unchanged if k_1 and k_2 are exchanged. In the future the relabeling of the k_i in all equivalent ways will be called symmetrization. Symmetrizing $K_2'(r)$ one has

$$K_2'(r) = L^{-1} \sum_{k_1}\sum_{k_2} \hat{U}(k_1)\hat{U}(k_2)\exp[i\,\tfrac{2\pi}{L}\,r(k_1+k_2)]\tfrac{1}{2}\left(\frac{k_1}{k_1+k_2} + \frac{k_2}{k_1+k_2}\right)$$

$$(1-\delta(k_1+k_2))\ (1-\delta(k_1))(1-\delta(k_2)). \tag{46}$$

$$K_2'(r) = \tfrac{1}{2}\,L^{-1} \sum_{k_1}\sum_{k_2} \hat{U}(k_1)\hat{U}(k_2)\exp[i\,\tfrac{2\pi}{L}\,r(k_1+k_2)]$$

$$(1-\delta(k_1)-\delta(k_2)-\delta(k_1+k_2)+2\delta(k_1)\delta(k_2)) \tag{47}$$

$$K_2'(r) = \frac{1}{2}\,[U(r)-\overline{U(r)}]^2 - \frac{1}{2}\,\overline{[U(r)-\overline{U(r)}]^2} \tag{48}$$

The symmetrization of the expression for $K_n'(r)$ is clearly vital to showing that $K_N(r) = K_N'(r)$. It has been shown that $K_1(r) = K_1'(r)$ and $K_2(r) = K_2'(r)$. It will also be shown that the assumption that $K_N(r) = K_N'(r)$ implies that $K_{N+1}(r) = K_{N+1}'(r)$, which will complete the proof that $K_N(r) = K_N'(r)$. Three Lemmas will be used in this proof, and they are presented next.

Lemma 1. Note, that in terms of Fourier expansions,

$$[U(r)-\overline{U(r)}]^N = L^{-\frac{N}{2}} \prod_{i=1}^{N} \sum_{k_i} \hat{U}(k_i)\, \exp[i\, \tfrac{2\pi}{L}\, rk_i](1-\delta(k_i)) \tag{49}$$

$$\overline{[U(r)-\overline{U(r)}]^\ell} = L^{-\frac{\ell}{2}}\, \delta(\sum_{j=1}^{\ell} k_j) \prod_{i=1}^{\ell} \sum_{k_i} \hat{U}(k_i) \exp[i\, \tfrac{2\pi}{L}\, rk_i](1-\delta(k_i)). \tag{50}$$

The truth of Eq. (49) is obvious. The truth of Eq. (50) is just as obvious if one notices that the product of the Fourier exponentials, $\exp(i\, \frac{2\pi}{L}\, rk_i)$ is always one, because of $\delta(\sum_{j=1}^{\ell} k_j)$. This term is included so that $K_N(r)$ in Eq. (39) may be written using only a single product symbol in the following way,

$$K_N(r) = \frac{(-1)^N}{N!} \sum_{m=o}^{N} \frac{N!}{(N-m)!m!} L^{-\frac{N}{2}} \prod_{i=1}^{N} \sum_{k_i} \hat{U}(k_i) \exp[i\, \frac{2\pi}{L}\, rk_i](1-\delta(k_i))$$

$$\sum_{\substack{\text{Partitions} \\ \text{of } m}} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{(-1)^p p!m!}{m_\ell!\ell!^{m_\ell}} \delta(\sum_{j=1}^{\ell} k_{[\ell(r-1)+j]} \tag{51}$$

Lemma 2.

$$\sum_{p\varepsilon s_N} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{\delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})k_{p(N)}}{m_\ell!\ell!^{m_\ell}[\sum_{j=1}^{N} k_{p(j)}]} =$$

$$\frac{1}{N-m} \sum_{p\varepsilon s_N} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{\delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})}{m_\ell!\ell!^{m_\ell}} \tag{52}$$

In Eq. (52), S_n is the set of all permutations among the integers, 1, 2, ..., n and $m = \sum_{\ell=1}^{m} \ell m_\ell$. This lemma is proved in Appendix II.

Lemma 3.

$$-\sum_{m=o}^{N} (-1)^{N+1} \overline{[U(r)-\overline{U(r)}]^{N+1-m}} \sum_{\substack{\text{Partitions} \\ \text{of } m}} \prod_{\ell=1}^{m} \frac{(-1)^p p!}{(N+1-m)!m_\ell!\ell!^{m_\ell}}$$

$$[\overline{(U(r)-\overline{U(r)})^\ell}]^{m_\ell} = (-1)^{N+1} \sum_{\substack{\text{Partitions} \\ \text{of } N+1}} \prod_{\ell=1}^{N+1} \frac{(-1)^{p'}p'!}{m'_\ell!\ell'!^{m'_\ell}}$$

$$[\overline{(U(r)-\overline{U(r)})^{\ell'}}]^{m'_\ell} \tag{53}$$

This lemma is proved in Appendix II.

Theorem 2.

$$K_N(r) = K_N'(r) \tag{54}$$

Proof:

It has been shown that $K_N(r) = K_N'(r)$ for N=1 and N=2. It is assumed that $K_N(r) = K_N'(r)$. $K'_{N+1}(r)$ may then be written as

$$K'_{N+1}(r) = (-1)^N L^{-\frac{N}{2}} \prod_{i=1}^{N} \sum_{k_i} \hat{U}(k_i)\exp[i\,\frac{2\pi}{L}\,rk_i]\,\frac{k_i}{\sum_{j=1}^{i} k_j}\,(1-\delta(k_i))$$

$$(1-\delta(\sum_{j=1}^{i} k_j))\{-L^{-1/2} \sum_{k_{N+1}} \hat{U}(k_{N+1})\exp[i\,\frac{2\pi}{L}\,rk_{N+1}]$$

$$\frac{k_{N+1}}{\sum_{j=1}^{N+1} k_j}\,(1-\delta(k_{N+1}))(1-\delta(\sum_{j=1}^{N+1} k_j))\}. \tag{55}$$

Using the assumption, $K_N(r) = K_N'(r)$, and Lemma 1, one has

$$K'_{N+1}(r) = (-1)^{N+1} L^{-\frac{N+1}{2}} \prod_{i=1}^{N+1} \sum_{k_i} \hat{U}(k_i)\exp[i\,\frac{2\pi}{L}\,rk_i](1-\delta(k_i))$$

$$\frac{(1-\delta(\sum_{j=1}^{N+1} k_j))k_{N+1}}{\sum_{j=1}^{N+1} k_j} \sum_{m=o}^{N} \sum_{\substack{\text{Partitions}\\ \text{of } m}} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell}$$

$$\frac{(-1)^p p!}{(N-m)!m_\ell!(\ell!)^{m_\ell}} \delta(\sum_{j=1}^{\ell} k_{[\ell(r-1)+j]}). \tag{56}$$

Symmetrizing among the k_i, using $\frac{1}{(N+1)!} \sum_{p\varepsilon S_{N+1}}$, and using Lemma 2, one has

$$K'_{N+1}(r) = (-1)^{N+1} L^{-\frac{N+1}{2}} \prod_{i=1}^{N+1} \sum_{k_i} \hat{U}(k_i) \exp[i \tfrac{2\pi}{L} rk_i](1-\delta(k_i))$$

$$\{\frac{1}{(N+1)!} \sum_{p\varepsilon S_{N+1}} [1-\delta(\sum_{j=1}^{N+1} k_{p(j)})] \sum_{m=o}^{N} \sum_{\substack{\text{Partitions} \\ \text{of } m}} \tag{57}$$

$$\prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{(-1)^p p!}{(N+1-m)!m_\ell!(\ell!)^{m_\ell}} \delta(\sum_{j=1}^{\ell} k_{p[\ell(r-1)+j]})\}.$$

Now, if one sums over Fourier indices and rewrites $K'_{n+1}(r)$ in r space, the permutations have no effect upon the form and one obtains

$$K'_{N+1}(r) = \frac{(-1)^{N+1}}{(N+1)!} \sum_{p\varepsilon S_{N+1}} \sum_{m=o}^{N} \{[U(r)-\overline{U(r)}]^{N+1-m} -$$

$$\overline{[U(r)-\overline{U(r)}]^{N+1-m}}\} \sum_{\substack{\text{Partitions} \\ \text{of } m}} \prod_{\ell=1}^{m} \frac{(-1)^p p!}{(N+1-m)!m_\ell!(\ell!)^{m_\ell}} \tag{58}$$

$$[\overline{(U(r)-\overline{U(r)})^\ell}]^{m_\ell}.$$

Since $\frac{1}{(N+1)!} \sum_{p \varepsilon S_{N+1}}$ sums the same expression (N+1)! times and then divides by (N+1)!, one may replace it with 1. Then using Lemma 3, one obtains

$$K'_{N+1}(r) = (-1)^{N+1} \sum_{m=o}^{N} (U(r)-\overline{U(r)})^{N+1-m} \sum_{\substack{\text{Partitions}\\ \text{of } m}} \prod_{\ell=1}^{m}$$

$$\frac{(-1)^p p!}{(N+1-m)!\, m_\ell!\, (\ell!)^{m_\ell}} [\overline{(U(r)-\overline{U(r)})^\ell}]^{m_\ell} (-1)^{N+1} \sum_{\substack{\text{Partitions}\\ \text{of } N+1}} \prod_{k=1}^{N+1}$$

$$\frac{(-1)^p p!}{m_k!\,(k!)^{m_k}} [\overline{(U(r)-\overline{U(r)})^k}]^{m_k} \tag{59}$$

or

$$K'_{N+1}(r) = K_{N+1}(r). \tag{60}$$

This completes the proof of Eq. (54) and thus the fact that the series, term (37), is a Boltzmann distribution.

It has been shown that the long time limit of the contracted, spatial distribution is equal to a Boltzmann distribution plus corrections. The Boltzmann distribution depends only upon the normalization of the initial spatial distribution and does not depend upon any of the details of that distribution. This corresponds with the behavior that one would expect of a macroscopic description of a real gas. In that case one expects the gas to go to a final equilibrium state which depends on the amount of gas present but not on the initial distribution of the gas. The system which is being studied here, however, has correction terms. These correction terms depend on both the normalization and on the details of the initial spatial distribution. One would expect these corrections to be related to the conservation of energy, and thus depend on the average, initial potential energy. One might guess that these corrections are such that the long time limit of the contracted, spatial distribution is a Boltzmann distribution in terms of a new parameter, β', which is an energy conserving renormalization of β. In order to examine this possibility, the first four terms of Eq. (27), the series representation of R(r,t), are calculated in the long time limit.

Is the Asymptotic, Spatial Distribution a Boltzmann Distribution in Terms of a Renormalized Temperature Parameter?

Calculation of the Terms of Eq. (27). From the results of Chapter II, Equations (14) through (20), it is clear that

$$\lim_{t\to\infty} R_o = L^{-1}. \tag{61}$$

The next term may be written as

$$\lim_{t\to\infty} R_1 = \lim_{t\to\infty} \int_{-\infty}^{\infty} dp \int_{o}^{t} ds_1 \exp[(s_1-t)\frac{p}{m}\frac{\partial}{\partial r}]\sum_{k_1} L^{-1/2}\hat{U}(k_1)i\,\frac{2\pi}{L}\,k_1$$

$$\exp[i\,\frac{2\pi}{L}\,rk_1]\,\frac{\partial}{\partial p}\,\exp[-\,\frac{s_1 p}{m}\,\frac{\partial}{\partial r}]\,\sum_{N} L^{-1/2}\,C_N$$

$$\exp[i\,\frac{2\pi}{L}\,rN]\;W_m(p) \tag{62}$$

and simplified to

$$\lim_{t\to\infty} R_1 = \sum_{k_1}\sum_{N} L^{-1}C_N\hat{U}(k_1)\exp[i\alpha mr(k_1+N)]$$

$$[NI^{(1)}(k_1,N) - \beta I^{(0)}(N) + \beta I^{(0)}(k_1+N)] \tag{63}$$

where

$$I^{(0)}(N) = \lim_{t\to\infty}\int_{-\infty}^{\infty} dp\;\exp[-i\alpha ptN]W_m(p) = \delta(N) \tag{64}$$

and

$$I^{(1)}(N,k_1) = \lim_{t\to\infty}\int_{-\infty}^{\infty} dpW_m(p)\int_{o}^{t} ds_1 s_1 m\alpha^2 k_1 \exp[i\alpha p(s_1 k_1 - t[k_1+N])]. \tag{65}$$

It is shown in Appendix III that

$$I^{(1)}(N,k_1) = \frac{\beta}{k_1}\,[\delta(N+k_1)-\delta(N)][1-\delta(k_1)] \tag{66}$$

and thus

$$NI^{(1)}(N,k_1) = \frac{\beta N}{k_1}\,(1-\delta(N))(1-\delta(k_1))(\delta(N+k_1)-\delta(N)). \tag{67}$$

It is important to include the exclusion, $(1-\delta(N))$, because the contribution to $I^{(1)}(N,k_1)$, for the case N=0, is zero. From Eq. (64) and Eq. (63) one has

$$-\beta I^{(0)}(N) + \beta I^{(0)}(k_1+N) = -\beta[\delta(N) - \delta(k_1+N)]. \tag{68}$$

Combining terms one may write Eq. (63) as

$$\lim_{t\to\infty} R_1 = \sum_{k_1}\sum_{N} L^{-1}C_N\hat{U}(k_1)\exp[i\alpha mr(k_1+N)](-\beta\delta(N))(1-\delta(k_1)) \tag{69}$$

or

$$\lim_{t\to\infty} R_1 = -L^{-1}\beta[U(r)-\overline{U(r)}]. \tag{70}$$

The next term, $\lim\limits_{t\to\infty} R_2$, is

$$\lim_{t\to\infty} R_2 = \lim_{t\to\infty}\int_{-\infty}^{\infty} dp \int_{o}^{t} ds_1 \int_{o}^{s_1} ds_2\, \exp[(s_1-t)\,\frac{p}{m}\frac{\partial}{\partial r}]\,\frac{dU(r)}{dr}\frac{\partial}{\partial p}$$

$$\exp[(s_2-s_1)\,\frac{p}{m}\frac{\partial}{\partial r}]\,\frac{dU(r)}{dr}\frac{\partial}{\partial p}\,\exp[-s_2\,\frac{p}{m}\frac{\partial}{\partial r}]R(r,o)W_m(p). \tag{71}$$

Equation (71) may be shown to simplify to

$$\lim_{t\to\infty} R_2 = \sum_{k_1} \sum_{k_2} \sum_{N} L^{-3/2}\hat{U}(k_1)\hat{U}(k_2)C_N \exp[i\alpha mr(k_1+k_2+N)]I \qquad (72)$$

where

$$I = \lim_{t\to\infty} \int_{-\infty}^{\infty} dp \int_{o}^{t} ds_1 \int_{o}^{s_1} ds_2[(s_1m\alpha^2Nk_1-(s_2-s_1)m\alpha^2k_1k_2-i\alpha pk_1\beta) \qquad (73)$$

$$(s_2m\alpha^2Nk_2-\beta \frac{d}{ds_2}) + \beta m\alpha^2k_1k_2]\exp[i\alpha p\{s_1k_1+s_2k_2-t(k_1+k_2+N)\}]W_m(p).$$

I may be shown to be

$$\begin{aligned} I &= NI^{(2)}(N,k_1,k_2) \\ &+ \beta N(\frac{k_2}{k_1+k_2} - \frac{k_1}{k_1+k_2})I^{(1)}(N,(k_1+k_2)) \\ &+ \beta(N+k_2)I^{(1)}(k_2+N,k_1)-\beta NI^{(1)}(N,k_2) \\ &+ \beta^2I^{(0)}(N) - \beta^2I^{(0)}(k_2+N) \\ &- \beta^2 \frac{k_2}{k_1+k_2} I^{(0)}(N) + \beta^2 \frac{k_2}{k_1+k_2} I^{(0)}(k_1+k_2+N) \end{aligned} \qquad (74)$$

where

$$I^{(2)}(N,k_1,k_2) \equiv \lim_{t\to\infty} \int_{-\infty}^{\infty} dp \int_{o}^{t} ds_1 \int_{o}^{s_1} ds_2 - S_2{}^2 k_1 k_2{}^2 m^2 \alpha^4$$

$$\exp[i\alpha p[s_1k_1+s_2k_2-t(k_1+k_2+N)]]W_m(p)$$

$$+ \lim_{t\to\infty} \int_{-\infty}^{\infty} dp \int_{o}^{t} ds_1 \int_{o}^{s_1} ds_2 \; k_1k_2(k_2+N)s_1s_2m^2\alpha^4$$

$$\exp[i\alpha p[s_1k_1+s_2k_2-t(k_1+k_2+N)]]W_m(p). \tag{75}$$

It is shown in Appendix III that

$$I^{(2)}(N,k_1,k_2) = \beta^2(1-\delta(k_1))(1-\delta(k_2))\{-\delta(N)\frac{2k_1{}^2+3k_1k_2}{3k_2(k_1+k_2)^2}$$

$$+ \delta(k_2+N)\frac{2}{3k_2} - \delta(k_1+k_2+N)\frac{k_2}{(k_1+k_2)^2}\}. \tag{76}$$

Using Equations (76), (66) and (64), Eq. (74) may be rewritten,

$$I = \beta^2 \{-\frac{2}{3}\delta(k_2+N) + \delta(k_1+k_2+N)\frac{k_2}{k_1+k_2}\}$$

$$- \beta^2 \frac{Nk_1}{(k_1+k_2)^2}\{[\delta(k_1+k_2+N)-\delta(N)](1-\delta(N))(1-\delta(k_1))\}$$

$$+ \beta^2 \frac{Nk_2}{(k_1+k_2)^2}\{[\delta(k_1+k_2+N)-\delta(N)](1-\delta(N))(1-\delta(k_2))\}$$

$$+ \beta^2 \frac{(N+k_2)}{k_1} \{[\delta(k_1+k_2+N)-\delta(k_2+N)](1-\delta(k_1))(1-\delta(N+k_2))\}$$

$$- \beta^2 \frac{N}{k_2} \{[\delta(k_2+N)-\delta(N)](1-\delta(N))(1-\delta(k_2))\}$$

$$+ \beta^2\delta(N)-\beta^2\delta(k_2+N)-\beta^2 \frac{k_2}{k_1+k_2} \delta(N)+\beta^2 \frac{k_2}{k_1+k_2} \delta(k_1+k_2+N). \quad (77)$$

Using Eq. (77), and symmetrizing with respect to k_1 and k_2, Eq. (72) may be rewritten as

$$\lim_{t\to\infty} R_2 = \frac{1}{2} \beta^2 L^{-1} [U(r)-\overline{U(r)}]^2 - \frac{1}{2} \beta^2 L^{-1} \overline{[U(r)-\overline{U(r)}]^2}$$

$$- \frac{2}{3} \beta^2 L^{-1} [U(r)-\overline{U(r)}] \overline{\overline{(U(r)-\overline{U(r)})}} \quad (78)$$

where

$$\overline{g(r)} \equiv \int_o^L R(r,o)g(r)dr \quad \text{for any} \quad g(r). \quad (79)$$

The final term which will be considered, $\lim_{t\to\infty} R_3$, may be obtained by a similar but much longer calculation.

Renormalization Procedure. In order to compare the long time limit of the contracted, spatial distribution with a Boltzmann distribution, containing a renormalized temperature parameter, the series expansion of both is written in the following table.

In calculating a renormalized temperature parameter,

Table 1. Series Comparison

Order of β	$\frac{1}{Q'}\exp[-\beta' U(r)]$	$R(r,\infty)$
0	L^{-1}	L^{-1}
1	$-\beta' L^{-1}(U(r)-\overline{U(r)})$	$-\beta L^{-1}(U(r)-\overline{U(r)})$
2	$+\frac{1}{2}\beta'^2 L^{-1}[(U(r)-\overline{U(r)})^2$ $-\overline{(U(r)-\overline{U(r)})^2}]$	$+\frac{1}{2}\beta^2 L^{-1}[(U(r)-\overline{U(r)})^2$ $-\overline{(U(r)-\overline{U(r)})^2}]$ $-\frac{2}{3}\beta^2 L^{-1}(U(r)-\overline{U(r)})\overline{\overline{(U(r)-\overline{U(r)})}}$
3	$-\frac{1}{6}\beta'^3 L^{-1}[(U(r)-\overline{U(r)})^3$ $-3(U(r)-\overline{U(r)})\overline{(U(r)-\overline{U(r)})^2}$ $-\overline{(U(r)-\overline{U(r)})^3}]$	$-\frac{1}{6}\beta^3 L^{-1}[(U(r)-\overline{U(r)})^3$ $-3(U(r)-\overline{U(r)})\overline{(U(r)-\overline{U(r)})^2}$ $-\overline{(U(r)-\overline{U(r)})^3}]$ $-\frac{2}{5}\beta^3 L^{-1}[(U(r)-\overline{U(r)})\{\overline{\overline{(U(r)-\overline{U(r)})^2}}$ $-\overline{(U(r)-\overline{U(r)})^2}\}]$ $-\frac{2}{3}\beta^3 L^{-1}[(U(r)-\overline{U(r)}\overline{(U(r)-\overline{U(r)})^2}]$ $+\frac{3}{5}\beta^3 L^{-1}\overline{\overline{(U(r)-\overline{U(r)})}}\{(U(r)-\overline{U(r)})^2$ $-\overline{(U(r)-\overline{U(r)})^2}\}$

β', it is assumed that

$$\beta' = \sum_{N=0}^{\infty} a_N \beta^N. \tag{80}$$

Comparing the left and right columns, one quickly sees that

$$a_0 = 0 \quad \text{and} \quad a_1 = 1. \tag{81}$$

A little calculation yields

$$a_2 = \frac{2}{3} \overline{\overline{(U(r) - \overline{U(r)})}}. \tag{82}$$

Thus, to second order, β' may be written as

$$\beta' = \beta + \frac{2}{3} \overline{\overline{(U(r)-\overline{U(r)})}} \beta^2 + \ldots. \tag{83}$$

The renormalization procedure is working! The coefficient 2/3 raises some questions, however. The equation for the conservation of energy may be written as

$$\frac{1}{2} \beta'^{-1} + \int_0^L \frac{1}{Q'} \exp[-\beta' U(r)] U(r) dr = \frac{1}{2} \beta^{-1} + \overline{U(r)}. \tag{84}$$

If one expands the Boltzmann distribution as a power series using Theorem 1, one may show

$$\beta = \beta' + \beta(2\beta'\overline{\overline{(U(r)-\overline{U(r)})}} + 2\beta'^2\overline{(U(r)-\overline{U(r)})^2} \tag{85}$$

$$+ \ldots \text{ higher order terms in } \beta').$$

Using Eq. (80), this equation may be rearranged to yield

$$\beta' = \beta - 2\overline{\overline{(U(r)-\overline{U(r)})}}\beta^2 + \ldots \text{ higher order terms in } \beta. \tag{86}$$

Not only is the coefficient which was found in Eq. (82) the wrong magnitude, but it is also the wrong sign. Equation (83) implies that a gas would cool as it "fell into a potential well." This very non-physical result prompts a careful reexamination of the interpretation of β'. This parameter has been interpreted as a kinetic energy temperature parameter of the type found in a Maxwellian momentum distribution. Although the initial momentum distribution is Maxwellian, the potential perturbs this distribution and there is no mechanism for returning the momentum distribution to a Maxwellian distribution. Without a Maxwellian momentum distribution, how can one discuss a kinetic energy temperature? Thus, the contracted, spatial distribution may approach a Boltzmann distribution, but the parameter, β', should not be interpreted as a kinetic energy temperature parameter.

Notice that the renormalization is related to the conservation of energy. The expression, $\overline{\overline{(U(r) - \overline{U(r)})}}$, is the difference between the average initial potential energy and the average potential energy for a uniform distribution. Continuing with the renormalization procedure, further calculation leads to the coefficient of the third order term,

$$
\begin{aligned}
a_3 = {} & \frac{2}{5}\,\overline{\overline{(U(r)-\overline{U(r)})^2}} - \frac{4}{15}\,\overline{(U(r)-\overline{U(r)})^2} \\
& + \frac{1}{15}\,(U(r)-\overline{U(r)})\;\overline{\overline{(U(r)-\overline{U(r)})}} \\
& + \frac{1}{15}\,(U(r)-\overline{U(r)})^{-1}\;\overline{(U(r)-\overline{U(r)})^2}\;\overline{\overline{(U(r)-\overline{U(r)})}}\,. \qquad (87)
\end{aligned}
$$

The third and fourth terms in a_3 are functions of r, and therefore violate the implicit assumption that β' is not a function of r. Therefore the contracted, spatial distribution does not approach a Boltzmann distribution even though the equilibrium distribution which it does approach has a strong Boltzmann character as demonstrated in Theorem 2.

Boltzmann → Boltzmann

In this section a check of the internal consistency of the previous calculation is made. This check is possible because there exists a distribution which is unchanged by the action of the Liouville operator for this system. That distribution is the Maxwell-Boltzmann distribution, $\frac{1}{Q}\exp[-\beta U(r)]W_m(p)$. Therefore, if the initial distribution is specified to be a Maxwell-Boltzmann distribution, then the contracted, spatial distribution would remain a Boltzmann distribution for all time. In order to be self consistent, the expression which was derived for the long time limit of the contracted, spatial distribution should be the same Boltzmann distribution, under these initial conditions. It has already been shown that the long time limit of the contracted, spatial distribution is the same Boltzmann distribution plus correction terms. These correction terms are non-zero but they are shown to sum to zero in this special case. The correction terms are a power series in β which starts at the β^2 order. If the initial distribution is a Maxwell-Boltzmann distribution, then the coefficients of the power series are functions of β. In order to see this, the long time limit of the contracted, spatial distribution is written out in terms of the Boltzmann distribution and the correction terms.

$$\begin{aligned}
\lim_{t\to\infty} R(r,t) = {} & Q^{-1}\exp[-\beta U(r)] - \tfrac{2}{3}\,\beta^2 L^{-1}(U(r)-\overline{U(r)})\,\overline{\overline{(U(r)-\overline{U(r)})}} \\
& - \tfrac{2}{5}\,\beta^3 L^{-1}(U(r)-\overline{U(r)})\{\overline{\overline{(U(r)-\overline{U(r)})^2}} - \overline{(U(r)-\overline{U(r)})^2}\} \\
& - \tfrac{2}{3}\,\beta^3 L^{-1}[(U(r)-\overline{U(r)})\ \overline{(U(r)-\overline{U(r)})^2}] \\
& + \tfrac{3}{5}\,\beta^3 L^{-1}\ \overline{\overline{(U(r)-\overline{U(r)})}}\ \{(U(r)-\overline{U(r)})^2 - \overline{(U(r)-\overline{U(r)})^2}\} \\
& + \ldots.
\end{aligned}$$

The initial average found in the first correction term is

$$\overline{\overline{(U(r)-\overline{U(r)})}} = \int_0^L (U(r)-\overline{U(r)})[\int_0^L \exp[-\beta U(r')]dr']^{-1}\exp[-\beta U(r)]dr. \tag{89}$$

Expanding in terms of β by means of Theorem I, Eq. (38), one has

$$\overline{\overline{(U(r)-\overline{U(r)})}} = -\overline{U(r)} + L^{-1}\int_0^L U(r)dr - L^{-1}\beta\int_0^L U(r)(U(r)-\overline{U(r)})dr + \ldots . \tag{90}$$

The first correction term is now written as

$$\frac{2}{3}\beta^3 L^{-1}(U(r)-\overline{U(r)})\overline{(U(r)-\overline{U(r)})^2} + \text{higher order terms in } \beta. \tag{91}$$

One sees that there is no contribution, from the first correction term, to order β^2. One also notices that the contribution which the first correction term makes at order β^3 exactly cancels the third correction term in Eq. (88). It remains to analyze the second and fourth correction terms. If they are expanded in a power series in β, as was done with the first correction term, one readily sees that these two terms make no contribution up to order β^3. Therefore it has been shown, that to the order calculated, the correction terms sum and cancel in this special case, yielding

$$\lim_{t \to \infty} R(r,t) = Q^{-1}\exp(-\beta U(r)). \tag{92}$$

This calculation verifies that the formalism used in this section is correct. It has been shown that the long time limit of the contracted, spatial distribution is not a Boltzmann distribution even though there is an approach to equilibrium. The equilibrium which is approached has correction terms which conserve energy and also depend on higher "moments" of the potential.

CHAPTER IV

IDEAL GAS IN THE PRESENCE OF AN EXTERNAL POTENTIAL, AND IMMERSED IN A BROWNIAN FLUID

In this chapter an attempt will be made to find a system which has a contracted, spatial distribution which approaches a Boltzmann distribution. In the last chapter, it was found that an ideal gas acted upon by conservative forces tended in that direction, but the conservation of energy prevented it. In this chapter, there is a "Brownian" fluid present in which the ideal gas is immersed, which continually returns the momentum distribution to a Maxwellian distribution as the distribution is perturbed. Because of the ability of the gas to exchange energy with the "Brownian" fluid, one would expect the phase space distribution to relax to a Maxwell-Boltzmann distribution.

This "Brownian" fluid is considered to be a fluid of particles which make their presence known only through a stochastic force, $\tilde{F}(t)$ and a damping coefficient, α, which is intimately related to $\tilde{F}(t)$. The results of this analysis have many physical applications. Kramers[3] used the results of a calculation for this system in the high viscosity limit to find chemical reaction rates. If the gas is assumed to be composed of noninteracting ions, the conservative force which acts is assumed to be a constant electric field, and finally the system is open instead of closed. Then the problem is that of ions in a drift tube such as might be found in a mobility experiment.

Another possible application is to the time evolution of molecules in solution. One might consider, for example, an enzyme and its associated substrate in aqueous solution. These macromolecules exist as ions and they will interact by means of their charge distributions. When they come into contact and reach the proper relative orientation, bonding will occur. It is possible that the charge distributions of these molecules aid in the establishment of this proper orientation. Such a question might be answered by means of the techniques which are developed in this section.

The time evolution of this system is given by its Liouville equation

$$\frac{\partial}{\partial t} D(r,p,t) = \left(- \frac{p}{m} \frac{\partial}{\partial r} + \frac{dU(r)}{dr} \frac{\partial}{\partial p} - \frac{\partial}{\partial p} \left[- \frac{\alpha}{m} p+\tilde{F}(t)\right]\right)D(r,p,t) \tag{93}$$

where the stochastic properties of $\tilde{F}(t)$ are those of Brownian motion:

$$\langle\tilde{F}(t)\rangle = 0 \quad \text{and} \quad \langle\tilde{F}(t)\tilde{F}(s)\rangle = 2 \frac{\alpha}{\beta} \delta(t-s). \tag{94}$$

Here $\delta(t-s)$ is a Dirac delta. The damping parameter, α, from Eq. (93), is found in the autocorrelation formula for $\tilde{F}(t)$ and that is the Einstein relation which connects α and $\tilde{F}(t)$.[9] The function of interest in this case is not the phase space distribution, but the stochastic average of the phase space distribution. The time evolution for this distribution is given by a Fokker-Planck type equation:

$$\frac{\partial}{\partial t} \langle D(r,p,t)\rangle = [- \frac{p}{m}\frac{\partial}{\partial r} + \frac{dU(r)}{dr}\frac{\partial}{\partial p} + \alpha\frac{\partial}{\partial p}(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p})] \langle D(r,p,t)\rangle. \quad (95)$$

This equation is derived from the Liouville equation in Appendix IV. The solution to Eq. (95) is given by

$$\langle D(r,p,t)\rangle = \exp[- \frac{pt}{m}\frac{\partial}{\partial r} + t\,\frac{dU(r)}{dr}\frac{\partial}{\partial p} + \alpha t\,\frac{\partial}{\partial p}(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p})] D(r,p,o). \quad (96)$$

Equation (95) is a caricature of the Boltzmann equation which can be written

$$\frac{\partial}{\partial t} f(r,p,t) = (- \frac{p}{m}\frac{\partial}{\partial r} + \frac{dU}{dr}\frac{\partial}{\partial p})f(r,p,t) + \mathrm{coll}(f(r,p,t)) \quad (97)$$

in which coll(f(r,p,t)) signifies the non-linear integral operator for collisions in the Boltzmann equation. This operation is known to drive the momentum distribution towards a Maxwellian form*[10] so that

$$f(r,p,t) \underset{t\to\infty}{\to} A(r)W_m(p) \tag{98}$$

where $W_m(p)$ is the Maxwellian momentum distribution. Asymptotically, coll(f(r,p,t)) = 0 and $\frac{\partial}{\partial t} f(r,p,t) = 0$ so that

$$\left(-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU}{dr}\frac{\partial}{\partial p}\right) A(r)W_m(p) = 0 \tag{99}$$

must hold and this implies that $A(r) = C\exp[-\beta U(r)]$ where C is an arbitrary constant. In equation (95) the operator $\alpha \frac{\partial}{\partial p}\left(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p}\right)$ drives $\langle D(r,p,t)\rangle$ to the asymptotic form

$$\langle D(r,p,t)\rangle \underset{t\to\infty}{\to} A(r)W_m(p) \tag{100}$$

with $\frac{\partial}{\partial t}\langle D(r,p,t)\rangle = 0$. Therefore, again $A(r) = C\exp[-\beta U(r)]$ because both the Boltzmann equation and equation (95) contain the same streaming operator, $-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU}{dr}\frac{\partial}{\partial p}$. In the following, the details of the dynamics of the approach to the Boltzmann distribution are examined. Operator techniques are used to

*This argument for the Boltzmann equation appears on page 80 of Lectures in Statistical Mechanics, G. E. Uhlenbeck and G. W. Ford (Amer. Math. Soc., 1963).

show that the series representation of the Boltzmann distribution given by equation (37) is obtained as the dynamical asymptotic limit of equation (96).

Simplification of the Propagation Operator

In the process of simplifying the exponential propagation operator, it will prove convenient to define several operators.

$$A = \frac{p}{m}\frac{\partial}{\partial r} \qquad B = \alpha \frac{\partial}{\partial p}\left(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p}\right)$$
$$C = 2\beta^{-1}\frac{\partial^2}{\partial p \partial r} \qquad D = -\frac{2}{\beta m}\frac{\partial^2}{\partial r^2} \tag{101}$$

The following relations will also be useful:

$$[A,B] = -\frac{\alpha}{m}(A+C)$$

$$[B,C] = -\frac{\alpha}{m}C$$

$$[A,C] = D$$
$$[A,D] = [B,D] = [C,D] = 0 \,. \tag{102}$$

Using the disentanglement theorem, Eq. (24), one may simplify Eq. (96).

$$\langle D(r,p,t)\rangle = \exp[-t(A-B)] \underset{\leftarrow}{T} \exp[\int_o^t \exp[s(A-B)]$$

$$\frac{dU(r)}{dr} \frac{\partial}{\partial p} \exp[-s(A-B)]ds]\ D(r,p,o) \tag{103}$$

This may be written in series form as

$$\langle D(r,p,t)\rangle = D_o + \sum_{N=1}^{\infty} D_N \tag{104}$$

where

$$D_o = \exp[-t(A-B)]\ D(r,p,o) \tag{105}$$

and

$$D_N = \int_o^t ds_1 \int_o^{s_1} ds_2 \ldots \int_o^{s_{N-1}} ds_N \exp[-(t-s_1)(A-B)]\frac{dU(r)}{r} \frac{\partial}{\partial p}$$

$$\exp[-(s_1-s_2)(A-B)] \ldots \frac{dU(r)}{dr} \frac{\partial}{\partial p} \exp[-s_N(A-B)]\ D(r,p,o). \tag{106}$$

Operators of the form, $\exp(-t(A-B))$, appear several times in Eq. (103) and Eq. (106) and these operators will now be simplified. Using the disentanglement theorem one obtains

$$\exp[-t(A-B)] = \exp[-tA] \underset{\leftarrow}{T} \exp[\int_o^t \exp[sA]B \exp[-sA]ds]. \tag{107}$$

The integrand in Eq. (107) will be simplified.

$$\exp[sA]B\ \exp[-sA] = B + \sum_{N=1}^{\infty} \frac{s^N}{N!} [A,\cdot]^N B \tag{108}$$

The operator, $[A,\cdot]$, in Eq. (108) is a commutator operator. Its action is illustrated in the following example:

$$[A,\cdot]^3 B = A^3B - 3A^2BA + 3ABA^2 - BA^3. \tag{109}$$

Using the commutation relations in equations (102) through (105), one may write Eq. (108), which truncates automatically after N = 2, as

$$\exp[sA]B\ \exp[-sA] = B - \frac{s\alpha}{m}(A+C) - \frac{s}{2}\left(\frac{s\alpha}{m}\right)D \tag{110}$$

and therefore Eq. (103) may be rewritten as

$$\exp[-t(A-B)] = \exp[-tA]\underset{\leftarrow}{T}\ \exp[\int_0^t B - \frac{s\alpha}{m}(A+C) - \frac{s}{2}\frac{s\alpha}{m} D\, ds]. \tag{111}$$

One may again use Eq. (102) and the disentanglement theorem to further simplify the integrand.

$$\exp[-t(A-B)] = \exp[-tA]\exp[-\frac{1}{6}t^3\frac{\alpha}{m}D]\exp[tB] \tag{112}$$

$$\underset{\leftarrow}{T}\ \exp[-\int_0^t \exp[-sB]\frac{s\alpha}{m}(A+C)\exp[sB]ds]$$

$$\exp[-sB]\,\frac{s\alpha}{m}\,(A+C)\exp[sB] = \frac{s\alpha}{m}\,(A+C) + \frac{s\alpha}{m}\sum_{N=1}^{\infty}\frac{(-s)^N}{N!}\,[B,\cdot]^N(A+C) \tag{113}$$

$$[B,\cdot]^N(A+C) = \begin{cases} (\frac{\alpha}{m})^N\ A \text{ if } N \text{ is odd} \\ (\frac{\alpha}{m})^N\ (A+C) \text{ if } N \text{ is even} \end{cases} \tag{114}$$

$$\exp[-sB]\,\frac{s\alpha}{m}\,(A+C)\exp[sB] = \frac{s\alpha}{m}\,\exp[-\frac{s\alpha}{m}]A + \frac{s\alpha}{m}\,\cosh[\frac{s\alpha}{m}]C \tag{115}$$

Thus one obtains

$$\exp[-t(A-B)] = \exp[-tA]\ \exp[-\frac{1}{6}\,t^3\,\frac{\alpha}{m}\,D]\ \exp[tB] \tag{116}$$

$$\underset{\leftarrow}{T}\ \exp[-\int_0^t \frac{s\alpha}{m}\,(\exp[-\frac{s\alpha}{m}]A + \cosh\,[\frac{s\alpha}{m}]C)ds].$$

Now the time propagation operator may be further simplified using a time ordered extension of Glauber's theorem, because of Eq. (102).

Introduction of a Time Ordered Glauber's Theorem

Glauber's theorem is true for two operators which do not commute with each other but do commute with their commutator,

$$\exp[f+g] = \exp[f]\exp[g]\exp[\frac{1}{2}[f,g]]. \tag{117}$$

A time ordered extension of this theorem is proved in

Appendix IV and is found to be

$$\underset{\leftarrow}{T}\exp[\int_0^t ds\; f(s)+g(s)] = \underset{\leftarrow}{T}\exp[\int_0^t ds\; f(s)]\underset{\leftarrow}{T}\exp[\int_0^t ds\; g(s)]$$
$$\underset{\rightarrow}{T}\exp[\int_0^t ds_1 \int_0^{s_1} ds_2\; [g(s_1),f(s_2)]]. \tag{118}$$

If this theorem is applied to Eq. (116), one obtains

$$\exp[-t(A-B)] = \exp[-tA]\;\exp[tB]\;\exp[\phi_1(t)A]$$
$$\exp[\phi_2(t)C]\;\exp[\phi_3(t)D] \tag{119}$$

where

$$\phi_1(t) = -\int_0^t \frac{s\alpha}{m}\exp[-\frac{s\alpha}{m}]ds = t\exp[-\frac{t\alpha}{m}] + \frac{m}{\alpha}[\exp[-\frac{t\alpha}{m}]-1], \tag{120}$$

$$\phi_2(t) = -\int_0^t \frac{s\alpha}{m}\cosh[\frac{s\alpha}{m}]ds = \frac{1}{2}[\phi_1(t) + \phi_1(-t)], \tag{121}$$

$$\phi_3(t) = -\frac{1}{6}t^3\frac{\alpha}{m} - \int_0^t ds' \int_0^{s'} ds'' s' \frac{\alpha}{m}\cosh[\frac{s'\alpha}{m}]s''\frac{\alpha}{m}\exp[-\frac{s''\alpha}{m}], \tag{122}$$

and

$$\phi_3(t) = -\frac{1}{4}[\phi_1(t)\phi_1(-t) + \phi_1^{\,2}(t) + \frac{m}{\alpha}\phi_1(t) - \frac{m}{\alpha}\phi_1(-t)]. \tag{123}$$

The terms in the series, Eq. (104), for the average phase space distribution may now be written out in terms of operators which act consecutively. Several lemmas will be useful in the further analysis of this problem.

Operator Identities

1. $$\frac{\partial \exp[\phi A]}{\partial p} = \frac{\phi}{m}\frac{\partial}{\partial r}\exp[\phi A] \qquad (124)$$

2. $$\exp[tB]\frac{\partial}{\partial p} = \frac{\partial}{\partial p}\exp[-\frac{t\alpha}{m}]\exp[tB] \qquad (125)$$

3. $$\exp[-t(A-B)]\frac{\partial}{\partial p} = (\frac{\partial}{\partial p}\exp[-\frac{t\alpha}{m}] + \frac{t-\phi_1(t)}{m}\frac{\partial}{\partial r})\exp[-t(A-B)] \qquad (126)$$

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4. $$\exp[b\frac{\partial}{\partial p}\frac{\partial}{\partial r}]\exp[ar]W_m[p+q] = \exp[ar]W_m[p+q+ab] \qquad (127)$$

5. $$\exp[tB]W_m(p+a) = W_m[p+a\exp[-\frac{t\alpha}{m}]] \qquad (128)$$

Simple Identities

6a. $$W_m(p)\exp[ap] = W_m[p - \frac{am}{\beta}]\exp[\frac{a^2m}{2\beta}] \qquad (129)$$

6b. $$W_m[p+b]\exp[ap] = W_m[p+b - \frac{am}{\beta}]\exp[\frac{a}{2\beta}(ma-2\beta b)] \qquad (130)$$

Lemmas 1, 2, and 5 are proved in Appendix I. Lemma 3 is an application of Lemma 1 and Lemma 2 to Eq. (119).

Analysis of the Series Expansion of D(r,p,t)

Analysis of D_o

D_o is the first term in the expansion of the average phase space distribution, but it is also the average phase space distribution for a system which consists of a particle acted on by a "Brownian" fluid but not subject to any other forces. It is assumed that the initial conditions are

$$D(r,p,o) = \sum_N L^{-1/2} C_N \exp[i \frac{2\pi}{L} r_N] W_m(p). \qquad (131)$$

D_o may then be written using Eq. (101) and Eq. (119) as

$$D_o = L^{-1/2} \sum_N C_N \exp[i \frac{2\pi}{L} Nr] \exp[\frac{2\pi^2 N^2}{L^2 \beta m} 4\phi_3(t)] \qquad (132)$$

$$\exp[-it \frac{2\pi}{L} N \frac{p}{m}] \exp[tB] \exp[i\phi_1(t) \frac{2\pi}{L} N \frac{p}{m}]$$

$$W_m(p+i\phi_2 \frac{2\pi}{L} N \frac{2}{\beta}),$$

or

$$D_o = L^{-1/2} \sum_N C_N \exp[i \frac{2\pi}{L} rN] W_m(p + \frac{i\,2\pi N}{\beta} \{t +$$

$$(2\phi_2(t) - \phi_1(t)) \exp[-\frac{t\alpha}{m}]\}) \exp[\frac{2\pi^2 N^2}{L^2 \beta m} \phi_4(t)], \qquad (133)$$

where

$$\phi_4(t) = 4\phi_3(t) + 4\phi_2{}^2(t) - (2\phi_2(t)-\phi_1(t))^2$$
$$-t^2-2t(2\phi_2(t)-\phi_1(t))\exp[-\frac{t\alpha}{m}] \tag{134}$$

$$\phi_4(t) = -2\frac{tm}{\alpha} + 2\frac{m^2}{\alpha^2}(1-\exp[-\frac{t\alpha}{m}]). \tag{135}$$

One notes that in Eq. (133)

$$t+(2\phi_2(t)-\phi_1(t))\exp[-\frac{t\alpha}{m}] = \frac{m}{\alpha}(1-\exp[-\frac{t\alpha}{m}]) \tag{136}$$

Since Einstein's relation for the diffusion constant is

$$D = \frac{1}{\beta\alpha}, \tag{137}$$

one may write Eq. (133) as

$$D_o = L^{-1/2}\sum_N C_N \exp[i\frac{2\pi}{L}rN]W_m(p+i\frac{2\pi}{L}Nm(1-\exp[-\frac{t\alpha}{m}])D)$$
$$\exp[-\frac{4\pi^2N^2}{L^2}D(t-\frac{m}{\alpha}+\frac{m}{\alpha}\exp[-\frac{t\alpha}{m}])]. \tag{138}$$

It is clear from the damping behavior of the last exponential that in the long time limit one has

$$\lim_{t\to\infty} D_o = L^{-1} W_m(p). \tag{139}$$

Thus, the average of the phase space distribution for a particle in a "Brownian" fluid but subject to no other forces, relaxes to a distribution which is uniform in position space and Maxwellian in momentum space, as was expected. One should also note that Eq. (138) contains in the last exponential the term $D(t- \frac{m}{\alpha} + \frac{m}{\alpha} \exp[- \frac{t\alpha}{m}]$ which is the diffusive behavior of a particle.

Analysis of D_1

$$D_1 = \{\ \}_1 \int_o^t ds_1 \exp[-(t-s_1)(A-B)]\exp[i \tfrac{2\pi}{L} r\ k_1] \frac{\partial}{\partial p}$$
$$\exp[-s_1(A-B)]\exp[i \tfrac{2\pi}{L} rN]W_m(p) \tag{140}$$

where

$$\{\ \}_1 = \sum_{k_1} \sum_{N} L^{-1} \hat{U}(k_1)C_N\ i \frac{2\pi}{L} k_1. \tag{141}$$

Using the result which was obtained in the analysis of D_o one may rewrite Eq. (140) as

$$D_1 = \{\ \}_1 \int_o^t ds_1 \exp[-(t-s_1)(A-B)] \frac{\partial}{\partial p} \exp[i \tfrac{2\pi}{L} r(N+k_1)]$$
$$W_m(p+f(s_1,N))\ F(s_1,N) \tag{142}$$

where

$$f(s_1,N) = \frac{i2\pi Nm}{L\beta\alpha}\left(1-\exp\left[-\frac{s_1\alpha}{m}\right]\right) \tag{143}$$

and

$$F(s_1,N) = \exp\left[\frac{2\pi^2N^2}{L^2\beta m}\phi_4(s_1)\right]. \tag{144}$$

One may now use Lemma 3, Eq. (126) and obtain

$$D_1 = \{\ \}_1 \exp\left[i\frac{2\pi}{L}r(N+k_1)\right]\int_o^t ds_1\{\ \}_2 \exp\left[-(t-s_1)\frac{i2\pi}{L}(N+k_1)\frac{p}{m}\right]$$
$$\exp[(t-s_1)B]\exp\left[\phi_1(t-s_1)\frac{i2\pi}{L}(N+k_1)\frac{p}{m}\right]\exp\left[\phi_2(t-s_1)i\frac{2\pi}{L\beta}(N+k_1)\right.$$
$$\left.2\frac{\partial}{\partial p}\right]\exp\left[\frac{2\pi^2}{L^2\beta m}4(N+k_1)^2\phi_3(t-s_1)\right]W_m(p+f(s_1,N))F(s_1,N) \tag{145}$$

where

$$\{\ \}_2 = \frac{\partial}{\partial p}\exp\left[-(t-s_1)\frac{\alpha}{m}\right] + \frac{t-s_1-\phi_1(t-s_1)}{m}i\frac{2\pi}{L}(N+k_1). \tag{146}$$

Next D_1 is simplified in a sequence of steps:

$$D_1 = \{\ \}_1 \exp\left[i\frac{2\pi}{L}r(N+k_1)\right]\int_o^t ds_1\{\ \}_2 \exp\left[-(t-s_1)\frac{i2\pi}{L}(N+k_1)\frac{p}{m}\right]$$
$$\exp[(t-s_1)B]\exp\left[\phi_1(t-s_1)i\frac{2\pi}{L}(N+k_1)\frac{p}{m}\right] \tag{147}$$

$$W_m[p+f(s_1,N)+i\ \frac{2\pi}{L\beta}\ (N+k_1)2\phi_2(t-s_1)]\exp[\frac{2\pi^2}{L^2\beta m}\ 4(N+k_1)^2\phi_3(t-s_1)]$$

$$F(s_1,N),$$

$$D_1 = \{\ \}_1\ \exp[i\ \frac{2\pi}{L}\ r(N+k_1)]\int_o^t ds_1\{\ \}_2\ \exp[-(t-s_1)i\ \frac{2\pi}{L}(N+k_1)\frac{p}{m}]$$

$$\exp[(t-s_1)B]W_m[p+f(s_1,N)+i\ \frac{2\pi}{L\beta}\ (N+k_1)(2\phi_2(t-s_1)-\phi_1(t-s_1))]$$

$$\exp[\frac{2\pi^2}{L^2\beta m}\ (4(N+k_1)^2\phi_3(t-s_1)-(N+k_1)^2\phi_1{}^2(t-s_1)+4(N+k_1)^2$$

$$\phi_1(t-s_1)\phi_2(t-s_1)]\exp[-f(s_1,N)\phi_1(t-s_1)i\ \frac{2\pi}{Lm}\ (N+k_1)$$

$$F(s_1,N), \tag{148}$$

$$D_1 = \{\ \}_1\ \exp[i\ \frac{2\pi}{L}\ r(N+k_1)]\int_o^t ds_1\{\ \}_2 W_m[p+f(s_1,N)\exp[-(t-s_1)\frac{\alpha}{m}]$$

$$+\ f(t-s_1,N+k_1)]F(t-s_1,N+k_1)F(s_1,N) \tag{149}$$

$$\exp[f(s_1,N)(i\ \frac{2\pi}{Lm}\ (N+k_1)(-\phi_1(t-s_1)+(t-s_1)\exp[-(t-s_1)\frac{\alpha}{m}])],$$

$$D_1 = \sum_{k_1}\ \sum_N L^{-1}\ \hat{U}(k_1)C_N i\ \frac{2\pi}{L}\ k_1\ \exp[i\ \frac{2\pi}{L}\ r(N+k_1)]\int_o^t ds_1$$

$$(\frac{\partial}{\partial p}\ \exp[-(t-s_1)\frac{\alpha}{m}]\ +\ \frac{t-s_1-\phi_1(t-s_1)}{m}\ i\ \frac{2\pi}{L}\ (N+k_1))$$

$$W_m[p+f(s_1,N)\exp[-(t-s_1)\frac{\alpha}{m}]\ +\ f(t-s_1,N+k_1)]$$

$$F(t-s_1,N+k_1)\ F(s_1,N)$$

$$\exp[\tfrac{m}{\alpha}\ f(s_1,N)\ \tfrac{i2\pi}{Lm}\ (N+k_1)(1-\exp[-(t-s_1)\ \tfrac{\alpha}{m}])]. \qquad (150)$$

Now the long time limit of D_1 will be examined and it will be found to depend on the initial spatial distribution only as far as the normalization. In the integrand, $\lim_{t\to\infty} F(t-s_1,N+k_1)$ is zero unless $s_1\to\infty$ or $N+k_1 = 0$. If $N+k_1 = 0$, the integrand contains a term $\lim_{t\to\infty} \exp(-(t-s_1)\ \frac{\alpha}{m})$ and the integrand is still zero unless $s_1\to\infty$. If $s_1\to\infty$ then the integrand is zero due to $F(s_1,N)$ unless $N = 0$. Therefore, only the $N = 0$ term in the sum over N contributes to the long time limit of D_1. From normalization requirements, Eq. (10), $C_o = L^{-1/2}$.

$$\lim_{t\to\infty} D_1 = L^{-1} \sum_{k_1} L^{-1/2}\ \hat{U}(k_1)\ \lim_{t\to\infty} \int_o^t ds_1\ \exp[-(t-s_1)(A-B)] \qquad (151)$$

$$i\ \frac{2\pi}{L}\ k_1\ \exp[i\ \frac{2\pi}{L}\ r\ k_1]\ \frac{\partial}{\partial p}\ W_m(p)$$

Using the definition of A and the fact that $B \exp[i\ \frac{2\pi}{L}\ r\ k_1]\ W_m(p) = 0$, one may write Eq. (151) as

$$\lim_{t\to\infty} D_1 = L^{-1} \sum_{k_1} L^{-1/2}\ \hat{U}(k_1)\ \lim_{t\to\infty} \int_o^t ds_1(-\beta)\exp[-(t-s_1)(A-B)] \qquad (152)$$

$$(A-B)\ \exp[i\ \frac{2\pi}{L}\ r\ k_1]\ W_m(p)$$

The integrand is now an exact differential! Integrating gives

$$\lim_{t\to\infty} D_1 = L^{-1} \sum_{k_1} L^{-1/2} \hat{U}(k_1)(-\beta)(\exp[i \tfrac{2\pi}{L} r\, k_1]-\delta(k_1))W_m(p) \tag{153}$$

or

$$\lim_{t\to\infty} D_1 = -\beta L^{-1} W_m(p) \; (U(r)-\overline{U(r)}). \tag{154}$$

Comparing D_o and D_1 with the table in the last chapter, one sees that to this order the asymptotic distribution is a Maxwell-Boltzmann distribution. In order to prove this relation to all orders one must analyze D_n for arbitrary n.

<u>Analysis of D_n</u>

From what has been learned in the analysis of D_o and D_1, D_n may now be evaluated. A very useful result may be abstracted from the analysis of D_1. From equations (142) and (150), one may show

$$\exp[-t(i \tfrac{2\pi}{Lm} K-B)] \; W_m(p+b) = W_m[p+b \exp[- \tfrac{t\alpha}{m}] \tag{155}$$

$$+ f(t,K)]F(t,k)\exp[\tfrac{m}{\alpha} b \tfrac{i2\pi}{Lm} K(1-\exp[- \tfrac{t\alpha}{m}])].$$

From Eq. (106) one has

$$D_N = \sum_{k_1} \sum_{k_2} \dots \sum_{k_N} \sum_{\ell} L^{-\frac{N+1}{2}} \hat{U}(k_1)\hat{U}(k_2)\dots\hat{U}(k_N)$$

$$C_\ell \; (i \; \frac{2\pi}{L})^N \; k_1 k_2 \dots k_N \int_o^t ds_1 \int_o^{s_1} ds_2 \dots \int_o^{s_{N-1}} ds_N$$

$$\exp[-(t-s_1)(A-B)] \; \exp[i \; \frac{2\pi}{L} \; r \; k_N] \; \frac{\partial}{\partial p}$$

$$\exp[-(s_1-s_2)(A-B)\exp[i \; \frac{2\pi}{L} \; r \; k_{N-1}] \; \frac{\partial}{\partial p} \; \dots$$

$$\exp[i \; \frac{2\pi}{L} \; k_1 r] \; \frac{\partial}{\partial p} \; \exp[-s_N(A-B)]$$

$$\exp[i \; \frac{2\pi}{L} \; r\ell]W_m(p). \tag{156}$$

Letting the A operators act, one obtains

$$D_N = \{ \; \}_1 \int_o^t ds_1 \dots \int_o^{s_{N-1}} ds_N \; \exp[-(t-s_1)(i \; \frac{2\pi}{Lm} \; p[\ell + \sum_{i=1}^{N} k_i]$$

$$-B)] \; \frac{\partial}{\partial p} \; \exp[-(s_1-s_2)(i \; \frac{2\pi}{Lm} \; p[\ell + \sum_{i=1}^{N-1} k_i]-B)] \; \frac{\partial}{\partial p} \; \dots \tag{157}$$

$$\frac{\partial}{\partial p} \; \exp[-s_N(i \; \frac{2\pi}{Lm} \; p\ell - B)]W_m(p)$$

where

$$\{ \; \}_1 = L^{-\frac{N+1}{2}} (\frac{i2\pi}{L})^N \sum_{\ell} C_\ell \prod_{i=1}^{N} \sum_{k_i} \hat{U}(k_i)\exp[i \; \frac{2\pi}{L} \; r \; k_i]. \tag{158}$$

Using Lemma 3, Eq. (126), one has

$$D_N = \{\ \}_1 \int_o^t ds_1 \ldots \int_o^{s_{N-1}} ds_N \{\ \}_2 \exp[-(t-s_1)(i \frac{2\pi}{Lm} p [\ell + \sum_{i=1}^{N} k_i]-B)] \exp[-(s_1-s_2)(i \frac{2\pi}{Lm} p[\ell+ \sum_{i=1}^{N-1} k_i]-B)]\ldots \exp[-s_N(i \frac{2\pi}{Lm} p\ell-B)]W_m(p) \tag{159}$$

where $\{\ \}_2$, the product obtained from commuting all the $\frac{\partial}{\partial p}$ operators to the left, is given by

$$\begin{aligned}\{\ \}_2 = {} & [\frac{\partial}{\partial p} \exp[-(t-s_1) \frac{\alpha}{m}] + (t-s_1-\phi_1(t-s_1))\frac{i2\pi}{Lm} [\ell+ \sum_{i=1}^{N} k_i]] \\ & [\frac{\partial}{\partial p} \exp[-(t-s_2) \frac{\alpha}{m}] + (t-s_1-\phi_1(t-s_1))\frac{i2\pi}{Lm} [\ell+ \sum_{i=1}^{N} k_i] \\ & \exp[-(s_1-s_2 \frac{\alpha}{m}] + (s_1-s_2-\phi_1(s_1-s_2)) \frac{i2\pi}{Lm} [\ell+ \sum_{i=1}^{N-1} k_i]] \\ & \ldots \\ & [\frac{\partial}{\partial p} \exp[-(t-s_N) \frac{\alpha}{m}] + (t-s_1-\phi_1(t-s_1)) \frac{i2\pi}{Lm} [\ell+ \sum_{i=1}^{N} k_i] \\ & \exp[-(s_1-s_N) \frac{\alpha}{m}] + \ldots + (s_{N-1}-s_N-\phi_1(s_{N-1}-s_N))\frac{i2\pi}{Lm}[\ell+k_1]].\end{aligned} \tag{160}$$

Using Eq. (155), one may rewrite Eq. (159) as

$$D_N = \{\ \}_1 \int_o^t ds_1 \ldots \int_o^{s_{N-1}} ds_N \ \{\ \}_2 \ W_m[p+f(s_N,\ell)\exp[-(t-s_N)\frac{\alpha}{m}]$$

$$+ f(s_{N-1}-s_N,\ell+k_1)\exp[-(t-s_{N-1})\frac{\alpha}{m}] + \ldots + f(t-s_1,$$

$$\ell + \sum_{i=1}^{N} k_i)] \ \{\ \}_3 \ \{\ \}_4 \qquad (161)$$

where

$$\{\ \}_3 = F(s_N,\ell)F(s_{N-1}-s_N,\ell+k_1) \ \ldots \ F(t-s_1,\ell + \sum_{i=1}^{N} k_i) \qquad (162)$$

and

$$\{\ \}_4 = \exp[\frac{i2\pi}{L} f(s_N,\ell)(1-\exp[-(s_{N-1}-s_N) \frac{\alpha}{m}](\ell+k_1)]$$

$$\exp[\frac{i2\pi}{L\alpha} \{f(s_N,\ell)\exp[-(s_{N-1}-s_N) \frac{\alpha}{m}] +$$

$$f(s_{N-1}-s_N,\ell+k_1)\}(1-\exp[-(s_{N-2}-s_{N-1}) \frac{\alpha}{m}])(\ell+k_1+k_2)]\ldots$$

$$\exp[\frac{i2\pi}{L\alpha} \{f(s_N,\ell)\exp[-(s_1-s_N) \frac{\alpha}{m}] + f(s_{N-1}-s_N,\ell+k_1)$$

$$\exp[-(s_1-s_{N-1}) \frac{\alpha}{m}] + \ldots + f(s_1-s_2, \ \ell + \sum_{i=1}^{N-1} k_i)\}$$

$$(1-\exp[-(t-s_1) \frac{\alpha}{m}])(\ell + \sum_{i=1}^{N} k_i)]. \qquad (163)$$

From the form of D_n it may be argued that the only term in the sum, $\sum_{\ell}$, which contributes to the long time limit of D_n is the term $\ell = 0$. This is due to the product, $\{\ \}_3$. $\lim_{t\to\infty} F(t-s_1, \ell + \sum_{i=1}^{N} k_i) = 0$ unless $s_1 \to \infty$. If $s_1 \to \infty$ then $\lim_{s_1\to\infty} F(s_1-s_2, \ell + \sum_{i=1}^{N-1} k_i) = 0$ unless $s_2 \to \infty$. This process continues until $\lim_{s_N\to\infty} F(s_N, \ell) = 0$ unless $\ell = 0$.

This chain of argument may be broken at some point if there is a sum which is zero, $\ell + \sum_{i=1}^{N-j} k_i = 0$. In this case the time variable, s_{j+1}, is not required to become infinite. This type of problem also occurred in the evaluation of D_1; see the arguments following Eq. (150). In this case the argument is similar. The chain of argument is assumed to be intact up until this first break. Thus, the time variables, t, s_1, s_2, ..., s_j, all become infinite while s_{j+1} is allowed to remain finite. $\{\ \}_2$ contains a term which is as follows

$$[\frac{\partial}{\partial p} \exp[-(t-s_{j+1}) \frac{\alpha}{m}] + (t-s_1-\phi_1(t-s_1)) \frac{i2\pi}{Lm} [\ell + \sum_{i=1}^{N} k_i] \exp[-(s_1-s_{j+1}) \frac{\alpha}{m}] + \ldots + (s_\ell - s_{\ell+1} - \phi_1(s_\ell - s_{\ell+1})) \frac{i2\pi}{Lm} [\ell + \sum_{i=1}^{N-j} k_i]]. \tag{164}$$

The exponentials in this term all damp to zero and only the last term remains. This last term, however, contains $[\ell + \sum_{i=1}^{N-j} k_i]$ which was assumed to be zero. Thus one sees that all such breaks in the chain of argument which has been constructed lead, inevitably, to a zero contribution. It has been shown then that $\lim_{t\to\infty} D_N$ may be written in terms of only the normalization information from the initial spatial distribution,

$$\lim_{t\to\infty} D_N = \lim_{t\to\infty} L^{-1} \int_0^t ds_1 \ldots \int_0^{s_{N-1}} ds_N \exp[-(t-s_1)(A-B)] \frac{dU(r)}{dr} \frac{\partial}{\partial p} \tag{165}$$

$$\ldots \frac{dU(r)}{dr} \frac{\partial}{\partial p} \exp[-s_N(A-B)] W_m(p).$$

Since

$$\frac{\partial}{\partial p} \exp[-s_N(A-B)] W_m(p) = \frac{\partial}{\partial p} W_m(p) = -\frac{\beta p}{m} W_m(p), \tag{166}$$

Eq. (165) may be written in a form similar to Eq. (151),

$$\lim_{t\to\infty} D_N = \lim_{t\to\infty} L^{-1}\{\ \}_1 \int_0^t ds_1 \ldots \int_0^{s_{N-2}} ds_{N-1} \exp[-(t-s_1)$$

$$(i \frac{2\pi}{Lm} p \sum_{i=1}^{N} k_i - B)] \frac{\partial}{\partial p} \ldots \frac{\partial}{\partial p} (-\beta)(i \frac{2\pi}{L} k_1)^{-1} \tag{167}$$

$$\int_0^{s_{N-1}} ds_N \exp[-(s_{N-1}-s_N)(i \frac{2\pi}{Lm} pk_1 - B)](i \frac{2\pi}{Lm} pk_1) W_m(p).$$

Since $-B\, W_m(p) = 0$, this quantity may be added to the integrand thereby making it an exact differential of s_N! Integrating one has

$$\lim_{t\to\infty} D_N = \lim_{t\to\infty} L^{-1}\{\ \}_1 \int_0^t ds_1 \cdots \int_0^{s_{N-2}} ds_{N-1} \exp[-(t-s_1)$$

$$(i\, \frac{2\pi}{Lm}\, p \sum_{i=1}^{N} k_i - B)]\, \frac{\partial}{\partial p} \cdots \exp[-(s_{N-2}-s_{N-1})$$

$$(i\, \frac{2\pi}{Lm}\, p\ (k_1+k_2)-B)]\, \frac{\partial}{\partial p}\ (-\beta)\ (i\, \frac{2\pi}{L}\, k_1)^{-1}$$

$$[1-\exp[-s_{N-1}\ (i\, \frac{2\pi}{Lm}\, pk_1 - B)]]W_m(p). \tag{168}$$

The part of the integrand which uses the 1 in the last bracket is already in the form of Eq. (167) and this integration procedure can be iterated. The part of the integrand which uses $\exp[-s_{N-1}\ (i\, \frac{2\pi}{Lm}\, pk_1 - B)]$ is of the form of Eq. (157) with ℓ replaced by k_1 and C_ℓ by $\hat{U}(k_1)$. It has been shown that for this form only k_1 contributes. Thus Eq. (168) may be rewritten as

$$\lim_{t\to\infty} D_N = L^{-1} \sum_{k_1} \sum_{k_2} \cdots \sum_{k_N} L^{-\frac{N}{2}}\, \hat{U}(k_1)(i\, \frac{2\pi}{L})^N$$

$$k_1 k_2 \ldots k_N \exp[i\, \frac{2\pi}{L}\, r \sum_{i=1}^{N} k_i](-\beta)^N (1-\delta(\sum_{i=1}^{N} k_i))$$

$$(1-\delta(\sum_{i=1}^{N-1} k_i)) \ \ldots \ (1-\delta(k_1))(\frac{i2\pi}{L})^{-N}(\sum_{i=1}^{N} k_i)^{-1}$$

$$(\sum_{i=1}^{N-1} k_i)^{-1} \ \ldots \ k_1^{-1} \ W_m(p) \tag{169}$$

or

$$\lim_{t\to\infty} D_N = L^{-1} \ K_N'(r)\beta^N \ W_m(p) \tag{170}$$

where $K_N'(r)$ is the same as Eq. (37) and was shown to be the N^{th} coefficient of the series expansion of a Boltzmann distribution. The exclusions, $(1-\delta(\sum_{i=1}^{N-j} k_i))$, in Eq. (169) enter that equation automatically and not as assumptions which are required for the integrations to be performed.

It has been shown that the long time limit of the phase space distribution is a Maxwell-Boltzmann distribution if the initial phase space distribution was Maxwellian in momentum space. Notice the way in which this result has occurred. The Boltzmann distribution which has been obtained is the same as the result obtained by the partial resummation in Chapter III, Eq. (36). Indeed it has also been obtained by a partial resummation of the same type of terms. The important difference is that the terms which have not been resummed, the correction terms, have been shown to be zero in this case. The arguments which have shown these correction terms to be zero are intimately related to the action of the

Brownian operator which was introduced in this section. This operator also provides physical justification for the presence of the original parameter, β, in the final Maxwell-Boltzmann distribution. This parameter is the kinetic energy temperature parameter for the Brownian fluid and the particle exchanges energy with the fluid so that this becomes the correct temperature parameter for the particle.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The contracted, spatial distribution for a noninteracting, ideal gas subject to an external potential achieves an equilibrium if the initial momentum distribution is Maxwellian.

2. The equilibrium reached by a noninteracting, ideal gas subject to an external potential is not a Boltzmann distribution.

3. The reason that this equilibrium distribution is not a Boltzmann distribution is related to the conservation of energy, or from another point of view, the lack of partitioning of the energy.

4. If the ideal gas subject to an external potential is allowed to exchange energy with a Brownian fluid, then the equilibrium reached by the phase space distribution is a Maxwell-Boltzmann distribution.

5. It has been shown that operator techniques such as have been used in this dissertation are powerful tools which can be used to analyze classical problems.

Recommendations

There are a number of systems to which analysis such as that found in Chapter IV might be applied. The problem of ion drift velocities in a neutral fluid under the influence of an electric field is one. The interaction of macromolecular ions in solution is another. A molecule migrating across the surface of a crystal to a binding site is a third.

Another problem which is related to those in this dissertation is that of 2, 3, 4, ... particles in a box interacting by means of interparticle potentials. I would expect such a system to show a closer approach to a renormalized Boltzmann distribution than the equilibrium of a one particle system.

It might prove possible to find the phase space distribution in Chapter IV for arbitrary time and apply that result to many types of rate problems. For example Kramers has solved this problem in the large viscosity limit and applied the results to the calculation of chemical reaction rates.

APPENDICES

APPENDIX I

MATHEMATICAL TOOLS

A. $\exp(a \frac{\partial}{\partial r})\exp(br) = \exp(br)\exp(ab)$

a, b, and r commute (171)

Proof:

$$\exp(a\frac{\partial}{\partial r})\exp(br) = \sum_{N=o}^{\infty} \frac{(a \frac{\partial}{\partial r})^N}{N!} \exp(br) =$$

$$\sum_{N=o}^{\infty} \frac{(ab)^N}{N!} \exp(br) = \exp(br)\exp(ab) \tag{172}$$

B. $$\int_{-\infty}^{\infty} \exp[\frac{ap}{m}]W_m(p)dp = \exp[1/2 \frac{a^2}{m\beta}] \tag{173}$$

Proof:

$$\int_{-\infty}^{\infty}\exp [\frac{ap}{m}]W_m(p)dp = \sum_{N=o}^{\infty} \frac{a^N}{N!} (\frac{\beta}{2\pi m})^{1/2} \int_{-\infty}^{\infty} (\frac{p}{m})^N \exp[-\beta \frac{p^2}{2m}]dp \tag{174}$$

Since the integral is zero if N is odd, let $N = 2\ell$.

$$= \sum_{\ell=o}^{\infty} \frac{(a^2)^\ell}{(2\ell)!} (\frac{\beta}{2\pi m})^{1/2} \int_{-\infty}^{\infty} (\frac{p^2}{m^2})^\ell \exp[-\beta \frac{p^2}{2m}]dp \tag{175}$$

This is the form of a Gaussian average and it is well known that

$$<\frac{p^2}{m^2}> = \frac{k_B T}{m} = \frac{1}{\beta m} \tag{176}$$

and

$$<(\frac{p^2}{m^2})^{\ell}> = \frac{(2\ell)!}{2^{\ell}\ell!} <\frac{p^2}{m^2}>^{\ell} \tag{177}$$

where

$$<f(p)> = (\frac{\beta}{2\pi m})^{1/2} \int_{-\infty}^{\infty} f(p)\exp[-\beta \frac{p^2}{2m}]dp \tag{178}$$

for any function f(p). Rewriting Eq. (175), one has

$$\int_{-\infty}^{\infty} \exp[a \frac{p}{m}]W_m(p)dp = \sum_{\ell=o}^{\infty} \frac{(a^2/2)^{\ell}}{\ell!} (\frac{1}{\beta m})^{\ell} \tag{179}$$

$$= \exp[\frac{1}{2} \frac{a^2}{m\beta}]. \tag{180}$$

C. $$\int_{-\infty}^{\infty} p^N \exp[ap]W_m(p)dp = \frac{m}{\beta} \frac{1}{2^{N-2}} \tag{181}$$

$$(\frac{\partial}{\partial x})^{N-1} [X \exp \frac{x^2 2m}{\beta}]\Big|_{X = \frac{a}{2}}$$

This result may be obtained by treating (p)exp(ap) as $\frac{\partial}{\partial a}\exp(ap)$.

D. Disentanglement Theorem

$$\exp[is(A+B)] = \exp(isA]\underset{\leftarrow}{T}\exp[i\int_0^s \exp[-is'A]B\exp[is'A]ds'] \tag{182}$$

Proof:

The two sides are equal when s = 0. Next, both sides are differentiated.

$$\frac{\partial}{\partial s}\exp[is(A+B)] = i(A+B)\exp[is(A+B)] \tag{183}$$

$$\frac{\partial}{\partial s}\exp[isA]\underset{\leftarrow}{T}\exp[i\int_0^s \exp[-is'A]B\exp[is'A]ds'] =$$

$$\{iA\exp[isA] + \exp[isA](i\exp[-isA]B\exp[isA])\} \tag{184}$$

$$\underset{\leftarrow}{T}\exp[i\int_0^s \exp(-is'A)B\exp(is'A)ds'] =$$

$$i(A+B)\exp(isA)\underset{\leftarrow}{T}\exp[i\int_0^s \exp[-is'A]B\exp[is'A]ds'] \tag{185}$$

Therefore, the two sides of Eq. (182) are equal for s = 0 and obey the same linear, first order, differential equation.

E. Lemma 1 from Chapter IV

$$\frac{\partial \exp[\phi A]}{\partial p} = \frac{\phi}{m} \frac{\partial}{\partial r} \exp[\phi A] \tag{186}$$

Proof:

The general formula for the parameter differentiation of exponential operators[10] is

$$\frac{\partial \exp[aH]}{\partial \lambda} = \int_o^a \exp[(a-u)H] \frac{\partial H}{\partial \lambda} \exp[uH]du \tag{187}$$

Using this identity, one has

$$\frac{\partial \exp[\phi A]}{\partial p} = \int_o^\phi \exp[(\phi-u)A] \frac{\partial A}{\partial p} \exp[uA]du \tag{188}$$

where

$$\frac{\partial A}{\partial p} = \frac{1}{m} \frac{\partial}{\partial r} \tag{189}$$

Simplifying, one has

$$\frac{\partial \exp[\phi A]}{\partial p} = \frac{1}{m} \frac{\partial}{\partial r} \exp[\phi A] \int_o^\phi du \tag{190}$$

$$= \frac{\phi}{m} \frac{\partial}{\partial r} \exp[\phi A] \tag{191}$$

F. Lemma 2 from Chapter IV

$$\exp(tB)\,\frac{\partial}{\partial p} = \frac{\partial}{\partial p}\,\exp[-\,\frac{t\alpha}{m}]\,\exp[tB] \tag{192}$$

Proof:

$$\exp[tB]\,\frac{\partial}{\partial p} = \sum_{N=o}^{\infty}\frac{t^N B^N}{N!}\,\frac{\partial}{\partial p} \tag{193}$$

$$B^N\,\frac{\partial}{\partial p} = \sum_{\ell=o}^{N}\frac{N!}{\ell!\,(N-\ell)!}\,[B,\cdot]^{\ell}\,\frac{\partial}{\partial p}\,B^{N-\ell} \tag{194}$$

$$[B,\cdot]^{\ell}\,\frac{\partial}{\partial p} = \frac{\partial}{\partial p}\,(-\,\frac{\alpha}{m})^{\ell} \tag{195}$$

$$\exp[tB]\,\frac{\partial}{\partial p} = \frac{\partial}{\partial p}\sum_{N=o}^{\infty}\sum_{\ell=o}^{N}\frac{t^N}{N!}\,\frac{N!}{\ell!\,(N-\ell)!}\,(-\,\frac{\alpha}{m})^{\ell}\,B^{N-\ell} \tag{196}$$

$$= \frac{\partial}{\partial p}\sum_{N=o}^{\infty}\frac{t^N}{N!}\,(B\,-\,\frac{\alpha}{m})^N \tag{197}$$

$$= \frac{\partial}{\partial p}\,\exp[-\,\frac{t\alpha}{m}]\,\exp[tB] \tag{198}$$

G. Lemma 5 from Chapter IV

$$\exp[tB]W_m(p+a) = W_m(p+a\,\exp[-\,\frac{t\alpha}{m}]) \tag{199}$$

Proof:

$$\exp[tB]W_m(p+a) = \left(\frac{\beta}{2\pi m}\right)^{1/2} \int_{-\infty}^{\infty} G(p,p')\exp[-\frac{\beta}{2m}(p'+a)^2]dp' \quad (200)$$

where G(p,p') is the Greens' function given by

$$G(p,p') = \frac{\beta}{2\pi m(1-\rho^2)} \exp[-\frac{\beta}{2m(1-\rho^2)}(p-p'\rho)^2] \quad (201)$$

and

$$\rho = \exp[-\frac{t\alpha}{m}] \quad (202)$$

Simplifying, one obtains

$$\exp[tB]W_m(p+a) = \frac{\beta}{2\pi m}(1-\rho^2)^{-1/2} \int_{-\infty}^{\infty} \exp[-\frac{\beta}{2m(1-\rho^2)}(p'-p)^2] \quad (203)$$

$$\exp[-\frac{\beta}{2m}p'(2a+2p(1-\rho)^{-1})]\exp[-\frac{\beta}{2m}a^2]dp'$$

let

$$\sigma^2 = \frac{m(1-\rho^2)}{\beta} \quad (204)$$

$$X = p'-p \quad (205)$$

$$C = \frac{\beta}{2m}(2a+2p(1+\rho)^{-1}) \quad (206)$$

Then Eq. (203) may be written as

$$\exp[tB]W_m(p+a) = \frac{\beta}{2\pi m}(1-\rho^2)^{-1/2}\exp[-\frac{\beta}{2m}a^2]\exp[-Cp] \tag{207}$$

$$\int_{-\infty}^{\infty}\exp[-cx]\exp[-\frac{x^2}{2\sigma^2}]dx$$

or

$$\exp[tB]W_m(p+a) = \frac{\beta}{2\pi m}(1-\rho^2)^{-1/2}$$

$$\exp[-\frac{\beta a^2}{2m}]\exp[-cp]\exp[\frac{c^2\sigma^2}{2}]\sigma\sqrt{2\pi} \tag{208}$$

If one substitutes for C and σ one obtains Eq. (199).

H. Time ordered extension of Glauber's Theorem

$$\underset{\leftarrow}{T}\exp[\int_0^t f(s)+g(s)ds] = \underset{\leftarrow}{T}\exp[\int_0^t f(s)ds] \tag{209}$$

$$\underset{\leftarrow}{T}\exp[\int_0^t g(s)ds]\ \underset{\rightarrow}{T}\exp[\int_0^t ds_1\int_0^{s_1} ds_2\ [g(s_1),f(s_2)]]$$

f(s) and g(s') both commute with their commutator

Proof:

Define:

$$F(t) = \underset{\leftarrow}{T}\exp[\int_0^t f(s)ds]\ \underset{\leftarrow}{T}\exp[\int_0^t g(s)ds] \tag{210}$$

$$\frac{\partial}{\partial t}F(t) = f(t)F(t) + \underset{\leftarrow}{T}\exp[\int_0^t f(s)ds]g(t)\ \underset{\leftarrow}{T}\exp[\int_0^t g(s)ds] \tag{211}$$

$$\frac{\partial}{\partial t} F(t) = \{f(t) + \underset{\leftarrow}{T} \exp[\int_0^t f(s)ds]g(t) \underset{\rightarrow}{T} \exp[\int_0^t -f(s)ds]\}F(t) \tag{212}$$

since

$$\underset{\rightarrow}{T} \exp\ [\int_0^t -f(s)ds]\ \underset{\leftarrow}{T} \exp[\int_0^t f(s)ds] = 1 \tag{213}$$

Equation (213) is easily proved since it is true for $t = 0$ and the derivative with respect to t is zero.

$$\underset{\leftarrow}{T} \exp[\int_0^t f(s)ds]g(t) \underset{\rightarrow}{T} \exp[\int_0^t -f(s)ds] =$$

$$g(t) + \int_0^t [f(s),g(t)]ds + \int_0^t ds_1 \int_0^{s_1} ds_2[f(s_1),[f(s_2),g(t)]] + \ldots. \tag{214}$$

or

$$\underset{\leftarrow}{T} \exp[\int_0^t f(s)ds]g(t) \underset{\rightarrow}{T} \exp[\int_0^t -f(s)ds] = \tag{215}$$

$$\underset{\leftarrow}{T} \exp\ [\int_0^t ds[f(s),\cdot]]g(t)$$

Using the fact that f and g both commute with their commutator and Eq. (215), one may rewrite Eq. (212) as

$$\frac{\partial}{\partial t} F(t) = \{f(t)+g(t) + \int_o^t [f(s),g(t)]ds\}F(t). \tag{216}$$

Equation (216) is now integrated to obtain

$$F(t) = \underset{\leftarrow}{T} \exp[\int_o^t (f(s)+g(s))ds] \; \underset{\leftarrow}{T} \exp [\int_o^t ds_1 \int_o^{s_1} ds_2 \; [f(s_2),g(s_1)]]. \tag{217}$$

Equation (217) is equivalent to Eq. (209) if

$$\underset{\leftarrow}{T} \exp[\int_o^t ds_1 \int_o^{s_1} ds_2[f(s_2),g(s_1)]]\underset{\rightarrow}{T} \exp[\int_o^t ds_1 \int_o^{s_1} ds_2 \; - [f(s_2),g(s_1)]] = 1. \tag{218}$$

This is easily proved using Eq. (213). Define I such that

$$\underset{\leftarrow}{T} \exp[\int_o^t f(s)ds] \; I = 1 \tag{219}$$

$$\underset{\rightarrow}{T} \exp[\int_o^t -f(s)ds]\underset{\leftarrow}{T} \exp[\int_o^t f(s)ds]I = \underset{\rightarrow}{T} \exp[\int_o^t -f(s)ds] \tag{220}$$

$$I = \underset{\rightarrow}{T} \exp[\int_o^t -f(s)ds] \tag{221}$$

APPENDIX II

A. A Boltzmann distribution is to be expanded in a series in powers of β.

$$\frac{\exp[-\beta U(r)]}{\int_0^L \exp[-\beta U(r)]dr} = L^{-1} \sum_{N=o}^{\infty} K_N(r)\beta^N \tag{222}$$

$$\frac{\exp[-\beta U(r)]}{\int_0^L \exp[-\beta U(r)]dr} = \frac{\exp[-\beta(U(r)-\overline{U(r)})]}{\int_0^L \exp[-\beta(U(r)-\overline{U(r)})]dr} \tag{223}$$

$$K_N(r) = \frac{1}{N!}\left(\frac{\partial}{\partial\beta}\right)^N [(\int_0^L \exp[-\beta(U(r)-\overline{U(r)})]dr)^{-1}\exp[-\beta(U(r)-\overline{U(r)})]]\Big|_{\beta=o} \tag{224}$$

One now uses the Leibnitz rule for product differentiation.

$$K_N(r) = \frac{1}{N!} \sum_{m=o}^{N} \frac{N!}{m!(N-m)!} \{(\frac{\partial}{\partial\beta})^{N-m} \exp[-\beta(U(r)-\overline{U(r)}]]\Big|_{\beta=o}\}$$

$$\{(\frac{\partial}{\partial\beta})^m [\int_0^L \exp[-\beta(U(r)-\overline{U(r)})]dr]^{-1}\Big|_{\beta=o}\} \tag{225}$$

$$(\frac{\partial}{\partial\beta})^{N-m} \exp[-\beta(U(r)-\overline{U(r)})]\Big|_{\beta=o} = (-1)^{N-m}(U(r)-\overline{U(r)})^{N-m} \tag{226}$$

Next, one uses di Bruno's Formula for the differentiation of a composite function.

$$\left(\frac{\partial}{\partial\beta}\right)^m \left[\int_o^L \exp[-\beta(U(r)-\overline{U(r)})]\right]^{-1}\Bigg|_{\beta=o} = \sum_{\substack{\text{Partitions}\\ \text{of } m}} \prod_{\ell=1}^{m}$$

$$\frac{m!}{m_\ell!(\ell!)^{m_\ell}} \left[\left(\frac{\partial}{\partial\beta}\right)^\ell \int_o^L \exp[-\beta(U(r)-\overline{U(r)}]dr\Big|_{\beta=o}\right]^{m_\ell} \left[\left(\frac{d}{dQ}\right)^p \frac{1}{Q}\Big|_{Q=L}\right] \tag{227}$$

where $Q = \int_o^L \exp[-\beta(U(r)]dr$ and $p = \sum_{\ell=1}^{m} m_\ell$

Combining terms one has

$$K_N(r) = \frac{(-1)^N}{N!} \sum_{m=o}^{N} \frac{N!}{m!(N-m)!} (U(r)-\overline{U(r)})^{N-m} \sum_{\substack{\text{Partitions}\\ \text{of } m}}$$

$$\prod_{\ell=1}^{m} \frac{p!m!(-1)^p}{m_\ell!(\ell!)^{m_\ell}} \left[\overline{(U(r)-\overline{U(r)})^\ell}\right]^{m_\ell} \tag{228}$$

B. Lemma 2 from Chapter III

$$\sum_{p\varepsilon s_N} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{\delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})k_{p(N)}}{m_\ell!\ell!^{m_\ell}[\sum_{j=1}^{N} k_{p(j)}]} =$$

$$\frac{1}{N-m} \sum_{p\varepsilon s_N} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{\delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})}{m_\ell!\ell!^{m_\ell}} \tag{229}$$

Definitions:

S_N is the group of all permutations among the integers 1, 2, ..., N. For a permutation $p \varepsilon S_N$, S^p_{N-m} is the set of all permutations of the integers p(m+1), p(m+2), ..., p(N).

Proof:

Note that $\prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})$ implies that

$$\sum_{j=1}^{m} k_{p(j)} = 0 \quad \text{and} \quad \sum_{j=1}^{N} k_{p(j)} = \sum_{j=m+1}^{N} k_{p(j)} \tag{230}$$

One may rewrite the left hand side of Eq. (229) as

$$\sum_{p \varepsilon S_N} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{\delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})}{m_\ell ! \ell !^{m_\ell}} \{\frac{k_{p(N)}}{\sum_{j=m+1}^{N} k_{p(j)}}\} = \tag{231}$$

$$\sum_{p \varepsilon S_N} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{\delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})}{m_\ell ! \ell !^{m_\ell}} \{\frac{1}{(N-m)!} \sum_{q \varepsilon S^p_{N-m}}$$

$$\frac{k_{q(p(N))}}{\sum_{j=m+1}^{N} k_{q(p(j))}}\} =$$

$$\sum_{p \varepsilon S_N} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{\delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})}{m_\ell ! \ell !^{m_\ell}} \{\frac{1}{(N-m)! \sum_{j=m+1}^{N} k_{p(j)}} \sum_{q \varepsilon S^p_{N-m}}$$

$$k_{q(p(N))}\} = \tag{232}$$

$$\sum_{p\varepsilon S_N} \prod_{\ell=1}^{m} \prod_{r=1}^{m_\ell} \frac{\delta(\sum_{j=1}^{\ell} k_{p(\ell(r-1)+j)})}{m_\ell!\,\ell!^{m_\ell}} \{\frac{1}{(N-m)!\,\sum_{j=m+1}^{N} k_{p(j)}\,(N-m-1)!\,\sum_{j=m+1}^{N} k_{p(j)}}\} \tag{233}$$

Equation (233) is equal to the right hand side of Eq. (229).

C. Lemma 3 from Chapter III

$$-\sum_{m=o}^{N} (-1)^{N+1}\,\overline{[U(r)-\overline{U(r)}]^{N+1-m}} \sum_{\substack{\text{Partitions}\\ \text{of } m}} \prod_{\ell=1}^{m} \frac{(-1)^p p!}{(N+1-m)!\,m_\ell!\,\ell!^{m_\ell}}$$

$$\overline{[(U(r)-\overline{U(r)})]}^{m_\ell} = (-1)^{N+1} \sum_{\substack{\text{Partitions}\\ \text{of } N+1}} \prod_{\ell=1}^{N+1}$$

$$\frac{(-1)^{p'} p'!}{m'_\ell!\,\ell'!^{m'_\ell}} \overline{[(U(r)-\overline{U(r)})^{\ell'}]}^{m'_\ell} \tag{234}$$

Proof:

Definition: $$f(\beta) = \int_o^L \exp[-\beta(U(r)-\overline{U(r)})]dr \tag{235}$$

$$f(o) = L,\ \left(\frac{\partial}{\partial\beta}\right)^k f(\beta)\Big|_{\beta=o} = (-1)^k L^k\ \overline{(U(r)-\overline{U(r)})^k} \tag{236}$$

From Appendix II, Eq. (227), one has

$$\left(\frac{\partial}{\partial\beta}\right)^k [f(\beta)]^{-1}\Big|_{\beta=o} = (-1)^k L^{-1} \sum_{\substack{\text{Partitions}\\ \text{of } k}} \prod_{j=1}^{k} \frac{(-1)^q q!k!}{m_j! j!^{m_j}}$$

$$\left[\overline{(U(r)-\overline{U(r)})^j}\right]^{m_j} \tag{237}$$

where

$$k = \sum_{j=1}^{k} j\ m_j \qquad\qquad q = \sum_{j=1}^{k} m_j \tag{238}$$

k, q, and m_j are used here to emphasize that Eq. (237) is an identity independent of this lemma. Equation (234) may then be written as

$$\sum_{m=o}^{N} \frac{(-1)^{m-1}}{(N+1-m)!m!}\left[\left(\frac{\partial}{\partial\beta}\right)^{N+1-m} f(\beta)\Big|_{\beta=o}\right]\left[(-1)^{-m}\left(\frac{\partial}{\partial\beta}\right)^m [f(\beta)]^{-1}\Big|_{\beta=o}\right] \tag{239}$$

$$= \frac{L}{(N+1)!}\left(\frac{\partial}{\partial\beta}\right)^{N+1}[f(\beta)]^{-1}\Big|_{\beta=o}$$

Multiplying both sides by (N+1)! and adding $-L\left(\frac{\partial}{\partial\beta}\right)^{N+1}[f(\beta)]^{-1}\Big|_{\beta=o}$ to both sides gives

$$-\sum_{m=o}^{N+1} \frac{(N+1)!}{(N+1-m)!m!}\left[\left(\frac{\partial}{\partial\beta}\right)^{N+1-m} f(\beta)\Big|_{\beta=o}\right]\left[\left(\frac{\partial}{\partial\beta}\right)^m [f(\beta)]^{-1}\Big|_{\beta=o}\right] = o \tag{240}$$

Or using Leibnitz rule, one has

$$- \left(\frac{\partial}{\partial \beta}\right)^{N+1} [f(\beta)[f(\beta)]^{-1}] = 0 \quad (241)$$

$$- \left(\frac{\partial}{\partial \beta}\right)^{N+1} [1] = 0 \quad (242)$$

which is true if N is greater than or equal zero.

APPENDIX III

Derivation of $I^{(1)}(N,k_1)$

$$I^{(1)}(N,k_1) = \lim_{t\to\infty} \int_{-\infty}^{\infty} dp\ W_m(p) \int_0^t ds_1\ s_1 m\alpha^2 k_1$$

$$\exp[i\alpha p(s_1k_1 - t(k_1+N))] \qquad (243)$$

Integrating, $k_1 \neq 0$

$$I^{(1)}(N,k_1) = \lim_{t\to\infty} \left(\frac{\beta}{2\pi m}\right)^{1/2} \frac{m}{k_1} A(\beta)(1-\delta(k_1)) \qquad (244)$$

where

$$A(\beta) = \int_{-\infty}^{\infty} dp\ \exp[-\beta \frac{p^2}{2m}] \frac{1}{p^2} \{\exp[-i\alpha ptN] - \exp[-i\alpha pt(k_1+N)]$$

$$-i\alpha ptk_1\ \exp[-i\alpha ptN]\} \qquad (245)$$

$$\lim_{\beta\to\infty} A(\beta) = 0 \qquad (246)$$

Therefore

$$A(\beta) = \int_\beta^{\infty} dx \int_{-\infty}^{\infty} dp\ \frac{d}{dx} \exp[-x \frac{p^2}{2m}] \frac{1}{p^2} \{\exp[-i\alpha ptN]$$

$$-\exp[-i\alpha pt(k_1+N)] - i\alpha ptk_1\ \exp[-i\alpha ptN]\} \qquad (247)$$

$$A(\beta) = (\frac{\pi}{2m})^{1/2} \int_{\beta}^{\infty} dx\ x^{-1/2} \{(1-t^2 \frac{mNk_1\alpha^2}{x}) \exp[-\frac{t^2 m\alpha^2 N^2}{2x}] - \exp[-\frac{t^2 m\alpha^2 (N+k_1)^2}{2x}]\} \quad (248)$$

Changing variables

$$x = \frac{1}{w^2} \qquad dx = -\frac{2}{w^2}\,dw \quad (249)$$

$$A(\beta) = (\frac{\pi}{2m})^{1/2} \int_{o}^{\beta^{-1/2}} \frac{2}{w^2} [(1-t^2 mNk_1\alpha^2 w^2)\exp[-1/2\ t^2 m\alpha^2 N^2 w^2] - \exp[-1/2\ t^2 m\alpha^2 (N+k_1)^2 w^2]]dw \quad (250)$$

Integrating by parts

$$A(\beta) = (\frac{2\pi}{m})^{1/2}[\beta^{1/2}\{\exp[-\frac{1}{2\beta}\ t^2 m\alpha^2(N+k_1)^2] - (1-t^2 m\alpha^2 Nk_1/\beta) \exp[-\frac{1}{2\beta}\ t^2 m\alpha^2 N^2]\} + t^2 B(\beta)] \quad (251)$$

where

$$B(\beta) = m\alpha^2 \int_{o}^{\beta^{-1/2}} (N+k_1)^2 \exp[-1/2\ t^2 m\alpha^2 (N+k_1)^2 w^2] - [(N^2+2Nk_1) - t^2 m\alpha^2 N^3 k_1 w^2] \exp[-1/2\ t^2 m\alpha^2 N^2 w^2] dw \quad (252)$$

Therefore

$$I^{(1)}(N,k_1) = \frac{\beta}{k_1}\,[\delta(N+k_1)-\delta(N)](1-\delta(k_1))$$

$$+ \lim_{t\to\infty} \left(\frac{\beta}{2\pi m}\right)^{1/2} \frac{m}{k_1}\,(1-\delta(k_1))t^2B(\beta) \quad (253)$$

Thus I (N,k_1) is finite if and only if $\lim_{t\to\infty} t^2B(\beta) = 0$. This will be proved next.

$$\lim_{t\to\infty} t^2B(\beta) = B_1(\beta)-B_2(\beta) \quad (254)$$

where

$$B_1(\beta) = \lim_{t\to\infty} t^2m\alpha^2 \int_0^\infty \{(N+k_1)^2\exp[-1/2\ t^2m\alpha^2(N+k_1)^2w^2]-$$

$$[N^2+2Nk_1-t^2m\alpha^2N^3k_1w^2]\exp[-1/2\ t^2m\alpha^2N^2w^2]\}dw \quad (255)$$

$$B_2(\beta) = \lim_{t\to\infty} t^2m\alpha^2 \int_{\beta^{-1/2}}^\infty \{(N+k_1)^2\exp[-1/2\ t^2m\alpha^2(N+k_1)^2w^2]-$$

$$[N^2+2Nk_1-t^2m\alpha^2N^3k_1w^2]\exp[-1/2\ t^2m\alpha^2N^2w^2]\}dw \quad (256)$$

In $B_2(\beta)$ the order of the limit and the integral may be exchanged and the limit of t^2 times the integrand is zero. Integrating $B_1(\beta)$

$$\lim_{t\to\infty} t^2 B(\beta) = \lim_{t\to\infty} t^2 \sqrt{\frac{2\pi}{m}}\sqrt{\frac{\pi}{2}}\ \left[\frac{t^2 m\alpha^2 (N+k_1)^2}{t\alpha(N+k_1)\ \sqrt{m}} - \frac{t^2 m\alpha^2 (N^2+2Nk_1)}{t\alpha N\sqrt{m}}\right.$$

$$\left. + \frac{t^4 m^2 \alpha^4 N^3 k_1}{t^3 \alpha^3 N^3 m^{3/2}}\right] \tag{257}$$

Thus

$$\lim_{t\to\infty} t^2 B(\beta) = 0 \tag{258}$$

$$I^{(1)}(N,k_1) = \frac{\beta}{k_1}\ [\delta(N+k_1)-\delta(N)][1-\delta(k_1)] \tag{259}$$

Derivation of $I^{(2)}(N,\ k_1,\ k_2)$

$$I^{(2)}(N,k_1,k_2) =$$

$$\lim_{t\to\infty} \int_{-\infty}^{\infty} dp \int_0^t ds_1 \int_0^{s_1} ds_2\ k_1 k_2 [(k_2+N)s_1 s_2 - k_2 s_2{}^2] m^2 \alpha^4$$

$$\exp[i\alpha p[s_1 k_1 + s_2 k_2 - t(k_1+k_2+N)]] W_m(p) \tag{260}$$

Integrating over the time variables

$$I^{(2)}(N,k_1,k_2) =$$

$$\lim_{t\to\infty} \int_{-\infty}^{\infty} dp \{m^2\alpha^4 k_1 k_2 (k_2+N)[(\alpha^4 p^4 k_2{}^2 (k_1+k_2)^3)^{-1}[\exp[-i\alpha ptN]$$

$$[-\alpha^2 p^2 t^2 k_2 (k_1+k_2)^2 - 2i\alpha ptk_2(k_1+k_2)$$

$$+3k_2+k_1-i\alpha pt(k_1+k_2)^2]$$

$$-\exp[-i\alpha pt(k_1+k_2+N)][3k_2+k_1]]$$

$$-(\alpha^4 p^4 k_1{}^2 k_2{}^2)^{-1}[\exp[-i\alpha pt(k_2+N)][1-i\alpha ptk_1]$$

$$-\exp[-i\alpha pt(k_1+k_2+N)]]]$$

$$-m^2\alpha^4 k_1 k_2{}^2[(\alpha^4 p^4 k_2{}^3 (k_1+k_2)^3)^{-1}[\exp[-i\alpha ptN]$$

$$[-\alpha^2 p^2 t^2 k_2{}^2 (k_1+k_2)^2 - 2i\alpha ptk_2{}^2(k_1+k_2)$$

$$+2k_2{}^2 - 2i\alpha ptk_2(k_1+k_2)^2 + 2k_2(k_1+k_2) + 2(k_1+k_2)^2]$$

$$-\exp[-i\alpha pt(k_1+k_2+N)][2k_2{}^2+2k_2(k_1+k_2)+2(k_1+k_2)^2]$$

$$-\exp[-i\alpha pt(k_2+N)][\frac{2}{k_1}(k_1+k_2)^3]$$

$$+\exp[-i\alpha pt(k_1+k_2+N)][\frac{2}{k_1}(k_1+k_2)^3]]]\}W_m(p) \qquad (261)$$

Simplifying

$$I^{(2)}(N,k_1,k_2) = \lim_{t\to\infty} \int_{-\infty}^{\infty} p^{-4}\ F(p,N,k_1,k_2)W_m(p)dp \qquad (262)$$

where

$$F(p,N,k_1,k_2) = \exp[-i\alpha ptN]P_1+\exp[-i\alpha pt(k_2+N)]P_2+$$

$$\exp[-i\alpha pt(k_1+k_2+N)]P_3 \qquad (263)$$

and where

$$P_1 \equiv \frac{m^2k_1}{k_2(k_1+k_2)^3}\ [-\alpha^2p^2t^2k_2N(k_1+k_2)^2+i\alpha pt(k_1+k_2)[k_2(k_1+k_2)$$

$$-N(3k_2+k_1)]-(3k_2+2k_1)(k_1+k_2)+N(3k_2+k_1)] \qquad (264)$$

$$P_2 \equiv \frac{m^2}{k_1k_2}\ [i\alpha ptk_1(k_2+N)+2k_1-k_2-N] \qquad (265)$$

$$P_3 \equiv \frac{m^2}{k_1(k_1+k_2)^3}\ [k_2{}^2(k_1+k_2)+Nk_2(3k_1+k_2)] \qquad (266)$$

Now applying the same technique as before

$$\int_{-\infty}^{\infty} p^{-4}\ F(p,N,k_1,k_2)W_m(p)dp\Big|_{\beta=\infty} = 0 \qquad (267)$$

Also

$$\left(\frac{\partial}{\partial\beta}\int_{-\infty}^{\infty} p^{-4}\, F(p,N,k_1,k_2) W_m(p)\, dp\right)\Big|_{\beta=\infty} = 0 \tag{268}$$

$$I^{(2)}(N,k_1,k_2) = \tag{269}$$

$$\lim_{t\to\infty} \left(\frac{\beta}{2\pi m}\right)^{1/2} \int_{\infty}^{\beta} dx \int_{\infty}^{x} dy \int_{-\infty}^{\infty} dp\, \frac{1}{4m^2} \exp\left[-y\, \frac{p^2}{2m}\right] F(p,N,k_1,k_2)$$

or defining the operator

$$\langle\cdot\rangle_y = \int_{-\infty}^{\infty} \left(\frac{y}{2\pi m}\right)^{1/2} \exp\left[\frac{-y}{2m}\, p^2\right] \cdot\, dp \tag{270}$$

$$\lim_{t\to\infty} \left(\frac{\beta}{2\pi m}\right)^{1/2} \frac{1}{4m^2} \int_{\infty}^{\beta} dx \int_{\infty}^{x} dy \left(\frac{2\pi m}{y}\right)^{1/2} \langle F(p,N,k_1,k_2)\rangle_y \tag{271}$$

Now changing variables

$$x = \frac{1}{z^2} \qquad y = \frac{1}{w^2} \tag{272}$$

and exchanging the order of integration

$$I^{(2)}(N,k_1,k_2) = \lim_{t\to\infty} \frac{\beta^{1/2}}{m^2} \int_{o}^{\beta^{-1/2}} dw \int_{w}^{\beta^{-1/2}} dz\, \frac{1}{w^2} \langle F(p,N,k_1,k_2)\rangle_{\frac{1}{w^2}}\, z^{-3} \tag{273}$$

Integrating over z and then by parts

$$I^2(N,k_1,k_2) = \lim_{t\to\infty} \frac{\beta^{1/2}}{m^2} \frac{1}{2} \left(\frac{2}{3} \beta^{3/2}\right) <F(p,N,k_1,k_2>_\beta \tag{274}$$

$$- \frac{\beta^{1/2}}{m^2} \frac{1}{2} \int_0^{\beta^{-1/2}} dw\left(\frac{\beta}{w} - \frac{1}{3w^3}\right) \frac{d}{dw} <F(p,N,k_1,k_2)>_{\frac{1}{w^2}}$$

Now the integral term will be shown to be zero

$$<F(p,N,k_1,k_2)>_{\frac{1}{w^2}} = \tag{275}$$

$$\exp[-1/2\ \alpha^2t^2N^2mw^2]\left[\frac{m^2k_1}{k_2(k_1+k_2)^3}\ [-\alpha^2t^2k_2N(k_1+k_2)^2(mw^2-\alpha^2t^2N^2m^2w^4)\right.$$

$$+ \alpha^2t^2Nmw^2(k_1+k_2)(k_2(k_1+k_2)-N(3k_2+k_1))$$

$$- (3k_2+2k_1)(k_1+k_2) + N(3k_2+k_1)]]$$

$$+ \exp[-1/2\ \alpha^2t^2(k_2+N)^2mw^2][\frac{m^2}{k_1k_2}[\alpha^2t^2mw^2k_1(k_2+N)^2+2k_1-k_2-N]]$$

$$+\exp[-1/2\ \alpha^2t^2(k_1+k_2+N)^2mw^2][\frac{m^2}{k_1(k_1+k_2)^3}[k_2^2(k_1+k_2)+Nk_2(3k_1+k_2)]]$$

$$\frac{d}{dw} <F(p,N,k_1,k_2)>_{\frac{1}{w^2}} = \tag{276}$$

$$\exp[-1/2\ \alpha^2t^2N^2mw^2]\ \frac{\alpha^2m^3t^2N^2k_1}{k_2(k_1+k_2)^3}\ [-w^5\alpha^4t^4N^3m^2k_2(k_1+k_2)^2$$

$$+w^3\alpha^2t^2Nm(k_1+k_2)\ [N(3k_2+k_1)+4k_2(k_1+k_2)]$$

$$-w[3k_2(k_1+k_2) + N(3k_2+k_1)]]$$

$$+\exp[-1/2\ \alpha^2t^2(k_2+N)^2mw^2]\frac{\alpha^2m^3t^2(k_2+N)^3}{k_1k_2}[-w^3\alpha^2t^2mk_1(k_2+N)+w]$$

$$-\exp[-1/2\ \alpha^2t^2(k_1+k_2+N)^2mw^2]\frac{\alpha^2m^3t^2(k_1+k_2+N)^2}{k_1(k_1+k_2)^3}[w[k_2{}^2(k_1+k_2)+Nk_2$$

$$(3k_1+k_2)]]$$

Now define

$$W_1 + W_2 = \lim_{t\to\infty}\int_0^{\beta-1/2} dw\ \left(\frac{\beta}{w} - \frac{1}{3w^3}\right)\frac{d}{dw} \langle F(p,N,k_1,k_2\rangle_{\frac{1}{w^2}} \quad (277)$$

where

$$W_1 = \lim_{t\to\infty}\alpha^2\int_0^{\beta-1/2} dw\ \frac{1}{w^2}\ G(\alpha,w) \quad (278)$$

where

$$G(\alpha,w) \equiv \exp[-1/2\ \alpha^2t^2N^2mw^2]\ \frac{t^2m^3N^2k_1}{3k_2(k_1+k_2)^3}\ [3k_2(k_1+k_2)+N(3k_2+k_1)]$$

$$-\exp[-1/2\ \alpha^2t^2(k_2+N)^2mw^2]\ \frac{t^2m^3(k_2+N)^3}{3k_1k_2}$$

$$+\exp[-1/2\ \alpha^2t^2(k_1+k_2+N)^2mw^2]\ \frac{t^2m^3(k_1+k_2+N)^2}{3k_1(k_1+k_2)^3}\ [k_2{}^2(k_1+k_2)+k_2N$$

$$(3k_1+k_2)] \quad (279)$$

$$W_2 = \int_0^{\beta^{-1/2}} G(w)\,dw \tag{280}$$

$$G(w) = \int_0^{\beta^{-1/2}} dw \, \exp[-1/2 \ \alpha^2 t^2 N^2 m w^2] \ \frac{\alpha^2 t^2 m^3 N^2 k_1}{k_2 (k_1+k_2)^3}$$

$$[-w^4 \beta\alpha^4 t^4 N^3 m^2 k_2 (k_1+k_2)^2$$

$$+ \frac{1}{3} w^2 \alpha^4 t^4 N^3 m^2 k_2 (k_1+k_2)^2$$

$$+ \beta w^2 \alpha^2 m (k_1+k_2) \{t^2 N^2 (3k_2+k_1) + 4t^2 N k_2 (k_1+k_2)\}$$

$$- \frac{1}{3} \alpha^2 m (k_1+k_2) \{t^2 N^2 (3k_2+k_1) + 4t^2 N k_2 (k_1+k_2)\}$$

$$- \beta\{3k_2(k_1+k_2) + N(3k_2+k_1)\}]$$

$$+\exp[-1/2 \ \alpha^2 t^2 (k_2+N)^2 m w^2] \ \frac{\alpha^2 t^2 m^3 (k_2+N)^3}{k_1 k_2} \ [\beta + \frac{1}{3} \alpha^2 t^2 k_1 (k_2+N) m$$

$$- \beta w^2 \alpha^2 t^2 k_1 (k_2+N) m]$$

$$-\exp[-1/2 \ \alpha^2 t^2 (k_1+k_2+N)^2 m w^2] \ \frac{\beta\alpha^2 t^2 (k_1+k_2+N)^2 m^3}{k_1 \ (k_1+k_2)^3}$$

$$[k_2{}^2 (k_1+k_2) + k_2 N (3k_1+k_2)] \tag{281}$$

Now W_1 will be analyzed

$$W_1 = \lim_{t\to\infty} \alpha^2 \int_o^\infty \frac{1}{w^2} G(\alpha,w)dw$$

$$- \alpha^2 \int_{\beta^{-1/2}}^\infty \frac{1}{w^2} \lim_{t\to\infty} G(\alpha,w)dw \tag{282}$$

$$\lim_{t\to\infty} G(\alpha,w) = 0 \quad \text{for all} \quad w \neq 0 \tag{283}$$

$$W_1 = \lim_{t\to\infty} \alpha^2 \int_o^\infty \frac{1}{w^2} G(\alpha,w)dw \tag{284}$$

$$G(\alpha,w)\Big|_{\alpha=o} = 0 \tag{285}$$

implies

$$W_1 = \lim_{t\to\infty} \alpha^2 \int_o^\alpha dx \frac{d}{dx} \int_o^\infty dw \frac{1}{w^2} G(x,w) \tag{286}$$

$$W_1 = \lim_{t\to\infty} \alpha^2 \int_o^\alpha dx \int_o^\infty dw \; [-\exp[-1/2 \; x^2t^2N^2mw^2] \frac{xt^4m^4N^4k_1}{3k_2(k_1+k_2)^3}$$

$$[3k_2(k_1+k_2)+N(3k_2+k_1)]$$

$$+ \exp[-1/2 \; x^2t^2(k_2+N)^2mw^2] \frac{xt^4m^4(k_2+N)^5}{3k_1k_2} \tag{287}$$

$$- \exp[-1/2 \; x^2t^2(k_1+k_2+N)^2mw^2] \frac{xt^4m^4(k_1+k_2+N)^4}{3k_1(k_1+k_2)^3}$$

$$[k_2^2(k_1+k_2)+k_2N(3k_1+k_2)]]$$

$$\int_{o}^{\infty} e[-aw^2]dw = 1/2\sqrt{\frac{\pi}{a}} \tag{288}$$

$$W_1 = \lim_{t\to\infty} \alpha^3\sqrt{\frac{\pi}{2m}}\ [\frac{-t^3m^4N^3k_1}{3k_2(k_1+k_2)^3}\ [3k_2(k_1+k_2)+N(3k_2+k_1)]$$

$$+\frac{t^3m^4(k_2+N)^4}{3k_1k_2} \tag{289}$$

$$\frac{-t^3m^4(k_1+k_2+N)^3}{3k_1(k_1+k_2)^3}\ [k_2{}^2(k_1+k_2)+k_2N(3k_1+k_2)]]$$

Now W_2 will be analyzed

$$W_2 = \lim_{t\to\infty}\int_{o}^{\infty} G(w)dw - \int_{\beta^{-1/2}}^{\infty}\lim_{t\to\infty} G(w)dw = \lim_{t\to\infty}\int_{o}^{\infty} G(w)dw \tag{290}$$

Integrating and simplifying

$$W_2 = \lim_{t\to\infty}\sqrt{\frac{2\pi m}{2}}\ \frac{1}{k_1k_2(k_1+k_2)^3}\ \{\alpha^3t^3m^3[\frac{1}{3}\ k_1(k_2+N)^3(k_1+k_2)^3$$

$$-\ \frac{1}{3}\ k_1{}^2N^3(k_1+k_2)(3k_2+k_1)$$

$$-\ k_1{}^2k_2N^2(k_1+k_2)^2]$$

$$+\ \alpha\beta tm^2[Nk_1{}^3(k_1+k_2)+k_1{}^2k_2(k_1+k_2)^2$$

$$-N^2k_1{}^3-3N^2k_1{}^2k_2+(-k_1+k_2+N)(k_2+N)(k_1+k_2)^3$$

$$-k_2{}^3(k_1+k_2+N)^2$$

$$-3k_1Nk_2{}^2(k_1+k_2+N)]\} \qquad (291)$$

After a little algebra the coefficient of t in the second term of W_2 is zero. Thus W_1 and W_2 are both of order t^3. Adding

$$W_1+W_2 = \lim_{t\to\infty} \frac{\sqrt{2\pi m}\ \alpha^3 t^3 m^3}{\sigma k_1 k_2 (k_1+k_2)^2} [(k_1+k_2+N)(k_2+N)^3(k_1+k_2)^2$$

$$-(k_1+k_2)^2\{N^4+N^3(k_1+4k_2)$$

$$+3N^2k_2(k_1+2k_2)+Nk_2{}^2(3k_1+4k_2)$$

$$+k_2{}^3(k_1+k_2)\}] \qquad (292)$$

$$W_1+W_2 = 0 \qquad (293)$$

Therefore

$$I^{(2)}(N,k_1,k_2) = \lim_{t\to\infty} \frac{\beta^2}{3m^2} \langle F(p,N,k_1,k_2)\rangle_\beta \qquad (294)$$

One may obtain $\langle F(p,N,k_1,k_2)\rangle_\beta$ from $\langle F(p,N,k_1,k_2)\rangle_{\frac{1}{w^2}}$ by replacing w^2 by β^{-1}. Taking the limit $t\to\infty$ one obtains

$$I^{(2)}(N,k_1,k_2) = \frac{\beta^2}{3m^2}\left[-\delta(N)\frac{m^2(3k_2+2k_1)}{k_2{}^2(k_1+k_2)^2} + \delta(k_2+N)\frac{2m^2}{k_1k_2{}^2}\right.$$

$$\left. - \delta(k_1+k_2+N)\frac{3m^2}{k_1(k_1+k_2)^2}\right] \tag{295}$$

$$I^{(2)}(N,k_1,k_2) =$$

$$\frac{1}{3}\beta^2 \left[-\delta(N)\frac{(3k_2+2k_1)k_1}{k_2(k_1+k_2)^2} + \delta(k_2+N)\frac{2}{k_2}\right.$$

$$\left. - \delta(k_1+k_2+N)\frac{3k_2}{(k_1+k_2)^2}\right](1-\delta(k_1)(1-\delta(k_2)) \tag{296}$$

APPENDIX IV

DERIVATION OF EQUATION (96)

$$\frac{\partial}{\partial t} D(r,p,t) = (E+\tilde{E})D(r,p,t) \tag{297}$$

where

$$E = -\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU(r)}{r}\frac{\partial}{\partial p} + \frac{\alpha}{m}\frac{\partial}{\partial p}p \tag{298}$$

$$\tilde{E} = -\frac{\partial}{\partial p}\tilde{F}(t) \tag{299}$$

Using time ordered cumulants,[12] one has

$$\frac{\partial}{\partial t} \langle D(r,p,t)\rangle = (E+\exp[tE]\sum_{N=1}^{\infty} G^{(N)}(t)\exp[-tE])\langle D(r,p,t)\rangle . \tag{300}$$

The average of the stochastic operator is zero and its autocorrelation function is proportional to a Dirac delta. In these circumstances, all of the cumulants $G^{(N)}(t)$ are zero except the second one.

$$\int_0^t G^{(2)}(s)ds = \int_0^t ds_1 \int_0^{s_1} ds_2 \langle\exp[-s_1E]\tilde{E}(s_1)\exp[(s_1-s_2)E]\tilde{E}(s_2)$$

$$\exp[s_2E]\rangle \tag{301}$$

$$= \int_0^t ds_1 \int_0^{s_1} ds_2 \exp[-s_1 E] \frac{\partial}{\partial p} \frac{2\alpha}{\beta} \delta(s_1 - s_2) \exp[(s_1 - s_2)E]$$

$$\frac{\partial}{\partial p} \exp[s_2 E] \tag{302}$$

$$G^{(2)}(t) = -\exp[-tE] \frac{\alpha}{\beta} \frac{\partial^2}{\partial p^2} \exp[tE] \tag{303}$$

Substituting back into Eq. (300) one has

$$\frac{\partial}{\partial t} \langle D(r,p,t) \rangle = \left(E - \frac{\alpha}{\beta} \frac{\partial^2}{\partial p^2}\right) \langle D(r,p,t) \rangle \tag{304}$$

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VITA

Joel Lamar Davis, Jr. was born on November 12, 1948 in Atlanta, Georgia. He attended North Cobb High School in Acworth, Georgia, graduating in 1966. He was a Merit Scholarship finalist and received the Lockheed Leadership Scholarship. He attended the Georgia Institute of Technology and graduated cum laude in Physics in 1970. Next he studied in the Air Pollution Studies Program at the Georgia Institute of Technology. He was supported during this work by a HEW traineeship. He completed a thesis entitled The Absorption of Sulfur Dioxide by Charged Aqueous Droplets and received his M.S. in Physics in 1972. He worked in business for eighteen months before returning to graduate school. He completed a dissertation entitled Maxwell $\underset{t\to\infty}{\to}$ Boltzmann and received his Ph.D. in Physics from the Georgia Institute of Technology in 1976.